SCANNING TRANSMISSION ELECTRON MICROSCOPY (STEM) AND X-RAY
ABSORPTION SPECTROSCOPY (XAS) INVESTIGATIONS OF CATALYTIC
SYSTEMS

BY

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DISSEMINATION

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ABSTRACT

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Because of their importance to energy production, understanding and improving catalytic materials is essential to further advances in their development and use. The following work discusses the experimental investigation of various supported and unsupported noble metal nanoparticles using, predominantly, X-ray absorption spectroscopy (XAS) and scanning transmission electron microscopy (STEM) or spherical aberration-corrected STEM (C₅-STEM). Although the majority of the work focuses on γ-Al₂O₃ supported nanoparticles because of their industrial importance for fuel production, several other systems are also addressed. These include understanding the structural characteristics of unsupported noble metal nanoparticles (Au, Ag, Pt, Pd, Ir and Rh) as a function of size and Pt-Pd nanoparticles formed in core-shell, reverse core-shell and alloy motifs. Regardless of the system investigated, all experiments revealed information about how the nanoparticle catalysts were structured and/or behaved under catalytic conditions.
ACKNOWLEDGMENTS

There are many people and places which contributed to the completion of this work. Foremost amongst those who have guided my efforts are my advisor (Dr. Ralph Nuzzo) and committee members: Dr. Andrew Gewirth, Dr. Catherine Murphy, and Dr. Jian-Min Zuo. Amongst the many others who have helped me with useful conversations/advice, I would specifically like to mention Dr. Anatoly Frenkel, Dr. Sergio Sanchez, Dr. Jian-guo Wen, Dr. Shankar Sivaramakrishnan; Dr. Amish Shah and the Nuzzo group members (Matthew Stewart, Michael Motala, Jennifer (Hanson) Shepherd, Jimin Yao, Hauibin Zhang, Xiaoying Guo, Lucas Thompson, Sergio Sanchez, Audrey Bowen, Evan Erickson, Eric Brueckner, Lanfang Li, Jason Goldman, Michael Cason, Peixi Yuan, Enes Oruc, So Mi Kang, Chris Corcoran, Jeremy Smith, David Wetzel, Lu Xu, and Joselle McCracken). Of course, I would also be remiss if I did not thank those institutions and staff that made things technically and financially possible: the University of Illinois Chemistry Department; the Fredrick Seitz Materials Research Laboratory (MRL); Brookhaven National Laboratory (BNL); Argonne National Laboratory; and the United States Department of Energy (DOE). Lastly, I would like to thank my friends and family for their support.
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CHAPTER 1
INTRODUCTION

1.1 Importance of Catalysts

Society relies on a myriad of different materials every day, but rarely does one think about how those products were made or what they contain. Yet how much of the technology that we take for granted would be viable without catalysts? Take a vehicle for instance. If it uses fuel, that fuel was likely produced at a refinery using catalysts. The catalytic converter on the vehicle is also filled with catalysts that reduce the number of unburned hydrocarbons, NO, NO₂, N₂O and CO emissions.¹⁻³ Even in the case of batteries, the power plants that generated the electricity to charge the vehicle likely used catalysts to limit the emission of harmful gases.³,⁴ Then there are the plastics used to make the vehicle, most of which are made using catalysts.⁵ Indeed, without a catalyst many of the reactions used to make plastics are so slow that anything produced from them would be prohibitively expensive. Pharmaceutical drugs, fertilizers, explosives, margarine and even we (our body produces a large number of biocatalysts) would not exist without catalysts.⁶ Because of their immense impact on our lives, obtaining a better understanding of how catalysts work, and how to improve their efficiency, has the possibility of altering the daily lives of everyone on the planet.

1.2 Goals and Motivation

My research has focused primarily on catalysts used in industry for hydrocarbon reforming reactions and electrochemical applications. So, although I have worked on
some unsupported nanoparticle systems, most of my work has revolved around the synthesis and characterization of supported, noble metal nanoparticles. Of the systems investigated, Pt/γ-Al₂O₃ was the catalyst of choice for many experiments due to it being one of the most widely used industrial catalysts.⁷

Although many catalytic studies exist, most are more interested in understanding how to obtain desired products and product distributions than with what structural changes in the catalyst are the source of the observed behavior.⁸⁻¹⁰ Fortunately, more research is now focusing on understanding how the catalysis process occurs and seeking ways to optimize the outcome.¹¹ Although these studies frequently use reactions and catalysts previously discovered to have superior performance¹²⁻¹⁵ the focus is shifted toward understanding how the catalyst behaves so that an even better catalyst can be designed.¹⁶,¹⁷

Similar to the efforts of others, my work aims to understand how catalytic systems are put together and how these systems change when exposed to different conditions. Thus my work ranges from identifying crystallinity and elemental allocation to studying how the catalyst behaves as it is heated or exposed to adsorbates. The goal is not to discover the next important catalyst for a process. Our goal is to understand catalysts at a level so fundamental that we can design the optimal catalyst for any desired reaction.
References


CHAPTER 2
EXPERIMENTAL CHARACTERIZATION METHODS


2.1 General Comments

Each technique mentioned below can fill volumes on its mode of acquisition and capabilities. Here I have only sought to highlight a few important aspects of each method and provide one or two of the more thorough references I have encountered for each technique. These references should provide a reasonable starting place for anyone interested in finding out more about the technique and/or are useful for quick reference.

2.2 X-ray Absorption Spectroscopy (XAS)

One of the only methods of conducting in situ experiments on catalysts under realistic reaction conditions with atomic level characterization is XAS. Measurements are made at a synchrotron “beamline” (Figure 2.1) by directing high intensity X-rays onto the sample of interest. Specific X-ray wavelengths can be chosen using a monochromator, allowing for a range of photon energies to be scanned. Because each
element has unique, discrete energy levels for photon absorption, scanning over a selected energy range will offer element specific information.

The process that is being measured is shown schematically in Figure 2.2. If a sufficiently energetic photon hits the atom, it will eject an electron (photoelectric effect). The ejected “photoelectron” can then scatter off surrounding atoms, and the energy of the backscattered electron wave measured. Because the surrounding atoms create potential wells that interact with the photoelectron, constructive and destructive interferences can be seen in the detected signal and are dependent upon the scattering species. As a result, after the initial X-ray absorption and electron ejection, an oscillating signal caused by the photoelectron scattering back to the excited atom is obtained (Figure 2.3). There is, of course, also a smooth, single atom contribution (dotted line, Figure 2.3) which would arise even if no backscattering species existed.

The XAS spectrum is broken down into two primary regions: the X-ray absorption near-edge structure (XANES) and X-ray absorption fine structure (EXAFS) regions (Figure 2.3). Although there is no well defined limit to these ranges, the XANES region is generally considered to extend from 20 eV below the absorption edge to 50 eV above the absorption edge. Thus the EXAFS region is the decaying signal at energies more than 50 eV above the absorption edge. These distinctions were created because both sections offer different information about the system. Specifically, the XANES region provides useful information on the electronic state of the system whereas the EXAFS region yields information regarding bond distances (R), the root mean square disorder (Debye-Waller factor, $\sigma^2$) and coordination numbers (N). The remaining factors that are used when fitting the XAS equation (Figure 2.3b) relate to the electron wave vector ($k$),
the backscattering amplitude \((F(k))\), an amplitude reduction factor \((S_0^2)\) accounting for many-body processes, the mean free path of the electron \((\lambda)\) and phase shifts caused by neighboring species \((\phi)\). A nice overview of XAS is provided in the paper by Koningsberger.³

### 2.3 Diffraction

A variety of diffraction techniques exist, however, the basic principle is the same: incident radiation is reflected from the different layers of the material and the reflected waves interfere constructively or destructively depending on the distance between the layers and composition. The simplest example (Figure 2.4) is Bragg scattering, where the distance between atomic planes \((d)\) can be calculated by examining the crystal at a known angle \((\theta)\) and wavelength \((\lambda)\). Useful references are the solid state physics books by Ashcroft and Mermin⁴ and Kittel.⁵

In the case of measuring electron diffraction with a transmission electron microscope, a diffraction pattern (Figure 2.5a) is obtained when the detector is placed in the diffraction plane \((\text{vide infra})\). In the case where there are multiple orientations present, the sharp spots seen in a diffraction pattern will turn into diffraction rings (Figure 2.5b), as seen in powder diffraction measurements. A useful reference on transmission electron microscopes and techniques is Williams and Carter.⁶

### 2.4 Transmission Electron Microscopy (TEM) and Scanning Transmission Electron Microscopy (STEM)
The two main modes of operating a transmission electron microscope (Figure 2.6) are TEM and STEM (Figure 2.7). In the former, the electrons used to probe the sample form a broad, parallel beam. For STEM mode, the electrons are focused into a fine point that is rastered across the sample. Deflection of the electrons is approximately that of Rutherford scattering

\[
\frac{d\sigma(\theta)}{d\Omega} = \frac{e^4 Z^2}{16(E_0)^2 \sin^4 \frac{\theta}{2}}. \tag{2.4.1}
\]

In the above equation, \(d\sigma/d\Omega\) is the angular distribution of elastically scattered electrons, \(\theta\) is the scattering angle, \(e\) is the electron charge, \(E_0\) is the potential of the electron beam, and \(Z\) is the nuclear charge of the scattering atom. The strong \(Z\)-dependence makes STEM exceptionally good for distinguishing small particles and small particles – both supported and unsupported – as well as offering a visual means to distinguish compositional differences within particles containing two or more elements with large differences in \(Z\).

Many methods exist that use transmission electron microscopes either with, or without, additional hardware: nanobeam diffraction (NBD), selected area diffraction (SAED), convergent beam diffraction (CBD), coherent nanoarea electron diffraction, electron energy loss spectroscopy (EELS), tomography and energy dispersive X-ray spectroscopy (EDX or EDS) are among a few of these methods. EDX is perhaps the simplest and directly useful for the elemental characterization of small samples, particularly for larger \(Z\) elements (though a case can be made for EELS due to its sensitivity to lower \(Z\) elements). When EDX is used in TEM mode, a broad area is
illuminated by the electron beam and excites X-rays over a “large” area, giving more ensemble-like information. In contrast, coupling EDX with STEM can provide very location specific elemental information and is especially useful for characterizing single particles. Again, Williams and Carter\textsuperscript{6} is a useful reference for all things microscopy related.

2.5 Spherical Aberration-corrected STEM (C\textsubscript{s}-STEM)

Improved electron optics have been developed to remove various types of aberrations associated with focusing electron beams. One of the most recent advances has been the ability to correct for spherical aberration (C\textsubscript{s}). Image distortions from spherical aberration in electron microscopes are similar to those seen in optical systems and arise from the lens(es) focusing the beam to different points depending on how close to the optic axis the incident electrons (or photons) were (Figure 2.8).\textsuperscript{7} By introducing a lens with a negative spherical aberration coefficient (commonly a hexapole system in electron microscopes) this small difference in focal lengths can be corrected for and probe sizes below 1 Å can be attained – allowing for atomic resolution micrographs to be acquired. There are many papers that that discuss aberration correction in (S)TEM instruments, and here are a few.\textsuperscript{8-10}
2.6 Figures

**Figure 2.1.** Brookhaven National Laboratory, National Synchrotron Light Source image. This shows the storage ring (red) as well as one of the beamlines tunnels (green) and the station/hutch (purple). Adapted from: http://www.bnl.gov/physics/history/images/1980s/NSLS-schematic-470.gif.
Figure 2.2. Graphical depiction of the XAS process, showing an a) X-ray interacting with an atom and b) the backscattered photoelectron. The excited atom is shown in blue, scattering atoms in green and electrons/electron waves in yellow. Adapted from: Koningsberger, D. C.; Mojet, B. L.; van Dorssena, G. E.; Ramaker, D. E. Top. Catal. 2000, 10, 143.
Figure 2.3. a) Generic, normalized XAS spectrum showing the relative location of the XANES and EXAFS regions. Note that to make this a general example the x-axis is given in eV energy relative to the absorption edge – not the actual X-ray energy absorbed (as is normally done). The single-atom contribution to the signal is given by the dotted line. b) XAS equation describing the contributions to the observed signal. Adapted from: Koningsberger, D. C.; Mojet, B. L.; van Dorssena, G. E.; Ramaker, D. E. Top. Catal. 2000, 10, 143.
Figure 2.4. Depiction of Bragg scattering (Bragg’s Law: $n\lambda = 2d \cdot \sin \theta$, $n=$integer number of wavelengths).

Figure 2.5. Sample electron diffraction image obtained using a JEOL 2010-F scanning transmission electron microscope (STEM) for IrPt nanoparticles supported on $\gamma$-Al$_2$O$_3$. Bright peaks are diffraction spots. a) shows, mainly, a single crystal diffraction pattern while b) shows an electron diffraction pattern obtained when multiple crystalline orientations are sampled.
Figure 2.6. Schematic of a transmission electron microscope. Image was created by Sanchez, S. I.
Transmission Electron Microscopy

Major classifications

Transmission electron microscopy (TEM)
Scanning transmission electron microscopy (STEM)

Key Differences

- Uses a broad, parallel electron beam
- Records interference of electron waves
- Good for large (>2 nm) samples

- Rasters a focused electron beam over sample
- Records number of scattered electrons
- Good for samples with small, high-Z particles

Figure 2.7. Depiction of the two primary transmission electron microscopy methods.
Figure 2.8. Depiction of spherical aberration and its mode of correction.\textsuperscript{7}
References


CHAPTER 3
ENHANCED ATOM IDENTIFICATION AND SHORT RANGE ORDER CHARACTERIZATION USING ABERRATION-CORRECTED SCANNING TRANSMISSION ELECTRON MICROSCOPY

3.1 Abstract

Analysis of aberration-corrected scanning transmission electron microscopy (CSTEM) images can be greatly improved by accounting for the isotropic scattering of individual atoms/columns. Herein we show how this approach can be used to assign confidence limits to the locations of atoms/columns and that a normalized, radial distribution function (RDF) and angular distribution of nearest neighbors can be used to identify ordering within both unsupported and γ-Al₂O₃ supported Pt nanoparticles.

3.2 Introduction

The distinction between real data and artifacts is usually defined by how far individual measurements deviate from some norm or smoothly varying function; with anything lying beyond a specified range considered an outlier. Despite the seemingly simple goal of separating these signals, a large amount of research effort has been devoted to developing methods that effectively parse artifacts/noise from data.¹⁻⁷ Unsurprisingly, many of the techniques used to improve the quality of microscopy images are similar to those used in astronomy or other image intensive fields. Three approaches used (or combined) to improve the quality of and/or analyze images are, 1) applying a threshold to select signal intensities within a desired range;⁵,⁸,⁹ 2) using a
kernel to limit noise by scaling each pixel’s intensity based on the intensity of those in its vicinity;\textsuperscript{1,3,10-12} and 3) removing background intensity by subtracting some contribution (e.g., a smoothly varying function, a gaussian blurred image, using fourier filtering, etc.).\textsuperscript{1,2,4,10,13,14} These methods work especially well when the supporting material or system have distinct differences, but experience limitations as the size of background intensity fluctuations and the object of interest become comparable.

Part of the difficulty in differentiating small particles on high-background specimens has been overcome by the creation of scanning transmission electron microscopy, which easily differentiates small, high atomic number (Z) particles from low-Z supports.\textsuperscript{10,15-17} Recent advances in electronic optics have led to further improvements, most notably the creation of aberration-corrected electron microscopes.\textsuperscript{18-21} These instruments are able to resolve individual atoms and have resulted in multiple studies that would have been extremely difficult – or impossible – using any other technique.\textsuperscript{22-24} Because aberration-corrected electron microscopy is such a nascent technique, its capabilities to obtain insights into the atomic structure of different systems are still being actively explored.\textsuperscript{14,23,25,26} As the technique matures, however, analytical methods must be developed to analyze the images acquired more quantitatively, much as diffractive imaging techniques have been used to expand the abilities of conventional transmission electron microscopy.\textsuperscript{27-29} Namely, the ability to resolve individual atoms/columns and their intensities offers a way to obtain detailed information about structural ordering within a system. There are reports that have used C\textsubscript{e}-STEM to determine the relative number of atoms within a region\textsuperscript{15,30,31} and measure surface relaxation.\textsuperscript{23} We are unaware, however, of any reports that attempt to determine the
extent of long – or short – range order within structures using only CSTEM images nor of any studies that seek to quantify the relative abundance of free atoms on supported materials.

3.3 Experimental Methods

Sample preparation, unsupported Pt: Samples were prepared by dissolving 26.1 mg of H₂PtCl₆·H₂O (Sigma-Aldrich) in 50 mL of deionized water along with 556.3 mg of polyvinylpyrrolidone (MW=40,000 g/mol, Sigma-Aldrich) (PVP) under N₂ and magnetic stirring. After stirring for 30 minutes at 0°C, 24.4 mg of NaBH₄ dissolved in 5 mL of deionized water was quickly added to the solution and allowed to react for 1 hour.

Sample preparation, Pt/γ-Al₂O₃: Samples were prepared using the incipient wetness method to impregnate γ-Al₂O₃ (Alfa Aesar, surface area 220 m²/g) with Pt to a loading of 0.5 wt % using the desired precursor: (NH₃)₄Pt(OH)₂ (Strem Chemicals, Inc.) or H₂PtCl₆ (Strem Chemicals, Inc.). Two different procedures were used to induce cluster formation. The first treatment method involved reducing the sample in H₂ for 30 minutes at room temperature followed by reduction in H₂ at 573 K for 1 hour and subsequent cooling to room temperature in H₂. The second treatment method was identical to the first with the exception that the sample was calcined in air for 1 hour at 573 K and allowed to cool to room temperature (in air) prior to undergoing the aforementioned reduction procedure.

CSTEM acquisition: CSTEM images were acquired using a JEOL model 2200-FS electron microscope operated at 200 kV. Ethanol suspensions of the appropriate
sample were deposited onto Cu TEM grids coated with a holey carbon film (Ted Pella, Inc.) for imaging.

*Atom identification:* Images were analyzed using an in-house Matlab program. Identification of atoms/atomic columns was accomplished by defining several parameters: 1) the atom diameter ($R_{\text{atom}}$); 2) a distance beyond the atomic radius to define the local background ($R_{\text{cut-off}}$); 3) the number of standard deviations ($n$) above the local background required to be considered as a possible atom/column; and 4) the number of standard deviations above the mean, probability-scaled intensity to constitute an atom/column.

Briefly, a circular area commiserate with the defined atom diameter is compared to a surrounding annular region. If the total intensity of the central region exceeds that of the surrounding region by the specified number of standard deviations (of the annular region) a probability-weighted intensity is assigned to that location. This value is based on the probability that the location’s average intensity is a statistical (gaussian) fluctuation of the annular region’s or the annular region’s average intensity is a fluctuation of the central region’s. The locus of the central region is then incremented by one pixel and the process repeated. Finally, the composite of “probable” atoms/columns is limited to only those with an intensity above a desired cut-off. This image can then be analyzed using in-house, open source or commercial image processing software. A pictorial description of steps 1-3 has been provided in Scheme 3.1.

For comparative purposes, the particle finding/analysis/filtering tools in DigitalMicrograph (Gatan, Inc.) were used to attempt a similar identification of atoms/columns. In one instance, simple thresholding was used to select high-intensity
regions. For the second approach, the difference between the image filtered once and twice using a standard 3x3 unsharp kernel was subjected to three 7x7 unsharp convolutions and thresholded to identify species. This procedure was found by trial-and-error to yield good results.

**RDF determination:** The image containing identified atoms/columns was further analyzed by our Matlab program to identify the center of each atom/column and find all pair distances up to a desired distance from each atom/column. To create the normalized RDF the pair distances were first separated into discrete bins. Then the area swept out by each bin from the point of origin up to the desired distance was determined. For this step it is necessary to correct for the finite size of the micrographs. Finally, the number of atoms/columns was normalized to the largest bin population.

**Angular distribution determination:** One atom/column is chosen. A search is then done to locate all combinations of two other atoms within a specified cut-off distance (in our case 3 Å). The smallest angle between these three locations (where the first location is then vertex) recorded. This process is repeated for all atoms/columns within the image. As an example, an equilateral triangle would have 6 measurements all yielding 60° (total number of measurements is: \(3C_1 \times 2C_1 \times 1C_1\), and all angles are equivalent in this example).

### 3.4 Results/Discussion

The introduction of C₅-STEM has allowed further resolution to be achieved, but it also means that previously minor or unobservable background contributions become apparent when trying to acquire a low noise image. Advantageous carbonaceous species,
non-zone axis particle orientation and thermal motion are just a few of the difficulties that are encountered. Attempts to mitigate these confounding factors have taken several approaches including the use of thinner support materials, fourier filtering and other background removal algorithms. One approach to improving atom/column identification is to customize the algorithm for atomic resolution systems. Specifically, the methods previously noted are versatile because they do not place restrictions on the shape of the species being identified. While this may be advantageous for images where the relative size and shape of interest may change, it does not take advantage of the nearly constant diameter and circular scattering profile of atoms/columns in atomically resolved C$_s$-STEM images. Toward this end, we have developed a Matlab program that automatically identifies atoms within an image, creates a RDF and analyzes the distribution of angles defined by three neighboring species. Initial identification of atoms/columns is accomplished by defining a circular region and comparing it to the immediate surroundings (Scheme 3.1). Comparison of the region to only the immediate surroundings offers a simple way to account for localized background fluctuations within the image. More important is the ability to define a priori specific limitations for what constitutes an atom/column based on region size and relative intensity. This permits quantitative control over what is considered an atom/column instead of simply enhancing aspects of an image (Figure 3.1).

One example of how our method compares to more traditional methods – analyzed using DigitalMicrograph (Gatan, Inc.) – is given for an unsupported Pt nanoparticle in Figure 3.2. Identification of atoms/columns in this sample image (Figure 3.2a) have been made using three different methods. The first method (Figure 3.2b) uses
only thresholding to select signal intensities within a desired range. As can be seen, the noise within the image leads to a rapid deterioration in the ability to resolve individual atoms/columns toward the center of the cluster. Figure 3.2c shows that a significant improvement can be obtained by using a combination of unsharp filters, image subtraction and thresholding of the final result. The chief limitation of this method is the need to qualitatively select a cut-off intensity for each image analyzed and the generation of asymmetric signals – making it difficult to determine a reasonable threshold (Figure 3.1). Figures 3.2d and 3.2e show the species identified using our method and a mapping of the original intensities onto these locations (displayed for clarity at a slight angle relative to Figure 3.2a), respectively. The initial selection criteria used was to have an atomic diameter of ~1.35 Å (based on the experimental images), and a mean intensity at least one standard deviation above the average background of an annular region extending 1.35 Å beyond the atom/column. Equivalently, there is less than a 16% chance that such a strong intensity could be caused by fluctuations in the background intensity. To make things even more quantitative, the intensities of the species found can be scaled based on the probability of being a statistical fluctuation of the background or that the background is a statistical fluctuation of the central region. This also offers a convenient means of emphasizing free atoms by extending the “background” region to overlap with distances seen in bulk materials. In the case of Figure 3.2d, we have limited our analysis to the top 76% of the scaled intensities calculated. As a result, easily identifiable atoms/columns weighted by their difference from background can be seen in Figure 3.2d.

In Figures 3.3a and 3.3b we show our filtered image, and how pair distances and angles are defined, respectively. For creation of the RDF (Figure 3.3c), atom/columns
pairs are calculated for distances up to 1.5 nm. Similarly, by choosing a single location to act as an origin and creating vectors to two other species (here limited to within 3 Å of the first to mimic nearest-neighbor selection), it is possible to determine the frequency of an angular relation, \( \theta \), between 0 and 180° (Figure 3.3d). For both Figures 3.3c and 3.3d the results from an ideal, 2 nm Pt crystal (truncated cuboctahedron) oriented along different zone axes is shown for comparison (see also Figure 3.4 and 3.5). Both Figures 3.3c and 3.3d show that the experimental data overlaps well with that expected for a [110] orientation. This is also in agreement with Figure 3.2a’s power spectrum (inset, Figure 3.2a).

Very rarely are ideal systems encountered in real applications. For example, \( \gamma \)-Al\(_2\)O\(_3\) supported Pt nanoparticles are heavily used in petroleum reforming\(^{32-36} \) and present a case wherein the topological support results in a background that can vary on the nanometer scale. Since the catalytic activity of this system is dictated by the number of Pt atoms accessible to reactants, the extent of metal dispersion is of particular concern. Industrial preparation of Pt/\( \gamma \)-Al\(_2\)O\(_3\) usually proceeds by impregnation of \( \gamma \)-Al\(_2\)O\(_3\) with an aqueous solution of H\(_2\)PtCl\(_6\) followed by drying, calcination and, finally, reduction of the catalyst.\(^{34,37,38} \) Previous reports have noted that the calcination procedure results in an increased dispersion, purportedly through the production of strong binding sites generated by dehydrating the alumina surface.\(^{34,38} \) On the other hand, PtO\(_x\)Cl\(_y\) species are implicated as the mobile species\(^{39-41} \) present during catalyst regeneration and should not be discounted. If calcination contributes to dispersion, irrespective of the presence of Cl species, then a difference in the level of atomically dispersed species on \( \gamma \)-Al\(_2\)O\(_3\) should be apparent if it is used during synthesis.
To investigate how different synthesis procedures affect the Pt dispersion, we have prepared several samples with similar particle sizes for C$_x$-STEM characterization using H$_2$PtCl$_6$ and (NH$_3$)$_4$Pt(OH)$_2$ (Figure 3.6). Each precursor was impregnated into the alumina support and either reduced or calcined and then reduced; producing a total of four samples (Scheme 3.2). If the presence of Cl and calcination are both relevant to atomic dispersion then the atomic dispersion should increase: (NH$_3$)$_4$Pt(OH)$_2$ (uncalcined) $<$ (NH$_3$)$_4$Pt(OH)$_2$ (calcined) ? H$_2$PtCl$_6$ (uncalcined) $<$ H$_2$PtCl$_6$ (calcined); where “?” indicates that the relative importance of calcination versus Cl on the final dispersion is unknown.

As a metric of comparison, we have chosen to use the ratio of free atoms observed to the number of clusters (FAC ratio) from a series of micrographs. Because of the large amount of variability between individual images caused by sample heterogeneity and the inherent limitations of using a localized measurement technique, the ratios reported are not absolute. They do, however, offer a way to compare the relative frequency of free atoms versus clusters for the different syntheses. By optimizing our algorithm’s parameters for one sample and applying them to the other three samples (acquired under identical conditions), we achieve a consistent comparison. Specifically, the atomic diameter was again taken to be 1.35 Å and the background was taken to extend 2.70 Å beyond this. Species were taken to be those regions with an intensity at least 1.5 standard deviations (<7% chance of misidentification) above background. Of the scaled intensities accounting for the variation in both the background and species, only the lowest 0.1% of the intensities were excluded.
Images showing the (approximately) mean FAC ratios obtained for all samples when excluding atoms within clusters are shown in Figure 3.7 (identified species circled in red). From the results, we can conclude that the FAC ratio is essentially unchanged except for the H$_2$PtCl$_6$ (calcined) sample. Examination of the 2D PDFs (Figure 3.8) shows an apparent disconnect between the calcined and uncalcined samples, with the calcined samples exhibiting a broader peak and a larger distance for the maximum Pt-Pt value. Using higher magnification images and loosening the atom/column identification criteria to include more central cluster atoms (0.75 standard deviations above background, background extending 1.35 Å) shows that the most common Pt-Pt distance is not shifted between samples (Figure 3.9). Instead, the apparent change in Pt-Pt distances is caused by the initial exclusion of many Pt-Pt distances toward the clusters’ cores. Both precursors, however, do have broadened Pt-Pt distance distributions when a calcination step is used. Such an observation is consistent with the calcined samples forming diffuse clusters relative to their uncalcined counterparts. Importantly, this indicates that the calcination step affects the morphology of clusters derived from different precursors but does not result in a high level of free atoms unless Cl is also present.

3.5 Conclusions

In conclusion, implementation of an algorithm designed to utilize known aspects of atomic dimensions and the symmetric scattering profile of atoms/columns allows for improved identification within C$_x$-STEM micrographs. Using this data to create a normalized radial pair distribution function promises to be a useful method for the
characterization of atomic resolution images. We have demonstrated the capabilities for structural characterization and selection of free atoms by examining both crystalline, unsupported Pt nanoparticles and Pt/γ-Al₂O₃ samples obtained via different synthesis methods. The results indicate the power of this method as a tool for gaining insight into the structure and ordering of nanoscale systems.

3.6 Acknowledgements

We would like to thank Dr. Jian-Min Zuo for several useful discussions. This work was sponsored in part by a grant from the U.S. Department of Energy (DE-FG02-03ER15476). Experiments were carried out at the Frederick Seitz Materials Research Laboratory Central Facilities, University of Illinois, which are partially supported by the U.S. Department of Energy under Grants DE-FG02-07ER46453 and DE-FG02-07ER46471.
Scheme 3.1. Depiction of atom identification method. R indicates a radius, I the intensity and n a number.
Figure 3.1. a) Random intensity pattern. b) Random intensity pattern analyzed using the same thresholding as Figure 3.2c (main text). c) Random intensity pattern analyzed using our algorithm and the parameters using in Figure 3.2d (blank image - no species found). d) Random series of “atoms” generated. e) RDF of d), demonstrating a lack of preferred atom/column pair distances for random atom/column arrangements. f) Normalized, angular distribution of the random points (3 Å cut-off).
**Figure 3.2.** Atomic columns and atoms of an unsupported Pt nanoparticle identified using different methods. For the different images: a) raw micrograph (20M magnification, power spectrum inset); b) threshold (green) analysis; c) analysis using a series of filters and thresholding; d) analysis using our method. e) 3D, angled view of the a) for areas satisfying filter conditions in d).
Figure 3.3. a) Species identified by our algorithm. b) Magnified view of a selected region of a) with sample pair distances and an angle defined. c) Spline graph showing the normalized RDF of the pair distances found in a). d) Spline graph showing the normalized occurrence of acute, 3-species angles (pair distance < 3 Å) for a).
Figure 3.4. Projections of Pt’s unit cell along select zone axes and the distances between the projected atoms/columns.
Figure 3.5. RDFs for ideal, truncated cuboctahedral, 2 nm Pt crystals oriented along select zone axes (projected potential inset) and the angular distribution of each crystal.
Figure 3.6. Particle size distributions and sample micrographs for the different samples:

a) H\textsubscript{2}PtCl\textsubscript{6}, calcined; b) (NH\textsubscript{3})\textsubscript{4}Pt(OH)\textsubscript{2}, calcined; c) H\textsubscript{2}PtCl\textsubscript{6}, uncalcined and d) (NH\textsubscript{3})\textsubscript{4}Pt(OH)\textsubscript{2}, uncalcined. Histogram insets detail average sizes and standard deviations for each sample.
Scheme 3.2. Synthesis methodology of $\gamma$-Al$_2$O$_3$ supported particles.
Figure 3.7. Atomic columns and atoms of γ-Al₂O₃ supported Pt nanoparticles identified (red circles) for samples synthesized using 4 different methods: a) H₂PtCl₆, calcined; b) (NH₃)₄Pt(OH)₂, calcined; c) H₂PtCl₆, uncalcined and d) (NH₃)₄Pt(OH)₂, uncalcined. Inset text gives the mean and median number FAC ratio from a series of images of each sample. All images were taken at a magnification of 10M.
Figure 3.8. Composite RDFs for multiple images taken at 10M for each sample plotted as a spline curve. Atoms are defined as being a region of 1.35 Å that is at least 1.5 standard deviations above the surrounding background (between 1.35 and 5.40 Å from atom center). a) H$_2$PtCl$_6$, calcined; b) (NH$_3$)$_4$Pt(OH)$_2$, calcined; c) H$_2$PtCl$_6$, uncalcined and d) (NH$_3$)$_4$Pt(OH)$_2$, uncalcined.
Figure 3.9. Composite RDFs for multiple images taken at 15M for each sample. Atoms are defined as being a region of 1.35 Å at least 0.75 standard deviations above the surrounding background (between 1.35 and 2.70 Å from atom center). Of the resultant, probability scaled, intensities the top 59% were considered to be “atoms”. a) H$_2$PtCl$_6$, calcined; b) (NH$_3$)$_4$Pt(OH)$_2$, calcined; c) H$_2$PtCl$_6$, uncalcined and d) (NH$_3$)$_4$Pt(OH)$_2$, uncalcined.
References


CHAPTER 4

STRUCTURAL CHARACTERIZATION OF Pt-Pd AND Pd-Pt CORE-SHELL NANOCLUSTERS AT ATOMIC RESOLUTION


4.1 Abstract

We describe the results of a study at atomic resolution of the structures exhibited by polymer-capped monometallic and bimetallic Pt and Pd nanoclusters—models for nanoscale material electrocatalysts—as carried out using an aberration-corrected scanning transmission electron microscope (STEM). The coupling of sub-nanometer resolution with Z-contrast measurements provides unprecedented insights into the atomic structures and relative elemental speciation of Pt and Pd within these clusters. The work further defines the nature of deeply quenched states that prevent facile conversions of core-shell motifs to equilibrium alloys and the nature of non-idealities such as twinning (icosahedral cores) and atomic segregation that these structures can embed. The nature of the facet structure present in these model systems is revealed by theory directed modeling in which experimental intensity profiles obtained in Z-contrast measurements at atomic resolution are compared to simulated intensity profiles using theoretically predicted cluster geometries. These comparisons show close correspondences between experiment and model and highlight striking structural complexities in these systems that are compositionally sensitive and subject to amplification by subsequent cluster growth
processes. The work demonstrates an empowering competency in nanomaterials research for STEM measurements carried out using aberration corrected microscopes, approaches that hold considerable promise for characterizing the structure of these and other important catalytic materials systems at the atomic scale.

4.2 Introduction

Understandings of homogeneous and heterogeneous catalysis have benefited greatly from the insights into materials structure developed through the use of electron microscopy.\textsuperscript{1-4} Using this analytical technique, it is possible to determine features critical to catalytic performance that include: supported catalyst particle mass distributions,\textsuperscript{5-8} crystallographic structure,\textsuperscript{1,3,4,9,10} and the speciation of specific forms of structural complexity and/or defects.\textsuperscript{11-14} Beyond such visual and diffraction centric forms of analysis, there have evolved additional techniques that strongly compliment and extend the analytical capacities of electron microscopy – ones yielding information pertaining to the chemical nature of catalytic materials as well as their electronic structure.\textsuperscript{15-19} Energy dispersive x-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS) are among the more common techniques paired with imaging and diffraction that serve to offer such forms of compositional and chemical information.\textsuperscript{14,15}

The deep capacities for structural characterization that analytical electron microscopy provides for studies of catalysts notwithstanding, there still remain some important limitations. The use of EDS to quantitatively probe the composition of materials, for example, is limited by the low detector collection efficiency. For small nanoparticles, the electron dosage required for successful EDS analysis is often too high and beyond the radiation damage thresholds of nanoparticles.\textsuperscript{20} The dearth of knowledge
concerning the surface structures (and composition) of small particles - features that are
difficult to characterize by microscopy - also presents a major hindrance to progress in
correlating such aspects with catalytic response to provide an atomistically rationalized
basis for the formulation of predictive structure-property and structure-rate correlations in
heterogeneous catalysis. This shortcoming is particularly significant given the likely
emergence of important forms of mesoscopic behaviors in material systems in this size
range. In addition to such pictures related to the size of a catalyst particle - which can
elicit changes to a cluster’s bonding geometry and catalytic behavior\textsuperscript{3,21,22} - hybrid
structures such as bi-(multi-) metallic catalysts present additional forms of complexity
where the nature and bonding of a metal surface is altered by the specific placements
adopted by the different atoms of a binary (or higher) composition\textsuperscript{23,24}. Such changes
from homo- to heterometallic coordination,\textsuperscript{25-28} in combination with the strain associated
with lattice mismatches,\textsuperscript{23,24} can further contribute to modifications of the catalytic nature
of a material and, unfortunately for all but highly specialized model systems, remain very
poorly understood. This larger deficiency provides a strong motivation for work seeking
to provide a more thorough understanding of a catalyst’s structure at the atomic scale, the
focus of the work reported here.

The conventional use of high-angle-annular-dark-field scanning transmission
electron microscopy (HAADF-STEM) allows one to probe the microstructures of
catalytic materials with resolution of a few angstroms.\textsuperscript{15} This method relies on the
detection of electrons that are scattered at high angles relative to the transmitted beam
(Rutherford scattering) using an annular detector.\textsuperscript{14,29} At large scattering angles the
scattering intensity is strongly and quantitatively dependent on the atomic number (Z) of
the element interacting with the electron beam, varying proportionally to $Z^4$ and with the thickness of the material (i.e. number of stacked atoms). The power factor, $X$, equals 2 for Rutherford scattering in the limit of electron single scattering. Electron multiple scattering and electron probe propagation in thick samples can lead to values of $X$ that are lower than 2. Nonetheless, the image contrast remains strongly dependent on $Z$. This strong dependence on $Z$ provides the quantitative foundation for so-called Z-contrast imaging; a technique that allows high-contrast imaging of high-Z elements (such as the noble metals in a heterogeneous catalyst) against the background of a low-Z material (such as a support phase). Such Z-contrast imaging results in more accurate size and composition determinations as compared to conventional bright-field transmission electron microscopy.

The present work explores the exceptional analytical capacities of Z-contrast microscopy extended to the limit of atomic resolution, applying it to the study of model binary clusters of interest in electrocatalysis. The data presented in this report follow from the advent of the spherical aberration (Cₐ) corrected electron microscopes, that provide dramatic improvements in image quality (subangstrom resolution and improved signal to noise ratios from the use of a large condenser aperture), pushing the limitations of atomic scale imaging and fostering new capacities for atomic level speciation of complex bonding motifs for materials. The enhancements afforded by Cₐ-corrected imaging are making accessible unprecedented forms of information regarding atomic scale structural features as well as enabling the discernment of elemental composition within a sample when employed in the HAADF-STEM mode.
This work utilizes these latter competencies, providing structural characterizations of Pd-Pt and Pt-Pd core-shell nanoclusters at atomic resolution. Recent work has exploited similar capacities to specify elemental variations within alloyed Pt-Co nanoparticles. In that study, line scans mapping the intensity across the diameter of the particles showed random fluctuations in the intensity of neighboring peaks, fluctuations ascribable to scattering from lower (Co) and higher (Pt) Z elements within a cluster. In work conducted by Li et al., an intensity diagram (obtained using a sub-angstrom probe) was combined with HAADF-STEM simulations to gain insight into the geometry of Au nanoparticles deposited by a soft-landing method onto an amorphous carbon support. Comprehensive studies conducted by Rosenthal et al. made use of the Z-contrast imaging and modeling to characterize compositional and structural features of biologically active Cd-Se nanoparticles. This latter study utilized Rutherford backscattering experiments and intensive imaging techniques to index the crystal facet planes of the Cd-Se/Zn-S nanocrystals and identify hierarchical structural motifs related to their core-shell structure.

In this report we use controlled synthetic techniques and C\textsubscript{s}-corrected imaging to describe the atomic structure and elemental segregation of both monometallic and bimetallic Pt and Pd nanoparticles, materials currently utilized as electrocatalysts. Using modifications of literature methods, we synthesized and subsequently analyzed Pt(core)-Pd(shell) and Pd(core)-Pt(shell) nanoparticles with cluster diameters lying in the range of 2-4 nm. Empirical examinations of the images and more quantitative analyses of integrated intensity profiles, when developed in conjunction with theory supported modeling, provides deep insights into the atomic-level structural features present in these
model binary metal nanostructures. We find striking, and also surprising, morphological differences between the monometallic Pt and Pd nanoparticles - a divergence in structure that is also reflected in and amplified by the structures of the bimetallic clusters formed from them via a seeded nucleated growth process. Fourier transforms (FT) of the atomic resolution images allow derivation of crystallographic data that in turn allow the assignment of truncating planes, crystal orientations, as well as specific forms of nanoparticle structure that are sensitive to and reflect the nature of metastable states in materials at this scale. The present data collectively support the importance of dynamical models - energy landscapes - to the atomic structures of metal nanoparticle catalysts and, potentially, for their catalytic behaviors as well.

4.3 Experimental Methods

*Nanoparticle preparation.* Polyvinylpyrrolidone (MW = 40,000 g/mol) (PVP)-capped monometallic Pt and Pd nanoparticles were synthesized using an alcohol reduction method. Metal precursors [266 mg of H$_2$PtCl$_6$ (FW = 409.82 g/mol) or 136 mg of Pd(OAc)$_2$ (FW = 224.50 g/mol) for Pt and Pd, respectively] were independently refluxed in a 300 mL ethylene glycol solution in the presence 2.5 g of PVP. Removal of excess PVP was accomplished by centrifuging aliquots of the PVP-capped Pt (or Pd) nanoparticle solution with 5 equivalents of acetone. After centrifugation, the isolated particles were resuspended and stored in ethanol.

The synthesis of core-shell nanoparticles was carried out using a method similar to that previously described by Toshima *et al.*, one involving the use of a “sacrificial hydrogen layer.” The premade, ethanol-stored monometallic Pt (or Pd) nanoparticles
were flushed with ultra-high purity H$_2$ (g) for 3 hrs followed by the purging of unadsorbed H$_2$ with N$_2$ (g) (2 hrs). Solutions of the hydrogen-coated Pt nanoparticles were then treated with a dilute degassed solution containing appropriate amounts Pd(OAc)$_2$ (~ 0.38 mM) dissolved in an acetone/H$_2$O mixture. Premade Pd nanoparticles were treated with a dilute degassed solution (~0.34 mM) containing appropriate amounts of H$_2$PtCl$_6$ (aq). The addition of the secondary metal solution in each case was paced at a rate no faster than 20 mL/hr under a N$_2$ flow.

A random alloy was obtained by the co-reduction of 271 mg of H$_2$PtCl$_6$ and 117 mg of PdCl$_2$ (FW = 177.31 g/mol) refluxed in a 300 mL methanol/H$_2$O mixture (1:1, v/v) degassed (N$_2$) solution containing PVP (3.02 g). All chemicals were purchased from Sigma-Aldrich ®.

**Electron microscopy.** Samples for low magnification STEM imaging were prepared by dip coating a holey carbon film supported on a Cu grid (SPI Supplies) into the nanoparticle suspensions. Size and energy dispersive x-ray spectroscopy (EDS) measurements were made on individual nanoparticles to ensure the presence of Pt and Pd atoms using a JEOL model 2010F electron microscope operated at 200 keV equipped with an Oxford INCA 30mm ATW detector for energy dispersion x-ray spectroscopy. The instrument used an electron beam focused to 0.5 nm as a probe during individual nanoparticle sizes and EDS measurements of the Pd L$_3$ and Pt M edges. The average sizes for the monometallic Pt and Pd nanoparticles were 2.36 +/- 0.44 and 2.44 +/- 0.37 nm, respectively (Figure 4.1). The average sizes for the bimetallic nanoparticle samples were; 3.29 +/- 0.62, 3.53 +/- 0.64 and 2.49 +/- 0.47 nm corresponding to the Pt(core)-Pd(shell), Pd(core)-Pt(shell) and Pt-Pd alloy samples, respectively (Figure 4.2). The
Pt(core)-Pd(shell) nanoparticles prepared at a 1:1 ratio (Pt:Pd) gave values of 49 atom % Pt with 51 atom % Pd (1.0 % error), respectively. The Pd(core)-Pt(shell) nanoparticles prepared at a 1:1 ratio (Pd:Pt) afforded corresponding EDS values of 53 atom % Pd with 47 atom % Pt (2.4 % error). The alloy yielded bulk EDS results of 45 atom % Pt with 55 atom % Pd (3 % error). Taken together these results present data in line with expectations based on the stoichiometric ratios used in the synthesis process. Particle sizes were determined by measuring the diameter cross-section of individual particles using DigitalMicrograph™ (Gatan Inc.) software. Samples for C₅-corrected imaging were similarly prepared by dip-coating ultrathin holey carbon films (Ted Pella Inc.) supported on Cu grids into the colloidal suspensions. These images were obtained using a JEOL model 2200-FS electron microscope operated at 200 keV.

**Theoretical modeling.** Several software programs were used to analyze and simulate the HAADF-STEM data. The structures of idealized crystals were created and manipulated using the Visual Molecular Dynamics (VMD) program to provide a structure that more accurately reflected the appearance of the experimental images. Optimized crystal structures were then deduced using the STEM image simulation program (ZMULT) developed by Zuo. This program is based on the multislice method of Cowley and Moodie.\(^ {42,43}\)

For the crystals under consideration, lattice constants of Pt (3.92 Å) and Pd (3.89 Å)\(^ {44}\) were used for cuboctahedral and icosahedral structures, respectively (see below). Models for both mono- and bimetallic nanoparticles were created based on these two limiting structural forms. For the bimetallic structures, the core structure was used to dictate the overall conformation of the particle. For the case of the Pd(core)-Pt(shell), this
required that the Pd core was taken to be an icosahedron; whereas for the Pt(core)-Pd(shell) structure had the growth of the Pd atoms occurred on a cuboctahedral core structure (see below).

To provide meaningful comparisons with the experimental data, the simulated structures were rotated such that the orientation of the nanoparticle used for the simulation was identical to that determined via analysis of the experimental image FT. This alignment was checked by validating that the FT of the simulated crystal’s projected potential gave the appropriate spatial frequencies. It should be noted that this procedure was not possible for the icosahedral particles due to the extensive twinning present in that case.

Scans were conducted using a box with an edge length 20 Å larger than the largest crystal examined. This box was then pixilated into a 512×512 region. Within this area, a sector of interest was chosen that comprised 10% of the y-axis (centered on the crystal) and 100% of the x-axis. Scanning/simulation of this region produced a potential map that was analyzed using DigitalMicrograph™ (Gatan, Inc.) for subsequent comparison with the experimental intensity profiles of the same region of the crystal.

**X-ray Diffraction.** The XRD data acquisition was carried out at the beamline 1ID at the Advanced Photon Source (APS), Argonne National Laboratory. Ethanol suspensions of monometallic and bimetallic Pt-Pd NPs were sealed in glass capillaries and measured with x-rays of energy 78.390 keV. The white synchrotron beam was dispersed by a combination of a pre-monochromator (two vertically-diffracting, asymmetrically-bent Laue crystals) and a 4-crystal, high-energy resolution (E/E~ 8 eV) monochromator. The monochromator was calibrated by measuring the K absorption edge of a thin foil of pure Au. Scattered x-rays
were collected by a Ge solid state detector coupled to a multi-channel analyzer. Integrated counts of these ranges were collected several times up to wave vectors of 25 Å⁻¹ and then averaged to improve the statistical accuracy. In total, the data collection time for a sample at a given energy was about 5 h.

4.4 Results/Discussion

Figure 4.3a shows a representative Cₜ-corrected HAADF-STEM image of a PVP-protected Pt nanoparticle. The inset to the figure is the FT (diffraction data) of the cluster, which indicates a [001] zone axis with the evident (002) lattice planes as indexed in the image. The sharp peaks in the FT indicate that a well ordered crystalline state characterizes these samples. A tabulation of the diffraction data for all samples analyzed is given in Tables 4.1 and 4.2. Several general trends are evidenced there. The Pt particles supported on the carbon film of the TEM grid were generally found to be oriented along either the [001] or the [011] zone axes, consistent with the polyhedral forms predicted by theory to be the most stable (cuboctahedron and cubes, respectively Figure 4.4). Integrated areal intensity profile measurements, and modeling describing the atomic structure of a particular Pt particle shown are given in Figure 4.5. The areal scans reflecting the number of Pt atoms lying within a single column, show a typical (and expected) hemispherical profile as the cluster diameter is traversed (quantitatively, the lower intensities at the peripheries indicate that fewer atoms are stacked at these positions). The model (Figure 4.5b) quantitatively replicates these effects by using the specific crystal orientation and truncating planes shown in Figure 4.5a. The profiles are those expected for a cuboctahedron cluster structure. The experimental and simulated
profiles show clearly discernable peaks, thereby enabling the measurement of interatomic pair distances by calculating the separation between intensity peaks up to the limit of the microscope scan precision. This analysis suggests a lattice constant for the Pt particles of $3.8 \pm 0.2$ Å along the [001] zone axis (Figure 4.3a), a value within the uncertainty limit of literature values for bulk Pt ($3.92$ Å).\textsuperscript{44}

The structures adopted by monometallic Pd nanoparticles are far more complex, their structures can be described using models of crystals embedded with a multitude of defects in the form of twins and dislocations (Figure 4.3b and Figure 4.6). Figure 4.3b shows a representative image of such a Pd nanoparticle. The image FT (inset) shows that these samples lack the single-crystalline qualities exhibited by the Pt clusters. The pattern in the inset demonstrates a non-crystallographic spectrum and significant broadening of the spatial frequencies in the FT as a consequence of the much finer crystalline grain, and multiple domains, that in turn result in a more ambiguous nature for the truncating lattice planes at the surface (Figure 4.6). Examinations of intensity profiles for the Pd clusters revealed Gaussian-like shapes, a finding qualitatively similar to that of the Pt cluster, albeit with the distinction that the spacings between atomic planes can not be resolved for the more distorted Pd particles. The disorder exhibited by the monometallic Pd nanoparticles can be explained by unusual examples of structural disorder imparted by the dimensional confinement of the particle as it decreases in size from its bulk state. One such example was offered by Gilbert et al.\textsuperscript{47} where competitive forces of surface relaxation give rise to “inhomogeneous internal strain.” Alternatively, it has been noted that Pd tends to adopt either an icosahedral or decahedral conformation within this size regime.\textsuperscript{48,49} Using Zmult we obtained the projected potential for both
icosahedral and decahedral structures at various orientations. Repeated application of a Gaussian blur convolution to the projected potentials allowed us to make semi-quantitative comparisons between the areal intensity maps of experimental images and images with similar appearances generated from the projected potential (Figure 4.7). Of the many images we were able to model using this protocol, we found that the structures of these monometallic Pd nanoparticles were best defined by an icosahedron. These simulations of experiment - representative examples of which are provided in Figure 4.7 - specifically show projections of symmetries (including the 2-fold axis) expected for icosahedra.

The samples in Figure 4.3a and b can be further modeled quantitatively to provide an estimation of the number of atoms contained within the particles, we analyzed images of many representative particles using the DigitalMicrograph™ program (Gatan, Inc.). By taking an average of the background-corrected intensity of a number of single atoms visible within an image, it is possible to calculate an average single atom scattering intensity calibration for each image (Figure 4.8). The averaged atom counts vs. cluster diameter data for the monometallic Pt and Pd particles examined are presented in Figure 4.9. The results given in Figure 4.9 clearly suggest some form of structure whose atomic ordering lies between the limits defined by cubic and cuboctahedral structures, a conclusion anticipated by previous work. We observe a structural divergence as mediated by the nature of the material. For the Pt nanoparticles, the crystal growth can be modeled by that of a cubic structure. Conversely, growth of Pd nanoparticles is bounded by icosahedral and cuboctahedral size dependences.
It is useful to consider the structural dissimilarities evidenced in these data and ask whether they might hold any resultant importance for catalytic behavior. For the Pt clusters, we observe well organized, single-crystalline structures accompanied by well-defined, truncating facets. Such motifs provide support for allocating structure-function properties to the cluster for structurally sensitive catalytic pathways, such as was previously shown for different geometrically shaped Pt nanoparticles by Chen et al.\(^1\) The situation for the Pd nanoparticles is far more complex, with the structures evidencing a significant degree of atomic disorder and bond strain. The lower degree of crystallinity for the Pd nanoparticles found here is supported by the results of past studies using x-ray based measurements of the atomic Pair Distribution Function (PDF).\(^{50,51}\) The data suggest rate/property-correlations that, in this case, would have to more fully consider the roles that might be played in reaction mechanisms by a richer population of structural defects.

The materials described above were then used to nucleate the growth of a secondary metal shell. In the one instance this was Pt on a Pd core and in the other Pd on a Pt core.\(^{40}\) Figure 4.10 shows representative images of these bimetallic Pt(core)-Pd(shell) and Pd(core)-Pt(shell) nanoparticles as synthesized using a sacrificial hydrogen layer to mediate the growth.\(^{40}\) The image in Figure 4.10a is exemplary of the structures adopted by Pt(core)-Pd(shell) nanoparticles, core-shell clusters that exhibit an exceptionally high contrast region in the HAADF-STEM image localized at its center. This demonstrates the retention of the Pt atoms within the cluster core. The spatial frequencies obtained from the image FT (Figure 4.10b) suggests that the particle is aligned along its [001] zone axis, which in turn allows the assignment of the various facet planes present (solid lines in Figure 4.10a). For these samples the most abundant zone
axis found in these images was along the [011] direction with (111) and (002) facets being the most abundant truncating lattice planes (Tables 4.1 and 4.2). Another important feature regarding these images is the Pd atoms use of the Pt core as a template for what appears to be an essentially epitaxial, and reasonably defect-free, form of overlayer growth. Evidence for this interpretation is provided by comparisons made between the data given in Figures 4.3a and 4.10a, where one notes the same truncating edges are exhibited for the shell and the core structures. Such trends epitomize the requirements for pseudomorphic growth\textsuperscript{23,52} and we conclude, as such, that the Pd atoms of the shell coherently match the lattice structure of the Pt core. This interpretation is well supported by the broader data taken from many clusters in the sample (Figure 4.11). The boxed region in Figure 4.10a presents an integrated intensity measurement made of the cluster (inset of Figure 4.10b). Surrounding the high intensity core region are areas significantly lower in intensity, ones presumably attributable to the lower Z Pd atoms. Such intensity profiles were consistently seen for the clusters in these Pt(core)-Pd(shell) samples (Figure 4.11).

Computer simulations of the HAADF-STEM potential were carried out to support these interpretations more quantitatively using an ideal Pt cuboctahedron structure oriented along its [001] zone axis with (002) facets terminating the crystal edges as the basis for the calculations. To mimic the image seen in Figure 4.10a, multiple layers of Pd atoms were added around this Pt core (Figure 4.1.10a). The projected potential of the simulated crystal was found to provide a reasonable representation of the actual image. Beyond the aesthetic appeal of the model, however, the simulated areal intensities of the cluster (inset of Figure 4.12a) exhibit profiles closely resembling those of experiment...
(e.g. the inset of Figure 4.10b). We see, for example, that there is a sharp decrease in the intensity of the edge peaks in comparison to the central region. This follows both the qualitative and quantitative contours of experiment. These data affirm the structure of a pseudomorphic cluster of high-Z Pt atoms encased by those of a lower-Z Pd shell.

A strong templating effect is also seen in the inverse plating sequence. Representative data for a Pd(core)-Pt(shell) nanoparticle and its corresponding FT are shown in Figures 4.10c and d, respectively. The pattern in Figure 4.10d indicates a [112] zone axis with the associated facets as annotated in Figure 4.10c. It is worth noting the presence of high index lattice planes truncating the particle in this case. For example, the (113) and (022) lattice planes are clearly discernable on this representative particle. These truncations are generally associated with higher surface energies for the facet structures, a surprising but not completely unprecedented outcome. We also note the attendant differences between the image in Figure 4.10c and its Pt(core)-Pd(shell) analogue (Figure 4.10a), observed here as an inversion of the intensity map. The greater contribution to the integrated intensity that resides at the periphery of these clusters implies a strong biasing placement of the Pt atoms at the exterior of the particle. A concave-shaped profile was observed for essentially all Pd(core)-Pt(shell) nanoparticles in the sample (Figure 4.13). We also found that the Pd nanoparticles do not generally sustain isotropic heteroepitaxy in the growth of the Pt overlayer. With the Pd(core)-Pt(shell) samples, we instead see more sporadic/discontinuous (perhaps nodular) plating of the Pt atoms onto the Pd core (Figure 4.13). The images given in Figure 4.13 show different examples of Pt coverage unevenly distributed over the Pd core’s surface. Areal scans of these clusters (inset in Figure 4.10d and Figure 4.13) show the unconventional
concave-like pattern quantitatively describing a complex Pd(core)-Pt(shell) structure for the image seen in Figure 4.10c. Despite the clearly anisotropic growth of the binary cluster structure, in this case we were able to model it in good consistency with experiment as an icosahedral Pd core overcoated by a trilayer of Pt atoms (Figure 4.12b). This model, a gross simplification, demonstrates that even isotropic coverage of Pt on a Pd core reproduces the unusual intensity profiles observed with the HAADF-STEM simulations showing an inverted concave intensity profile (inset of Figure 4.12b) similar to what was found experimentally (inset of Figure 4.10d and Figure 4.13). It should be noted that a simulated monometallic Pd particle exhibiting the experimentally observed intensity profile can be produced. This latter case is easily discounted, however, because exclusion of the higher Z Pt scattering centers would require physically unreasonable nanoparticle geometries.

These results, then, lead us into an important conclusion pertaining to the templating effects of the various monometallic cores. With Pt at the core, we see essentially single-crystalline structures and tendencies toward uniform nucleated growth by the Pd atoms. In contrast, Pd cores promote irregular growth of the Pt shell, a result that amplifies the structural complexity of the nascent nucleating clusters. We also demonstrate the crystalline nature of the metal atoms in the shell regions rich in Pt (Figure 4.10c and Figure 4.13) - a characteristic feature not seen for the monometallic Pd nanoparticles. This observation suggests that the Pt atoms might act to reconstruct the cluster motifs in these regions. Conversely, high Pd content regions appear to retain the high density of structural defects evidenced by the disordered cluster cores (Figure 4.3b and Figures 4.6, 4.7 and 4.13). The data indicates that this tendency toward order is an
element-specific property that is capable of strongly influencing secondary growth patterns, and may indicate the significance of subtle details of bonding in the differences seen in the catalytic behaviors of closely related alloy/binary compositions.23,24,26,27

A control experiment, conducted by the coreduction of Pt and Pd precursors, was performed to contrast the features seen in clusters formed through a random alloying of Pt and Pd atoms versus those of the organized core-shell structures described above. Figures 4.14a and b show representative data for a Pt-Pd nanoparticle with Pt and Pd atoms statistically dispersed within the crystal and the derived diffraction pattern, respectively. The nanoparticle in this image is oriented along its [011] axis with randomly located regions of high and low contrast, indicating areas with a slight degree of phase segregation as well as adoption of an ordered, essentially single-crystalline, structure. The vast majority of the clusters in this sample were found to be oriented along their [011] zone axes with crystal facets defined by the (111) and (002) planes (Figure 4.15). The high degree of crystallinity is striking given the general tendency towards defect incorporation evidenced by the monometallic Pd clusters. These coreduced samples resemble more the monometallic Pt and bimetallic Pt(core)-Pd(shell) clusters as they appear single crystalline complete with well-defined truncating edges. X-ray diffraction data collected for all the samples examined further iterates the degree of crystallinity embedded within these crystals (Figure 4.16). Of note is the significant broadening of diffraction peaks for the monometallic Pd nanoparticles compared to all the other samples. In striking contrast, the diffraction data produced by the Pt-Pd alloy resulted in the sharpest Bragg peaks despite being the smallest of the bimetallic samples (~ 2.5 nm) indicating the dominance of Pt in the diffraction signals. The observed dispersion of the
metal atoms seen here is expected given the miscibilities predicted by the Hume-Rothery rules: 1) the atomic radii are within 15% (1.4% for Pd and Pt, 1.37 and 1.39 Å, respectively); 2) both metals adopt an FCC packing structure; and 3), they have similar electronegativities (2.20 and 2.28 for Pd and Pt on the Pauling electronegativity scale, respectively). Another interesting structural consequence revealed by these images is the placement of Pt and Pd atoms in direct juxtaposition, a structural feature unavailable in the idealized core-shell motifs. For example, an examination of the integrated intensities (the intensity profile inset of Figure 4.14b) show an oscillatory pattern as modulated by the presence of both Pt and Pd atoms within the encased region of 5a. Such qualitative features have recently been attributed to the formation of a random alloy in Pt-Co nanoparticles. It is unquestionably clear, however, that the nanoalloys do not exhibit the structural features associated with a phase-segregated core-shell structure, a result validating the synthetic techniques implemented in this study and the deeply quenched metastable character of the energy landscape that serves to direct (and here preclude) the structural evolution of these materials.

### 4.5 Conclusions

To summarize, we have used C$_s$-corrected STEM imaging as a technique to distinguish between different nanoscale structural features in metal clusters. This has allowed the atomic characterization of structures in bimetallic Pt-Pd nanoparticles. Pt(core)-Pd(shell) clusters displayed strong intensity patterns concentrated at the center with weak scattering atoms along the periphery. Pd(core)-Pt(shell) nanoparticles show an inverted intensity map when compared to the Pt(core)-Pd(shell) sample, while the
random nanoalloys studied reveal alternating intensities in their line scans. ZMULT simulations of the regular polyhedral structures commonly predicted for Pt and Pd nanoparticles verified that the dark-field detector dependence on heavy element scattering was the source of the experimentally observed variations in intensity. This emerging method of analysis offers the potential to provide important insights into the structures and compositional morphologies of nanoscale materials. We believe the methodologies described here will find broad application in studies of catalysis while advancing fundamental understandings of atomic bonding relevant to structure-function correlations.

Equally important, however, are the differences in crystallinity observed between the monometallic Pt and Pd nanoparticles. As was demonstrated, Pt atoms tend to activate the assembly of precise ordered features in a cluster, while Pd atoms were less effective in this respect. The observations developed here further provide future insights that will serve to guide the development of protocols that will yield more fully quantitative analyses of data of the type presented here, efforts that are in progress and that we hope to report shortly.

4.6 Acknowledgements

This work was sponsored in the part by the grants from the U.S. Department of Energy Grant No. DEFG02-03ER15476 (R.G. Nuzzo) and Grant No. DEFG02-01ER45923 (J. Zuo). Experiments were carried out in part at the Frederick Seitz Materials Research Laboratory Central Facilities, University of Illinois, which is partially supported by the U.S. Department of Energy under Grant No. DE-FG02-07ER46453
and DE-FG02-07ER46471. The authors would also like to thank Valeri Petkov for acquiring and interpreting the X-ray diffraction data in the Supporting Information.
4.7 Figures and Tables

Monometallic Pt Nanoparticles

Monometallic Pd Nanoparticles

Figure 4.1. Low magnification STEM images of PVP-Capped (a) Pt and (b) Pd nanoparticles with their corresponding size distribution histograms.
Figure 4.2. Low magnification STEM images of the bimetallic (a) Pt-Pd Alloy, (b) Pd(core)-Pt(shell), (c) Pt(core)-Pd(shell) nanoparticles and their respective size distribution histograms (d-f).
Figure 4.3. Representative C₄-corrected HAADF-STEM images of PVP-capped monometallic (a) Pt and (b) Pd nanoparticles. The inset diffraction patterns were obtained from their respective images. The solid lines in (a) identify the facet planes defined by the diffraction data.
Table 4.1. Tally of the zone axis rendered by the different nanoparticle samples.

<table>
<thead>
<tr>
<th>Zone Axis</th>
<th>Monometallic Platinum&lt;sup&gt;24&lt;/sup&gt;</th>
<th>Bimetallic Pt (core)-Pd (shell)&lt;sup&gt;30&lt;/sup&gt;</th>
<th>Bimetallic Pt (core)-Pt (shell)&lt;sup&gt;*&lt;/sup&gt;</th>
<th>Bimetallic Pt-Pd (Coreduced)&lt;sup&gt;30&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>[011]</td>
<td>54 %</td>
<td>60 %</td>
<td>45 %</td>
<td>57 %</td>
</tr>
<tr>
<td>[001]</td>
<td>38 %</td>
<td>6.7 %</td>
<td>33 %</td>
<td>23 %</td>
</tr>
<tr>
<td>[112]</td>
<td>8 %</td>
<td>30 %</td>
<td>22 %</td>
<td>17 %</td>
</tr>
<tr>
<td>[111]</td>
<td>None</td>
<td>3.3%</td>
<td>None</td>
<td>3 %</td>
</tr>
</tbody>
</table>

Table 4.2. Tabulation of the population of crystal facets determined using the diffraction data.

<table>
<thead>
<tr>
<th>Crystal Facets</th>
<th>Monometallic Platinum&lt;sup&gt;24&lt;/sup&gt;</th>
<th>Bimetallic Pt (core)-Pd (shell)&lt;sup&gt;30&lt;/sup&gt;</th>
<th>Bimetallic Pt (core)-Pt (shell)&lt;sup&gt;*&lt;/sup&gt;</th>
<th>Bimetallic Pt-Pd (Coreduced)&lt;sup&gt;30&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>(111)</td>
<td>75 %</td>
<td>93 %</td>
<td>67 %</td>
<td>70 %</td>
</tr>
<tr>
<td>(002)</td>
<td>100 %</td>
<td>60 %</td>
<td>78 %</td>
<td>67 %</td>
</tr>
<tr>
<td>(022)</td>
<td>42 %</td>
<td>37 %</td>
<td>33 %</td>
<td>20 %</td>
</tr>
<tr>
<td>(113)</td>
<td>8.3 %</td>
<td>13 %</td>
<td>11 %</td>
<td>None</td>
</tr>
</tbody>
</table>

*Monometallic Pd nanoclusters contained multiple defects and the image FT did not provide crystallographic information regarding truncating planes. In the case of a Pd (core)/Pt (shell) nanoparticles the disorder inherent in the Pd core translated to the overall bimetallic structure. Of the 4 nanoparticles examined, only nine contained definite faceted planes.
Figure 4.4. Representative C₆-corrected images of PVP-capped Pt nanoparticles with inset diffraction data and accompanying intensity profiles for (a) and (b) with crystal orientations along the [011] zone axes. Two adjacent particles are observed in (c) with varying geometric features (oriented along their [011] and [001] zone axes) and their respective diffraction data.
Figure 4.5. (a) C$_s$-corrected HAADF-STEM image of PVP-capped Pt nanoparticle from Figure 1a complete with diffraction data and intensity profile measurements. (b) Shows a modeled Pt cluster reproducing the experimentally observed data using simulated HAADF-STEM measurements to produce the resultant intensity profile (inset).
Figure 4.6. (a-d) Multiple images of monometallic PVP-capped Pd nanoparticles showing crystal defects observed directly and crystallographically using the inset diffraction data.
Figure 4.7. A Comparison between experimentally observed PVP-capped Pd nanoparticles and the projected potentials of an icosahedron viewed from two different directions. In (a) the icosahedron is in a randomly chosen orientation with a Gaussian blur convolution applied 100 times to the projected potential. The top-right most inset is the unblurred projected potential of the icosahedron and the inset in the bottom-right is an areal intensity profile of the boxed region in (a). Figures (b) and (c) are experimental images (resembling the theoretical image in (a)), with areal intensity profiles of their respective boxed regions shown below the image. Figure (d) is a Gaussian blurred (100 times) icosahedron projected potential viewed along its two-fold axis. The top-right inset indicates the unblurred projected potential, while the bottom-right inset shows the areal intensity profile of the boxed region. Lastly, (e) shows an experimental image and its areal intensity profile reflective of that observed theoretically in (d).
Figure 4.8. Atom quantification done by measuring areal intensity of an individual atom as well as an entire cluster. Several individual atoms were measured and averaged before dividing the integrated intensity of the cluster. A total of ten different clusters were measured for both Pt and Pd nanoparticles.
Figure 4.9. Atom count measurements for 10 monometallic Pt and Pd nanoparticles (symbols) plotted as a function of their experimentally measured diameter. The lines depict different, ideal geometries. For the case of the cube and cuboctahedron these represent the smallest geometric diameter. However, the icosahedron diameter was chosen to be the mean of the maximum and minimum theoretical diameters due to the difficulty of accurately distinguishing between these dimensions within the experimental images. Lastly, the bilayer was viewed as the top of a truncated cube, dictating that the diameter be measure as the length of an edge when viewed from above.
Figure 4.10. Bimetallic nanoparticles synthesized using a sacrificial hydrogen layer. (a) Image of a Pt(core)-Pd(shell) nanoparticle complete with labeled crystal facets and the areal integrated intensity measurement made within the boxed region. Diffraction data and annotated zone axis with the intensity profile represented as the inset in (b). (c) Pd(core)-Pt(shell) nanoparticle with defined truncating planes and areal integrated intensity measurement made within the boxed region. Corresponding diffraction data and integrated intensity profile measurement shown as the inset in (d).
Figure 4.11. More representative images of the bimetallic Pt(core)-Pd(shell) sample showing the crystalline nature of the cluster as defined by the inset diffraction data. The particle in (a) is oriented along its [001] zone axis with the associated truncating planes. The intensity scan shows a region of high contrast localized in the center of cluster and a drop intensity toward its outer shell. In (b) two Pt clusters oriented along their [011] zone axis encased within a Pd shell are shown with diffraction data and intensity measurements.
Figure 4.12. Simulated bimetallic nanoparticles modeling the (a) Pt(core)-Pd(shell) and the (b) Pd(core)-Pt(shell) samples. The Pt(core)-Pd(shell) sample was directly modeled using crystallographic data to mimic the image seen in Figure 2a with intensity scan (boxed region) and corresponding profile (inset in (a)). An icosahedral structure was assumed for the Pd(core)-Pt(shell) sample with attendant line scan (boxed region) and intensity profile (the inset in (b)).
Figure 4.13. Multiple images of Pd(core)-Pt(shell) nanoparticles showing the alternating growth patterns of Pt. (a) Shows an example of the uniform growth of Pt on a Pd core. In (b) we depict a Pd nanoparticle capped with Pt growth at three different regions. The particle in (c) demonstrates the asymmetric growth of Pt on the Pd core. All the images are accompanied by inset diffraction patterns and areal intensity scans (boxed regions). The profile scans traversing the particles all show a dependence on intensity that generates concave-like patterns.
Figure 4.14. (a) Representative image of a coreduced bimetallic Pt-Pd nanoparticle with indexed facet planes (solid lines) and the areal intensity scanned region (boxed region). Diffraction data for the coreduced sample with lattice planes and zone axes denoted with the integrated intensity measurement shown as the inset.
Figure 4.15. C$_s$-corrected HAADF-STEM images of bimetallic Pt-Pd nanoparticles synthesized using a coreduction method. Both images (a and b) contain inset diffraction data and annotated intensity scan regions with resultant integrated areal intensity measurements shown.
Figure 4.16. X-ray diffraction data illustrating the differences in crystallinity between the series of nanoparticle systems examined.
References


CHAPTER 5

THE EMERGENCE OF NONBULK PROPERTIES IN SUPPORTED METAL CLUSTERS: NEGATIVE THERMAL EXPANSION AND ATOMIC DISORDER IN Pt NANOCLUSTERS SUPPORTED ON γ-Al₂O₃


5.1 Abstract

The structural dynamics -- cluster size and adsorbate dependent thermal behaviors of the metal-metal (M-M) bond distances and interatomic order -- of Pt nanoclusters supported on a γ-Al₂O₃ are described. Data from scanning transmission electron microscopy (STEM) and x-ray absorption spectroscopy (XAS) studies reveal that these materials possess a dramatically non-bulk-like nature. Under a inert atmosphere small, sub-nanometer Pt/γ-Al₂O₃ clusters exhibit marked relaxations of the M-M bond distances, negative thermal expansion (NTE) with an average linear thermal expansion coefficient $\alpha = (-2.4 \pm 0.4) \times 10^{-5}$ K$^{-1}$, large static disorder and dynamical bond (interatomic) disorder that is poorly modeled within the constraints of classical theory. The data further demonstrate a significant temperature-dependence to the electronic structure of the Pt clusters; thereby suggesting the necessity of an active model to describe the cluster/support interactions mediating the cluster’s dynamical structure. The quantitative dependences of these non-bulk-like behaviors on cluster size (0.9 nm to 2.9 nm), ambient
atmosphere (He, 4% H₂ in He or 20% O₂ in He) and support identity (γ-Al₂O₃ or carbon black) are systematically investigated. We show that the non-bulk structural, electronic and dynamical perturbations are most dramatically evidenced for the smallest clusters. The adsorption of hydrogen on the clusters leads to an increase of the Pt-Pt bondlengths (due to a lifting of the surface relaxation) and significant attenuation of the disorder present in the system. Oxidation of these same clusters has the opposite effect, leading to an increase in Pt-Pt bond strain and subsequent enhancement in non-bulk-like thermal properties. The structural and electronic properties of Pt nanoclusters supported on carbon black contrast markedly with those of the Pt/γ-Al₂O₃ samples in that neither NTE nor comparable levels of atomic disorder are observed. The Pt/C nanoclusters do exhibit, however, both size- and adsorbate-induced trends in bond strain that are similar to those of their Pt/γ-Al₂O₃ analogues. Taken together, the data highlight the significant role that electronic effects -- specifically charge exchange due to both metal-support and metal-adsorbate interactions -- play in mediating the structural dynamics of supported nanoscale metal clusters that are broadly used as heterogeneous catalysts.

5.2 Introduction

Supported metal clusters are widely used as catalysts, finding application in diverse technologies that are critical to the growth of the American economy.¹⁻³ Prominent examples of processes in which supported metal catalysts play an indispensable role include petroleum refining,²,³ environmental remediation (e.g. automotive exhaust stream processing),⁴,⁵ chemical synthesis³,⁶ and fuel-cell-based power generation.⁷⁻¹⁰ Materials of this type are inherently complex systems where the activity
and selectivity are determined by the chemical and structural nature of catalytically-active surface sites.\textsuperscript{4,11,12}

One critical parameter that influences the characteristics of the surface sites present on a metal cluster is its size. A decrease in the cluster size results in geometrical changes (e.g. the relative areas of exposed (100) and (111) surface facet planes) and, perhaps equally important, changes in its corresponding electronic structure.\textsuperscript{3,11-13} These perturbations are expressed most dramatically at the smallest particle sizes, a fact that has motivated numerous studies that have managed to characterize such materials in a variety of contexts down to sub-nanometer dimensions.\textsuperscript{14-17} Studies that have focused on catalytic activity as a function of nanoparticle size typically find correlations that are highly reaction dependent. Au, while essentially inert in its bulk form, shows significant activity for CO oxidation when dispersed as a nanoparticle on an appropriate support.\textsuperscript{18-20} In a model Au/TiO\textsubscript{2}(001) system, for example, the activity for CO oxidation varies with cluster size and peaks at a cluster diameter of ca. 3 nm.\textsuperscript{21} In contrast, the activity of Pt/C nanoparticles in the electrochemical oxygen reduction reaction was recently reported to show no significant dependence on nanoparticle size, save perhaps for that due to surface area effects.\textsuperscript{22} Current literature paints a complex story as to how metal particle sizes influence the diverse range of properties that are central to catalytic efficiency in real process applications — notable among these are sensitivities related to poisoning or deactivation,\textsuperscript{2,3,23,24} stability against sintering,\textsuperscript{2,3,25,26} and the efficacy of regeneration.\textsuperscript{2,3,27-29} In such contexts, understanding contributions to structure-property correlations associated with the nature of the metal-support interactions remains amongst the most important and, as of yet, incompletely developed aspects of the problem.\textsuperscript{30-35} Questions
such as the precise atomistic nature of the bonding that governs these interactions, and the impacts that follow for the electronic structure and structural dynamics of supported metallic clusters, comprise what are perhaps the most difficult problems in the field.

The catalytic behaviors of very small clusters, systems where the electronic and structural consequences of the support interaction would be most heavily weighted, are expected to show pronounced sensitivity to the nature of the metal-support bonding.\textsuperscript{30-35} The present work addresses itself to structural, dynamic and electronic features exhibited in a highly prototypical catalytic system of this type: Pt clusters supported on $\gamma$-Al$_2$O$_3$. This material is a heterogeneous catalyst used in the processes that produce essentially all the liquid hydrocarbon fuels consumed world-wide.\textsuperscript{2,3} This report follows and expands upon an earlier study that demonstrated the surprising onset of non-bulk-like mesoscopic structural behaviors in this system at nanometer particle sizes.\textsuperscript{17} That work suggested that the support interactions are not “passive,” but instead convolve electronic effects that significantly perturb the atomic structure of the clusters. We present results that define dramatic, and in some respect non-intuitive, chemical sensitivities of the structural behaviors seen in this system. These results include the occurrence of negative thermal expansion (NTE) in the M-M Pt bond distances, as well as the impacts of nanoparticle size (average sizes of 0.9±0.2 nm, 1.1±0.3 nm and 2.9±0.9 nm) and the presence of either reactive (H$_2$, O$_2$) or inert (He) atmospheres. Our findings illustrate which trends are size and adsorbate-dependent and further confirm the importance of charge-transfer in describing the emergent mesoscopic behaviors of the Pt/$\gamma$-Al$_2$O$_3$ system.

5.3 Experimental Methods
**Preparation of Supported Pt Clusters:** Pt clusters were prepared on $\gamma$-Al$_2$O$_3$ (Aldrich, surface area 220 m$^2$/g) by impregnating the Pt$^{2+}$ precursor, Pt(NH$_3$)$_4$(OH)$_2$·H$_2$O (Strem Chemicals, Inc.), onto the support from an aqueous solution using the incipient wetness method to yield a Pt weight loading of 1%. The supported precursor was dried under vacuum, pressed into a pellet and mounted in an *in-situ* XAS cell. The sample was heated under a stream of H$_2$ (4% in He) to a final temperature of 573 K to remove the ligands and reduce the precursor to metallic clusters. This resulted in a final average cluster size of 0.9 nm. In order to obtain a slightly larger average cluster size (1.1 nm) a second pellet of the supported precursor was subjected to a similar treatment, except a final reduction temperature of 687 K was used. A third, commercial Pt on $\gamma$-Al$_2$O$_3$ sample with an average particle size of 2.9 nm and a weight loading of 5% (Sigma-Aldrich) was also pressed into a pellet from the commercial powder and activated under H$_2$ flow at 573 K prior to taking XAS measurements.

Small Pt clusters on carbon black (Cabot, Vulcan® XC72, surface area 250 m$^2$/g) were prepared in a similar manner from the Pt(NH$_3$)$_4$(OH)$_2$·H$_2$O precursor, followed by reduction under H$_2$ at 450 K, to yield clusters with an average diameter of 1.0 nm and a Pt weight loading of 1%. Commercial Pt nanoparticles supported on carbon black (XC72) with an average particle size of 1.8 nm and a 10% weight loading (ETEK, Inc.) was also pressed into a pellet and activated by reduction under H$_2$ flow at 573 K prior to XAS measurements. The reduction process for all samples described above was monitored by scanning the Pt L$_3$ absorption edge.

**Particle Size Determination and Atom Quantification Using Scanning Transmission Electron Microscopy (STEM):** The samples for STEM were prepared by
suspending the supported Pt particles in acetone and placing a drop of the suspensions on copper grids coated with an ultra-thin carbon film on holey carbon (Ted Pella, Inc.). Dark field images were obtained on a JEOL 2010F (S)TEM operating at 200 kV with an electron probe focused to 0.5 nm. The images were analyzed using Digital Micrograph (Gatan, Inc.) and the diameters of individual particles were determined from intensity profiles. The irregular intensity of the high-surface-area support materials precludes automated particle analysis routines. The error associated with measurement of the average cluster size was taken as one standard deviation (Figure 5.1).

Quantitative atom counting was also carried out using Digital Micrograph in the analysis of integrated areal intensities of well isolated Pt clusters using a previously described procedure. Our results indicated accurate measurements within 7% of the intensity-correlated atom counts. For instance, a calculation of a 700 atom cluster was uncertain by approximately 22 atoms for our larger clusters while for smaller sized clusters a 16 atom cluster count was uncertain by 1 atom (Fig 5.2)

**X-Ray Absorption Spectroscopy**: XAS measurements were performed at the XOR-UNI beamline 33BM-B at the Advanced Photon Source, Argonne National Laboratory. Some samples were also independently measured at beamline X18B at the National Synchrotron Light Source, Brookhaven National Laboratory. Results obtained at the two different synchrotrons for identical samples and experimental conditions were unchanged, within the measured uncertainties. The same in situ cell, suitable for experiments with low temperature (using a liquid-nitrogen-filled container with a cold finger) and for high temperature (using a resistive heater) measurements as in our previous work was used in these experiments. Samples were mounted at a 45° angle
to the beam for spectra to be collected simultaneously in transmission and fluorescence modes. A Pt foil sample was also mounted in the beam between the transmission and reference ion chambers to collect a reference spectrum for absolute energy calibration and alignment of spectra collected from the Pt cluster samples.

Each sample was blanketed under flowing 4% H\textsubscript{2} in He and then heated using a variable autotransformer (Staco Energy Products, Co.) and thermocouple at the rate of 100 K/h. Upon reaching the target reduction temperature, the extent of reduction was monitored by x-ray absorption near edge structure (XANES) measurements at the Pt L\textsubscript{3} edge. After stabilizing the white line intensity for 30 minutes, full scans of the extended x-ray absorption fine structure (EXAFS) for the Pt L\textsubscript{3} edge were taken at a series of temperatures (165-573 K), starting at the highest temperature and then cooling and stabilizing the sample’s white line intensity at successively colder temperatures. A liquid nitrogen Dewar with a cold finger was inserted in place of the heater, for sub-ambient temperature measurements. The data were collected after the temperature stabilized to within 5 degrees to the lowest temperature possible, depending on the sample. Multiple scans were collected for signal averaging purposes. After completing the measurements under H\textsubscript{2}, the gas flow was switched to ultra-high purity He, the temperature raised, XANES scans collected and monitored until a new steady state was achieved followed by full scans made at various temperatures. At the conclusion of the measurement series, the temperature was returned to the highest value used in the series and a scan performed again to check whether the observed changes were reversible. All data presented below have passed these stringent tests of reversibility (Figure 5.3).
These same Pt on γ-Al₂O₃ samples were then subjected to an oxygen atmosphere (leading to a partial oxidation of the clusters but with the retention of significant M-M bonding) in the in-situ XAS cell. After complete reduction at high temperatures under 4% H₂ (as monitored by XANES), the samples were then oxidized under a flowing stream of 20% O₂, balanced by He, for one hour. In the case of the 0.9 and 1.1-nm supported cluster samples this oxidation occurred at 573 K, while the 2.9-nm commercial sample was oxidized at 673 K. The gas was switched to ultra-high purity He at the elevated temperature followed by scanning of the XANES region. Once the XANES spectra indicated a steady state had been reached, full spectra were collected for each sample over a series of temperatures (177-573 K) from highest temperature to lowest as before. At the conclusion of these measurements, the sample was heated to the initial (highest) temperature under H₂ and a full spectrum collected to confirm the reversibility of the observed changes (Figure 5.4).

Finally, spectra were collected from a standard Pt foil over a series of temperatures (154-700 K) similar to those used for the nanoparticle samples in order to allow a comparison of the nanoparticle dynamics and structure with bulk thermal behavior.

**EXAFS Data Analysis:** Data processing and analysis were performed using the IFEFFIT package, as previously described. The spectra were aligned using the simultaneously collected Pt foil standard spectra and the multiple scans for a given sample under identical conditions were merged. The background subtraction of the absorption edge to yield the EXAFS oscillations was performed using the AUTOBK code which implements cubic spline interpolation with an adjustable frequency cutoff to fit the
The data were \( k^2 \)-weighted and Fourier transformed to give a pseudo-radial distribution function (oxidized Pt/\( \gamma \)-Al\(_2\)O\(_3\) and Pt/C data were treated slightly differently, see below). The spectra were fitted in R-space by varying the coordination number (N), the photoelectron half-path length (R), the correction to the threshold energy (\( \Delta E_0 \)), the EXAFS Debye-Waller factor (\( \sigma^2 \)) and the third cumulant (\( \sigma^{(3)} \), which takes into account the anharmonic correction to the interatomic pair potential). Our data analysis demonstrated the significant role of anharmonic effects in the observed bond contraction and thus validated the use of the third cumulant in the data analysis. The passive electron reduction factor (\( S_0^2 \)) was set to 0.86 as determined from analysis of the Pt foil spectra collected at multiple temperatures where this parameter was found to be equal to 0.86±0.02. The effective scattering amplitude, phase shift and inelastic loss functions were calculated from the bulk Pt structure using a FEFF6 code.\(^{41,42}\)

In order to limit the number of variables, the fitting analysis was performed simultaneously on all the spectra collected at multiple temperatures for a given sample under a given atmosphere. Furthermore, several physically reasonable constraints were made during the fitting process and will be described in greater detail in the main text. After verifying that the coordination number (N) and threshold energy correction (\( \Delta E_0 \)) did not vary with any statistical significance as a function of temperature (Figure 5.5), these parameters were each fit to a single temperature-independent value across all temperatures. For all spectra, the data analysis was limited to the first-nearest-neighbor (1NN) single scattering paths because of their isolation from longer single- and multiple-scattering paths in the Fourier-transformed spectra.
For data where a low-Z scattering contribution was present, both Pt-Pt and Pt-low-Z paths were fit using a difference file k-weighting technique.\textsuperscript{43} Specifically, the data were weighted by $k^3$ to emphasize the Pt-Pt contribution and minimize errors from overlap from the Pt-O contribution - and the R-range was constrained to ca. 2.1-3 Å to fit solely the Pt-Pt contribution. This best-fit theoretical contribution was then subtracted from the experimental data in k-space and the residual Pt-O contribution fit in the R-range of ca. 1.4-2 Å. Theoretical standard for the Pt-O path used in the analysis of the oxidized Pt on $\gamma$-Al$_2$O$_3$ samples was calculated using a FEFF6 code from the PtO$_2$ structure while that for the Pt-C path used in the analysis of the Pt on carbon black samples was calculated from a platinum carbide structure.\textsuperscript{44,45} Because the parameters $R$, $\sigma^2$ and $\sigma^{(3)}$ are temperature-dependent, they were allowed to vary in the fits. No anharmonic correction was applied in the Pt-low-Z scattering path fit.\textsuperscript{46} The thermal dependence of $\sigma^2$ was also modeled using a correlated Einstein model which represents the mean-square deviation of bond length as a superposition of static ($\sigma_s^2$) and dynamic ($\sigma_d^2$) terms:

\[
\sigma^2 = \sigma_s^2 + \sigma_d^2
\]

\[
\sigma_d^2 = \frac{\hbar}{2\omega\mu} \left( \frac{\exp(-\Theta_E/\hbar)}{1 + \exp(-\Theta_E/\hbar)} \right)
\]

where $\omega$ is the bond vibration frequency, $\mu$ is reduced mass of the absorber-scatterer pair, $\Theta_E$ is the Einstein temperature ($\Theta_E = \hbar\omega_e/k_B$), $k_B$ is the Boltzmann’s constant and $T$ is the measurement temperature.\textsuperscript{47}

Representative plots for all the data and their best fits are presented as Figures 5.6-5.10.
5.4 Results

In this section we discuss the experimental results obtained using XAS (in both inert and reactive atmospheres) and STEM for Pt nanoclusters with narrow size distributions in the range of 0.9 nm – 2.9 nm supported on either γ-Al₂O₃ or carbon. High angle annular dark field (HAADF) STEM imaging was used to establish both the size distributions of the clusters and specific counts of metal atoms present in an average Pt cluster for each sample. These data provide strict constraints and points of comparison for cluster characterizations made using XAS and verifies that the latter ensemble-average determinations of the local atomic environment provide a relevant atomic-level structural description of an individual cluster.

Particle Size Distributions: STEM results.

HAADF-STEM micrographs of three different Pt on γ-Al₂O₃ samples obtained after high-temperature reduction are shown in Figure 5.1. Reduction of the supported Pt²⁺ precursor at 573 K, at a loading weight of 1 wt % Pt, resulted in the smallest mean particle diameter and the narrowest size distribution - as evident from the data of Figure 5.1a and the inset of Figure 5.1b (0.9 ± 0.2 nm). Quantitative analysis of intensity maps for the individual nanoparticles in the images provided an approximate atom count contained per cluster (Figure 5.2). Figure 5.1b shows that on average the number of Pt atoms contained within the 0.9 nm clusters is approximately 16 (N_{avg} = 16). This suggests that the structural motif of these clusters must be, in fact, an oblate rather than spherical particle.²⁷ Performing the reduction with the same loading at 687 K gave a larger mean
particle diameter with a slightly broader width to the distribution, as seen in Figure 5.1c and the inset of Figure 5.1d (1.1± 0.3 nm). Quantitative analyses of the HAADF-STEM data shows that the average cluster contains a significantly larger number of Pt atoms, \( N_{\text{avg}} = 30 \) (Figure 5.1d). We also examined a commercial sample, 5% Pt on \( \gamma\text{-Al}_2\text{O}_3 \), and found that it exhibited the largest and broadest distribution of particle sizes, 2.9 ± 1.0 nm (Figure 5.1e and the inset of Figure 5.1f), of the three \( \gamma\text{-Al}_2\text{O}_3 \) samples. These data demonstrate that most of the Pt atoms in such a cluster will experience more bulk-like bonding given the rather large number of atoms that it contains, \( N_{\text{avg}} = 700 \) (Figure 5.1f).

Analogous HAADF-STEM micrographs for two Pt/C nanocluster samples were recorded and size-distribution histograms analyzed (Figure 5.11). Samples prepared using a protocol similar to that employed for the Pt/\( \gamma\text{-Al}_2\text{O}_3 \) samples yielded comparable results as to the distribution of cluster sizes obtained (1.0 ± 0.3 nm). We also examined a commercial Etek, Inc. sample of Pt/C and found it to have an average diameter of 1.8 ± 0.5 nm (Figure 5.8).

**Electronic and Atomic Structural Characterization of Pt/ \( \gamma\text{-Al}_2\text{O}_3 \)**

We start with a consideration of EXAFS results in two stages, both complementing the data reduction and analysis processes. First we examine the raw data to draw qualitative guidance regarding the nature of the demonstrated structural and dynamical behaviors. We then present raw quantitative data that has been analyzed in a manner that does not make any assumptions about the particles under consideration (e.g. particle shape). The discussion that follows organizes these analyses along three major headings that serve to highlight the interplay of the main factors that direct the
temperature dependent structural responses of supported Pt nanoparticles. These factors are: (a) cluster size; (b) effects of adsorbates; and (c) the chemistry-specific effects of the metal-support interactions. On the subject of metal-support interactions, it is important to recognize the role of sample preparation as it relates to the absence of low-Z scattering contributions (conventionally associated with particle-support bonding)\textsuperscript{32,49-52} in the FT magnitudes of our samples. The lack of a Pt-O contribution to the radial distribution function has been observed in a previous study\textsuperscript{53} in which a similar synthetic protocol was employed in the preparation of Pt/\(\gamma\)-Al\(_2\)O\(_3\).

(a) Structural Dynamics as Influenced by Cluster Size

The raw EXAFS data, in terms of the phase \(\chi(k)\) or the Fourier Transform amplitude, provide useful insights pertaining to the influences of particle size on the structural dynamics. It is difficult, in general, to discriminate uniquely between the effects of temperature and size based on the Fourier transform magnitude alone (Figure 5.12 for Pt/\(\gamma\)-Al\(_2\)O\(_3\) and Figure 5.13 for Pt/C). Consideration of the k-space data (Figures 5.12a,c), however, allows a quantifiable discrimination between these two factors. One notes, for example, that the EXAFS data collected for the three different sized Pt samples (Figure 5.12a), when measured at the same temperature, appear to scale uniformly in intensity throughout the entire k-region. This sensitivity to cluster size permits the extraction of quantitative information about particle sizes by varying the coordination numbers in the fits (Figure 5.12b), thus providing direct points of comparison to the results obtained using microscopy.\textsuperscript{37} In the present case, the qualitative assessment described above suggests that the samples adopt self-similar atomic scale structures (i.e.
that variation of particle size within this range does not lead to exaggerated atomic reconstructions). The influences of temperature within a given sample, however, are quite different. For example, temperature dependent EXAFS data for the 2.9 nm Pt/γ-Al₂O₃ sample is characterized by a monotonic increase of the disorder parameter (σ²) with temperature. This is revealed as a dampening of the EXAFS oscillation intensity at higher k values (Figure 5.12c). Such trends denote the dominating effects of thermal disorder (Figure 5.12d).³⁷ And as we show below, the quantitative aspects of the data are also very sensitive to the surface chemistry of the particles, such as might occur in either oxidizing or reducing atmospheres (Figure 5.14).

We turn now to a more quantitative analysis of the EXAFS data. The quantitative results of the data analyses for all the samples are summarized in Tables 5.1-5.3. Using a previously described geometric model,⁵⁴,⁵⁵ we find the behavior of the average first-nearest-neighbor (1NN) M-M coordination numbers for the three nanocluster samples consistent with that of the average particle sizes obtained by TEM. Specifically, the extended atom counting analyses demonstrate the adoption of a more oblate shape of the particles with decreasing particle size (Figures 5.1b,d,f and Figure 5.2). This strict validation of the analysis procedure supports a more detailed quantitative assessments where the assumption is made that the distribution of clusters in the sample can be represented by an “equivalent cluster”, i.e. that the size distribution is narrow enough that EXAFS-based characterizations accurately exemplify properties that are intrinsic to a cluster of that size.⁵⁴,⁵⁵

Figure 5.15a provides a full comparison of the temperature dependences of the 1NN Pt-Pt bond lengths for all three Pt/γ-Al₂O₃ samples measured under He, along with
data for a Pt foil used as a reference. The Pt foil exhibits the expected positive thermal bond length expansion with an average linear thermal expansion coefficient $\alpha = (1.1 \pm 0.1) \times 10^{-5} \text{ K}^{-1}$, an experimental value that agrees well with one derived from x-ray diffraction measurements ($\sim 0.88 \times 10^{-5} \text{ K}^{-1}$ at 298 K). The thermal behavior of the smallest 0.9-nm Pt/$\gamma$-Al$_2$O$_3$ sample provides marked contrasts with the bulk behaviors when measured under an inert He atmosphere. These clusters show two strong effects: first, a substantial relaxation of the static Pt-Pt pair distance compared to the bulk (by ca. 3%, denoted by $R_{RT}$, the Pt-Pt pair distances at room temperature in Table 5.1); and, second, a dynamic decrease of the pair distance with increasing temperature, with the former having been observed for many types of nanoparticle-support systems.

The average measured NTE coefficient $\alpha$ is $(-2.4 \pm 0.4) \times 10^{-5} \text{ K}^{-1}$. The data also revealed a non-bulk-like thermal behavior for the 1.1-nm Pt/$\gamma$-Al$_2$O$_3$ nanoclusters qualitatively similar to, but less dramatic than, that of the smaller 0.9 nm clusters. In this case the measured $\alpha$ was $(-1.4 \pm 0.5) \times 10^{-5} \text{ K}^{-1}$. The data for the 2.9-nm Pt/$\gamma$-Al$_2$O$_3$ particles suggest a transition point to more bulk-like properties as marked by an apparent positive expansion coefficient, $\alpha = (0.2 \pm 0.1) \times 10^{-5} \text{ K}^{-1}$ (Table 5.1).

The functional dependences of the EXAFS Debye-Waller factors ($\sigma^2$) on temperature are also informative. These results are presented in Figure 5.15b. The data points correspond to the $\sigma^2$ values determined independently for each sample (under He) at a specific temperature while the lines are the corresponding fits made using a correlated Einstein model. The Pt foil data displays a very small contribution from static disorder, $\sigma_s^2$ (a measure of the temperature-independent, configurational disorder present in the sample), since its $\sigma_s^2$ (T) curve extrapolates to a value just slightly above zero,
0.0017 ± 0.0008 Å² at T = 0. This displacement from zero (the value expected for a perfectly ordered structure) is within the accuracy expected in such calculations. The calculated Θₑ (179±2 K) is in excellent agreement with literature values (~180 K). The 2.9-nm Pt/γ-Al₂O₃ nanoclusters exhibit a larger σᵢ² (0.0021±0.0001 Å²), and also a higher Θₑ (203±2 K). The 1.1-nm Pt clusters exhibit further increases in both the σᵢ² (0.0045±0.0002 Å²) and Θₑ (226±7 K). The data for the 0.9-nm clusters exhibit the largest perturbations, with σᵢ² increasing to 0.0069±0.0003 Å² and an apparent Θₑ of 298±24 K.

Thermal perturbations of electronic structure are also evidenced in the larger sized samples. In the absence of specific temperature-dependent electronic effects, (e.g., metal-insulator transition) the XANES data should have little, if any, temperature dependence in terms of absorption edge position and shape, or white line intensity. Such insensitivity has been demonstrated previously for Pt foil samples. We found that the 2.9 nm diameter Pt/γ-Al₂O₃ sample yielded XANES data with a thermal dependence (Figure 5.15c) that is qualitatively similar to that of Pt foil. In contrast, we observed substantial temperature-dependent changes in the XANES region of spectra measured in a He atmosphere for the 1.1-nm (Figure 5.15c), and even more dramatic ones for the 0.9-nm (Figure 5.15c), Pt/γ-Al₂O₃ nanocluster samples. In each case, the anomalous behavior was manifested as a progressive red shift of the edge position and slight increase in the white line intensity with increasing temperature. We defer further comment on these points to the discussion section.

(b) Structural Dynamics as Influenced by Adsorbates
Experiments were carried out to explore the influences that adsorbates exert over the structural and dynamical responses of supported Pt catalysts. For the particle sizes considered here, such effects are expected to be significant given the considerable fraction of atoms residing at (or near) surface sites (particularly for the 0.9 and 1.1 nm clusters). In the present study, this examination is particularly critical as the current literature does not present a clear picture regarding such interactions nor the mediating role they may play in modifying details of the interatomic bonding in very small clusters. For this reason, and to compliment the XAS measurements made under an inert He atmosphere (where the cluster present is presumably adsorbate free), we performed a similar set of measurements for samples maintained in a background pressure of hydrogen gas or after oxidation of the clusters in a dilute mixture of O₂ in He.

The impact of oxidation on the EXAFS spectra collected at room temperature for the three Pt/γ-Al₂O₃ samples are compared with their reduced counterparts in Figure 5.14. Oxidation leads to marked decrease in the peak magnitude of the Fourier transform plots in the 2-3 Å range of the EXAFS data, which indicates a decrease in Pt-Pt coordination number and/or an increase of atomic disorder in the cluster. The scattering contribution seen between ca. 1.5-2 Å is due to the Pt-O 1NN single scattering paths.

The influences of the H₂ atmosphere on the data are less dramatic. To provide a more quantitative analysis of the data we consider in order the results of the temperature-dependent behaviors of the Pt-Pt bonds in three distinct chemical states as depicted in Figure 5.16: (1) oxidized clusters (O₂, in green) measured in helium; (2) reduced clusters after hydrogen desorption measured in helium (He, in blue); and 3) reduced clusters measured under a hydrogen atmosphere (H₂, in red). These data provide a basis to
In comparison, the associated structural dynamics for two types of adsorbates, O and H (Figure 5.16a). Of the three cluster sizes studied, the 0.9-nm Pt nanoclusters were impacted the most dramatically by the oxidative treatment (Table 5.3). Most important is the fact that the oxidative treatment induces a pronounced static contraction in the 1NN Pt-Pt bonds relative to either He or H\textsubscript{2} samples at all temperatures (Figure 5.16a). These clusters also exhibit NTE, but the value of $\alpha$ for the oxidized case is larger ($(-2.9 \pm 0.4) \times 10^{-5}$ K\textsuperscript{-1}, Tables 5.1, 5.3). A lesser oxidation-induced bond contraction was observed for the 1.1-nm Pt nanoclusters, and there was no observable effect of oxidation in the 1NN Pt-Pt bond lengths found for the largest 2.9-nm Pt/\(\gamma\)-Al\textsubscript{2}O\textsubscript{3} nanoclusters compared to the Pt foil (as reflected by the $R_{RT}$ values found in Table 5.3). The influence of temperature on the bond lengths also diminishes with increasing cluster size (Tables 5.1, 5.3).

Figure 5.16b in conjunction with Tables 5.1 and 5.3, present data that demonstrate that the $\sigma_s^2$ term and the values of $\Theta_E$ (calculated for each Pt/\(\gamma\)-Al\textsubscript{2}O\textsubscript{3} system) are well correlated across all cluster sizes, for each of the various (He, H\textsubscript{2} and O\textsubscript{2}) treatments. For all of the nanoparticle samples, the presence of H\textsubscript{2} in the ambient atmosphere results in a decrease of $\sigma_s^2$ for the Pt-Pt atom pairs (Table 5.1), consistent with the lifting of a surface relaxation due to hydrogen adsorption and resultant bulk-like dynamics of the Pt atoms. For example, the 0.9-nm clusters under H\textsubscript{2} exhibit $\sigma_s^2$ of 0.0052$\pm$0.0002 Å\textsuperscript{2} and $\Theta_E$ of 207$\pm$6 K. In the inert environment (He), the $\sigma_s^2$ increases to 0.0069$\pm$0.0003 Å\textsuperscript{2}, with an apparent $\Theta_E$ of 298$\pm$24 K. For purposes of comparison, we also present the 1NN Pt-Pt $\sigma^2$ values for the oxidized samples in Figure 5.16b. The $\sigma_s^2$ and $\Theta_E$ determined from the correlated Einstein models for this sample are given in Table 5.3. The characteristics of $\sigma^2$ for the 0.9-nm Pt/\(\gamma\)-Al\textsubscript{2}O\textsubscript{3} nanoclusters are markedly different than those of the H\textsubscript{2} and
He cases. First, oxidation results in a statistically-significant increase in the $\sigma^2$ in the Pt-Pt bonds in the nanoclusters. Second, there is an apparent increase in $\Theta_E$. Notably, the correlated Einstein model does not appear to suitably correlate with the $\sigma^2$ determined independently at each measurement temperature. This is inferred by the large uncertainty that attends the calculation of the $\Theta_E$ (Table 5.3) within the Einstein model used in the data analysis.

The effects of adsorbates on the electronic structures of the clusters, as revealed by the changes appearing in XANES data, are illustrated by the spectra presented in Figure 5.16c. As expected, the impacts evidenced in the oxidized samples are qualitatively different from those found in either H$_2$ or He atmospheres (Figure 5.16c). The main difference between measurements made in each case is the correlated increase of the white line intensity. The dramatic nature of this electronic perturbation is further demonstrated by the marked blue shift of the isosbestic point seen with the increasing oxidation state of the Pt atoms in the cluster.

Systematic measurements of the size-, substrate- and adsorbate-dependent thermal properties of the Pt clusters allow discrimination between the charge transfer effects of the substrate and adsorbates (O vs H) on the apparent contraction of the Pt-Pt bond lengths. The smallest $\gamma$-Al$_2$O$_3$ supported clusters exhibit NTE regardless of the atmosphere. The 2.9 nm clusters, however, illustrate a crossover region where these two effects (support and adsorbate interactions) can be quantitatively separated: the Pt-Pt bond length in these clusters expands positively under He atmosphere and negatively under H$_2$ (Table 5.1). The origin of the latter behavior is rooted in the temperature dependent hydrogen coverage which decreases with increasing temperature. Due
to the cluster-support and cluster-adsorbate interactions, the ensemble-average from the EXAFS signal affords a weighted average of the electronic contributions of surface Pt atoms over the Pt atoms at the cluster-support interface. The proportion of each contribution is directly related to the relative fraction of surface atoms to interface atoms. Thus, it is plausible to find a combination of particle size and hydrogen coverage such that the particle demonstrates a bulk-like response (conventional thermal expansion) under inert conditions while, exhibiting NTE under H\(_2\). We independently verified this prediction in control experiments that examined thermal behaviors of Pt/\(\gamma\)-Al\(_2\)O\(_3\) clusters of a similar size but at a higher (1 atm) background pressure of H\(_2\). These control experiments (Figure 5.17) confirmed that the higher pressure provides a near saturation coverage of hydrogen to temperatures as high as 573 K and a more bulk-like response of the average Pt-Pt bond lengths. These data therefore define a size-dependent scaling of the electronic contributions of the metal-support interface within the ensemble average properties of a supported cluster.

\textit{(c) Structural Dynamics as Influenced by the Support}

The FT magnitudes of the EXAFS data for two Pt/C nanocluster samples measured under He at room temperature are given in Figure 5.13 along with data taken for a Pt foil standard. Of note in these data is the presence of a low-Z scattering contribution at R<2.0 Å that is not observed in the data for the Pt/\(\gamma\)-Al\(_2\)O\(_3\) systems under similar conditions (Figures 5.6-5.8). This contribution was fit to a Pt-C scattering interaction involving the support (Table 5.2).
The temperature independent 1NN Pt-Pt coordination numbers for the carbon supported samples are presented in Table 5.2. These values are consistent with the microscopy-determined size distributions and favor a faceted hemispherical structure (Figure 5.2).

The temperature-dependences of the bond lengths of the Pt/C nanoclusters, as measured under an inert He atmosphere, are presented in Figure 5.18a. It is immediately apparent that the 1.0 nm Pt/C sample does not exhibit NTE. Its thermal expansion coefficient \((0.2 \pm 0.4) \times 10^{-5} \text{ K}^{-1}\) stands in contrast to the behavior of the 0.9 nm Pt/\(\gamma\)-Al\(_2\)O\(_3\) sample described above. The Pt/C nanoclusters do show size-dependent bond length relaxations compared to the bulk however (Figure 5.18a; see also \(R_{RT}\) values in Tables 5.1, 5.2). The 1.8-nm Pt/C nanoclusters under He exhibit bond length relaxations of ca. 0.4% from the bulk value. The presence of H\(_2\) has little influence on the temperature dependence of the Pt-Pt bond lengths as indicated by an \(\alpha = (1.0 \pm 0.2) \times 10^{-5} \text{ K}^{-1}\) under both H\(_2\) and He, a value quantitatively similar to that for bulk metal (Table 5.2). The bond lengths measured for the smaller 1.0-nm Pt/C nanoclusters under He are more significantly contracted by an apparent surface relaxation mechanism (ca. 1.1% relative to the bulk value). These data show that hydrogen adsorption increases the average bond lengths of the 1NN Pt atoms, consistent with the lifting of a surface relaxation by adsorbate (Table 5.2).

For Pt/C clusters, the best fit values of \(\sigma^2\) for the Pt-C bonds were indistinguishable from zero, to within the uncertainties \((0.004-0.006 \text{ Å}^2\), Table 5.2). Even though these parameters cannot be accurately fit within the confines of the structural model, the larger inference remains that this bond is relatively stiff as compared to the Pt-
O interaction in the Pt/γ-Al₂O₃ samples. The values of σ² for the Pt-Pt bond calculated from the data for the 1.0 nm Pt/C and 0.9 nm Pt/γ-Al₂O₃ samples are graphically presented in Figure 5.18b. The σ² and Θₑ for Pt/C as determined from the correlated Einstein models are provided in Table 5.2. The experimentally determined σ² value for the 1.0 Pt/C sample is larger than that of the bulk. Even so, this measure of bond-length disorder is substantially smaller than that found for the 0.9 nm Pt/γ-Al₂O₃. The magnitude of the σ² of the 1NN M-M bond lengths of the 1.0 nm Pt/C clusters is significantly reduced by H₂ adsorption, a behavior similar to that found for all of the Pt/γ-Al₂O₃ samples (Tables 5.1, 5.3). There was no statistically-significant dependence of Θₑ value calculated from the data that results from H₂ adsorption, a result that markedly differs from those for the γ-Al₂O₃-supported clusters. Finally, we note that the σ² values measured for the 1.8-nm Pt/C nanoclusters were not impacted by H₂ adsorption (Tables 5.1, 5.2).

Figure 5.18c shows five XANES spectra, representing data collected under a He atmosphere at all measurement temperatures for the 1.0-nm Pt/C and 0.9-nm Pt/γ-Al₂O₃ samples (taken from Figures 5.15c and 5.16c) and plotted on the same scale to aid in their comparison. These spectra are qualitatively and quantitatively different. Most notably, there is a marked red shift and an increase in the normalized absorption intensity seen for the γ-Al₂O₃ supported sample. These thermally driven trends are not seen in the Pt/C system. Figure 5.15 shows these perturbations attenuate with increasing dimensions of the Pt/γ-Al₂O₃ clusters. The γ-Al₂O₃ support is therefore distinguished in this comparison by the significant electronic perturbations evidenced in the Pt clusters supported on it.
The latter is a feature that is directly correlated with the occurrence of charge transfer, a topic addressed in the discussion section.

Taken together the data establish several points for comparison that are central to the size-dependent scaling of the structural dynamics of supported Pt nanoclusters. These trends are illustrated graphically in the plots given in Figure 5.19, where the metal cluster size is represented by the 1NN M-M coordination number determined by EXAFS (Tables 5.1, 5.3). First, the particles exhibit significant contractions in their 1NN Pt-Pt bond distances relative to that of bulk metal, irrespective of the support (γ-Al_{2}O_{3} or C). The magnitudes of these static bond length contractions correlate inversely with particle size. Second, small clusters (again irrespective of the support) also embed significant levels of disorder in their M-M bonding relative to bulk state, the magnitude of which is largest in the smallest clusters. Third, support interactions appear to contribute to electronic effects (in ways that are different for the Pt/γ-Al_{2}O_{3} and Pt/C systems) that can strongly influence the structural dynamics of supported nanoscale clusters.

5.5 Discussion

The most significant finding coming from the measurements reported in this study is the unexpected complexity of the structural dynamics of supported metal nanoparticles, systems that well model important classes of industrial catalysts. Our results suggest marked structural sensitivities to three dominating factors: (a) particle size; (b) the chemistry of adsorbates; and (c) the nature of their interactions with the support. That the atomic structure of metallic clusters would be sensitive to such features is not a new idea. Such notions deeply inform long-adopted, albeit qualitative, models of structure-property
relationships in catalysis.\textsuperscript{30,32-34,50,52,69} There remain, though, critical deficiencies in these models and a general lack of understanding of structure at the atomic level that complicates a formal method of explaining the associated dynamics. It is therefore useful to start with a consideration of model structures and bridge from these ideas to the more important concepts developed by the current work.

It is now well appreciated that qualitative models of metal clusters that idealize them as polyhedra with atoms occupying regular lattice positions are inadequate. From a structural standpoint, a number of studies have revealed increased strain in nanoparticles relative to the bulk metal, being manifested in such cases as significantly contracted bond distances and increased static structural disorder.\textsuperscript{15,32-34,37,52,57-61,63,70-74} A variety of phenomenological models have been described in the literature that offer more atomistic detail such as those that include the relaxation of atoms in clusters due to surface effects,\textsuperscript{75,76} reconstruction due to adsorbate-cluster interactions\textsuperscript{34,50,61,69} and, most importantly, the basic principles involved in structural development that arise as a consequence of metal-support interactions.\textsuperscript{30,32-34} Recent reports\textsuperscript{77,78} applied new computational approaches toward the analysis of cluster-support interactions and the strong influences they exert on the structural dynamics of supported metal clusters. These studies, and the present work, demonstrate that the physical properties of a prototypical supported metal clusters, at least within a narrow size range of 1-3 nm, can exhibit striking forms of complexity. The diversity of the effects established in this work -- including: adsorbate-mediated atomic reconstruction of the cluster; significant examples of bond disorder; thermal mediation of electronic structure; and, most notably, cluster-size and support-dependent behaviors that lead to NTE -- challenge current
understandings of structural dynamics in nanoscale materials. Our studies specifically suggest that competing interactions are central in directing the mesoscopic behaviors found in Pt/$\gamma$-Al$_2$O$_3$ nanoparticles. In the sections that follow we develop these ideas and highlight quantitative and qualitative features associated with the chemical properties of this catalytic system.

Platinum is an indispensable catalyst, being among the most active metals known for the activation of H$_2$ for hydrogenation catalysis.$^{1-3}$ It also exhibits, along with a few other noble metals (e.g. Ir), the highest rates and selectivities in C-H and C-C bond activation and capacities for regeneration that lead to enhanced on-stream lifetimes.$^{2,3}$ For these reasons, Pt catalysts are essential for the efficient production of hydrocarbon fuels. Unfortunately there remain significant deficiencies in current understandings of the atomistic details involved in the processes that this metal catalyst promotes.$^{37}$ This lack of basic understanding is only amplified by the complexities that attend its use in supported forms for processes involving chemically demanding environments.$^{30,32-34,50,52,61,69}$

The present work examines fundamental dynamical behaviors in well-defined $\gamma$-Al$_2$O$_3$ supported Pt clusters in the size range of 0.9-2.9 nm. The acidic nature of this support promotes useful forms of C-C bond isomerization and, for this reason, finds ubiquitous use in hydrocarbon processing. The synergistic qualities of the $\gamma$-Al$_2$O$_3$ support and the Pt catalyst result in improved usage of the carbon content of feedstocks, resistance to deactivation by coking/sintering, improved processing lifetimes and facility of regeneration.$^{2,3}$ The present work demonstrates interesting behaviors for Pt on this support, highlighting the catalyst’s dependence on cluster size along with its sensitivity to
the chemical influences of adsorbates and electronic perturbations to the cluster’s M-M bonding that result from the cluster-support interactions. The latter serve to illustrate the requirements for more complex models to fully account for the bonding in such supported catalysts.\textsuperscript{77,78}

The most interesting result coming from the EXAFS measurements is the anomalous thermal behavior of the 1NN Pt-Pt bond distances seen in our supported nanoclusters (Figures 5.15a, 5.16a and 5.18a). The occurrence of NTE for Pt/\(\gamma\)-Al\(_2\)O\(_3\) nanoclusters is unexpected given that the cluster bonding is expected to conform to a close-packed metal system. The most fundamental requirement for close-packed bonding, due to the anharmonicity of the interatomic potential, is that of thermal expansion in which the average M-M bond length increases with rising temperature. In rare cases, where bond bending can contribute, the vibrational motion can lead to a decrease in the volume of a solid material with temperature.\textsuperscript{79} A classic example of such behavior is that of cubic zirconium tungstate, in which its open framework structure allows low-frequency transverse vibrational modes to contribute more strongly to the thermal properties of the crystal lattice than high-energy longitudinal modes, with the result being a net NTE.\textsuperscript{79-82} Such forms of vibrational anisotropy cannot be supported within a close-packed metallic structure however.\textsuperscript{83} The qualitative models typically used to describe the bonding of supported clusters (e.g. a cube-octahedral structure) establish the M-M bonding in a way that is directly related to the FCC structure of bulk Pt. For this reason normal (i.e. more bulk-like) thermal properties are to be expected.\textsuperscript{37} Recent work has demonstrated, however, that size effects can complicate this picture. Bond relaxations (contractions in Pt-Pt bond distances), for example, provide prominent
contributions to the structure of small clusters -- a feature intuitively expected for systems heavily weighting the low-coordination environments of surface atoms within their net bonding.\textsuperscript{13,67,75,76,84} More recent theory-based studies have demonstrated a striking capacity for anisotropy in such relaxations -- that the bond relaxation need not occur uniformly in a single atomic layer at an interface but, instead, exhibit a broad variation among an array of sites on the cluster surface.\textsuperscript{77,78} These ideas are depicted schematically in Figure 5.20, which presents molecular dynamics models that summarize in a qualitative fashion essential ideas related to the structures our data define for one of the Pt/\textgamma-Al\textsubscript{2}O\textsubscript{3} systems examined in this work. The scheme shows one model for a truncated cuboctahedron shape, here depicting an orientation of the cluster along the 001 axis relative to the support. The model further assumes an energetic preference for terminating the cluster along low-index planes. The structure at center is a baseline unrelaxed model in which all atomic positions are placed at the average M-M bond distance found by EXAFS (2.747±0.002Å) at room temperature. The remaining two structures show two of several plausible versions for relaxing the M-M bond framework of this structure. The model on the left depicts a uniform contraction of all surface atoms. The structure on the right is one in which specific low M-M coordination environments (vertices, plane edges etc.) are relaxed. The point of interest here is that EXAFS analysis does not allow us to discriminate between the two models of disorder. The difference between the models translates into different populations of Pt-Pt bond lengths which are all be characterized by values of $\sigma^2_s$ that we experimentally measure. More definitive answers can be obtained by first principle calculations that take into account mesoscopic effects and can, therefore, be directly verified by EXAFS analysis.
It is not unexpected that adsorbates substantially modify the quantitative aspects of the static Pt-Pt bond relaxations (Figure 5.16b). Under reducing conditions for example, the cluster surfaces dissociate H₂ and bind H atoms. These interactions soften the non-dynamic bond contractions, relieving the strain due to relaxation of the surface Pt atoms. Under oxidizing conditions (O₂) the Pt-Pt bonds are more strongly contracted, exhibiting intense strain relative to bulk Pt-Pt distances of as much as 2.8% due to the electronic consequences of O adatoms terminating the cluster surface. Inert atmospheric conditions (He) afford Pt-Pt bond lengths lying between these two limiting cases. These general trends follow simple models for electronic structure in M-M bonding, namely changes to the d-state occupancy increasing/decreasing bonding character. Charge transfer, due to adsorbates, leads to changes in the electron density of these states. This results in a heightened static contractive force in the case of O-adatoms (electron withdrawing) when compared to H-adatoms (electron donating). We note here that the data in Figure 5.16 demonstrate these features persuasively. Furthermore, Tables 5.1 and 5.3 illustrate the significant cluster-size-dependencies of these contributions. These non-dynamic contractions, ones due to surface-sensitive relaxations of the Pt-Pt bond distances, are an aspect of structure that can be accounted for within a close-packed bonding model.

The EXAFS data presented above also demonstrate the size-dependent nature of the disorder that characterizes nanoparticle structure (Figure 5.15). As noted above, some aspects of non-homogeneous distribution of static Pt-Pt bond contractions within the cluster can be attributed to low coordination sites, such as atoms at an edge or vertex, where atoms regress inward toward the particle (relaxation). It follows intuitively that
the disorder must arise as a consequence of a population of bond-relaxations that broaden the width of bond length distributions. It was our interest in characterizing these latter influences that led us to originally examine the thermal dependence of the EXAFS data -- a requirement to deconvolute static and dynamic contributions to the value of $\sigma^2$. One also assumes that the heterogeneity that likely characterizes the cluster-support interactions could also accentuate the trends evidenced in the (size-dependent) degree of disorder present in the Pt-Pt interatomic bonding. The latter trends, though, are ones that can still be accommodated within a formal close-packed model of the cluster bonding. The origins of NTE in this system therefore must be more complex and involve factors other than vibrational anharmonicity. The nature of the electronic contributions that are likely involved is revealed by a systematic analysis of the NTE observed. First, the data show that it is a support dependent phenomenon -- of consequence for $\gamma$-Al$_2$O$_3$ supports and, from our data, essentially absent for carbon. Second, NTE scales with cluster size as the smallest clusters are those that are most significantly influenced by the energetics of the metal-support interactions. The transition range for the mesoscopic behavior of the Pt/$\gamma$-Al$_2$O$_3$ system is exceptionally narrow. One notes, for example, that the EXAFS data for the 2.9 nm clusters, while still showing appreciable Pt-Pt bond length contractions relative to the bulk, display a thermal dependence of the bond lengths that is similar to that measured for bulk Pt with one notable exception: measurements made under a H$_2$ atmosphere (which convolve a stronger contribution from the temperature dependence of the hydrogen coverage). The data obtained under He essentially deconvolutes this coverage-dependent effect from other contributions and reveals a more bulk-like (i.e., positive thermal expansion) response of the Pt-Pt bond lengths for the 2.9 nm samples
(Table 5.1). It is striking that the smaller particles exhibit NTE under all ambient conditions explored in this work. This demonstrates a crossover between perturbation sensitive and more bulk-like thermal effects in the 1.1 to 2.9 nm size range. A similar crossover between nanoscale and bulk-like responses was recently reported in a separate study of Au nanoclusters -- an NTE attributed in this instance to electronic influences dominating over vibrational effects as particle size decreased.\(^{59}\)

What then are the electronic origins of the NTE observed for the smallest particles? To answer this question, it is instructive to consider the temperature-dependent changes seen in the XANES spectra presented in Figure 5.18c. It is well established that XANES reports sensitively on perturbations of electronic structure that are common to nanoscale materials. For example, varying the acidity of the metal oxide support has been found to impact the edge position, white line intensity, and edge shape of Pt-XAS data due to polarization and charge transfer effects.\(^{32,51,71,85,86}\) As noted above, dynamic features of the particle/support interactions must also play a critical role in the observed temperature-dependent XANES spectra.\(^{77,78}\) Considering the 0.9 nm Pt/\(\gamma\)-Al\(_2\)O\(_3\) sample as a specific example, the HAADF-STEM data show that a representative cluster contains only on the order of 10-15 atoms;\(^{17}\) given the relatively low (experimental) 1NN coordination number of 5.5 (Table 5.1), one infers that essentially every atom in one of these particles resides either at the surface or support interface. The energetics, in this instance, must weight the contributions of such sites significantly.

We believe the XANES data demonstrate a flow of charge between the Pt nanoparticles and the \(\gamma\)-Al\(_2\)O\(_3\) support. The data in Figures 5.15c, 5.16c and 5.18c show that white line intensity increases at elevated temperatures, indicating a progressive
depletion of the occupied electronic states at the Fermi level, while at lower temperatures a decrease and broadening is observed, features consistent with the occurrence of a temperature-mediated charge-transfer. Two possible origins for this behavior are: (a) a charge transfer from the support to the particle that dissipates at high temperatures; or (b) a charge transfer from the particle to the support that progressively increases with temperature. The XANES data offer a model-independent basis for concluding that the underlying effect is one involving a decrease of charge on the nanoparticle at heightened temperatures as discussed below.

It is frequently noted in literature that the edge shift can be used to discriminate between mechanisms involving charge transfer either on to (negative, or red, shift) or from (positive, or blue, shift) an absorbing atom. Such relationships do indeed exist for many bulk materials -- most notably oxides, where the main contributor to the edge shift comes from changes in the core hole screening upon charge transfer (a final state effect). In nano-scale metal clusters, changes in the Fermi level due to charge transfer can also give rise to a set of opposing trends: red shifts with a decline of electron density and blue shifts with its accumulation. Since the two effects (screening and Fermi level change) can exert opposing influences on the x-ray absorption edge position, the sign of the direction of an edge shift with temperature alone cannot be used to determine the path of charge transfer. Other considerations, then, must be brought to bear to account for the trends seen in the XANES data (Figures 5.15c, 5.16c and 5.18c). It is instructive to consult literature precedent for thermal effects of the form established in the present work.
In a leading study, nearly identical thermally-driven changes in the XANES spectra (a red shift, increase in white line intensity and edge narrowing at increasing temperatures) were reported to occur for Pt/SiO$_2$ catalysts under both He and H$_2$ atmospheres by Lytle et al. (no information on the thermal influences on the Pt-Pt bond distances was provided however). They ascribed these changes to the progressive thermal breaking of bonds to surface oxygen atoms of the support, a hypothesis supported by the disappearance at high temperature of a Pt-O scattering contribution observed at the lowest measurement temperatures (90 K). An alternative explanation, and one supported by recent DFT/MD calculations, involves significantly increased disorder in the Pt-O bonding at higher temperatures that serves to essentially “wash out” the EXAFS from the Pt-O scattering pair subsequently modifying the interfacial structure associated with the transfer of charge. These are important consequences that support the idea of charge-transfer from the support as an underlying mechanism.

Theoretical studies examined a model Pt$_{10}$ cluster on the “d” layer of the [110] surface of $\gamma$-Al$_2$O$_3$. This work successfully reproduced many of the puzzling behaviors documented in the present (and notable past) work, including NTE and corresponding XANES related electronic effects detailed above. This study emphasized the interrelatedness of these phenomena, providing new and general insights into the dynamics of supported metal nanoclusters. The simulations reveal dynamical consequences for bonding that derive from a differentiated structure, one comprising discrete layers of “oxidized” Pt atoms (those bonded to support oxygen atoms, designated Pt$_O$) and metallic-like Pt atoms (with solely Pt neighbors, designated Pt$_M$). These calculations showed that as the temperature increased from 165 K to 573 K (i.e. identical
to the experimental temperature range described above) the average distances of the interlayer PtO-PtM bonds expanded markedly but was offset by larger contractions of the intralayer PtO-PtO and PtM-PtM bonds. These structural behaviors, as dictated by M-supported charge-transfer, result within the theoretical model in a net and progressive NTE of the average Pt-Pt bond distances. The most significant finding that emerges from this work, one that finds some support in the current literature, is that the structures adopted by nanoscale supported metal clusters embed significant amounts of disorder. The discussion above touches on one component of this disorder, the aspects that follow from the vibrational dynamics of specific M-M bonding pairs and their interactions with non-metal-center bonding contacts involving either support or adsorbate atoms. This theoretical study suggested that additional dynamical components are involved and merit careful consideration – i.e. significant impacts on bonding can result as a direct consequence of highly fluxional, non-vibrational dynamics. The present work demonstrates explicit cases where supported metal clusters can exhibit large amplitude librational motions that strongly impact the cluster’s atomic and electronic structures, aspects not previously considered in the context of supported metal catalyst particles. Future work is warranted to more completely examine the role of librational atomic motion in real catalytic systems, thereby establishing how they might modify site-specific forms of reactivity and/or stabilize clusters against sintering amongst other possibilities.

We now turn to a discussion of the surprisingly complex forms of bond disorder (as defined by $\sigma_s^2$) that can contribute to the ensemble structural properties of supported nanoclusters. The data presented above demonstrate that the Pt atoms in the nanoclusters
exhibit disorder as non-vibrational deviations from their idealized atomic positions on fcc sites -- an embedded disorder. Such deviations have been noted by others and ascribed to a variety of effects including surface tension,\textsuperscript{75,76} adsorbate induced strain,\textsuperscript{50,54,61,74} as well as non-vibrational dynamics (such as the long period librational motions discussed above).\textsuperscript{77,78} For all of the $\gamma$-Al$_2$O$_3$ supported clusters examined here, exposure to H$_2$ resulted in a significant decrease of $\sigma_s^2$ for 1NN Pt atom pairs quantitatively correlating with a lifting of surface relaxation. Consistent with this model, the data show that the 0.9-nm clusters exhibit the largest response to hydrogen, presumably due to the higher fraction of metal atoms residing at surface sites. The anomalously high $\Theta_E$ (207 K under H$_2$ vs. 298 K under He) in this case suggest that, while the correlated Einstein model can adequately fit the experimental data, the underlying assumption that vibrational degrees of freedom strictly embody cluster dynamics neglects important aspects of the physics involved. The latter conclusion is one that is strengthened by the non-bulk-like anomalies noted in thermal expansion (the apparent NTE), XANES data (red shift), and large librational and static structural disorder revealed in DFT/MD and FEFF8 simulations.

The anomalous nature of $\sigma^2$ and the high values of $\Theta_E$ in such cases are difficult to reconcile within a simple model involving solely thermal populations of vibrational states of a single underlying equilibrium structure. If the latter were the case, the materials would be characterized by a temperature-independent anharmonic effective pair potential (a model often used in textbooks to visualize conventional thermal expansion). The temperature-dependent charge transfer, as strongly evidenced in the XANES data, implicitly establish the importance of interactions that serve to continuously modify the
total energy of the supported clusters (doing so on \( \gamma \)-Al\(_2\)O\(_3\) in ways that lead to NTE). As a result, the data require that the effective pair potential curve would need to be redefined at each temperature. Vila et al.\textsuperscript{77} confirmed this idea, revealing that the simulated nanocluster structure was in fact dynamic, with transient bonding and topology exhibiting stochastic motion of the center of mass on time scales long compared with internal vibrations. These librational motions lead to Pt-O bond breaking and formation very much in line with the prescient notion of Lytle \textit{et al.},\textsuperscript{88} producing a level of disorder in the simulations that is consistent with the results found in experiment and the low amplitudes that preclude direct characterization of Pt-O bonding in the EXAFS. More importantly, their temperature-dependent, non-vibrational contribution to the bond disorder fully accommodates contributions that cannot be accounted for by the correlated Einstein model used to fit the experimentally determined \( \sigma^2 \) (Eq. 1,2). One must instead substitute time- and configuration-dependent averaging to characterize static and dynamic contributions to the Debye-Waller factors.\textsuperscript{37,47}

We now turn our attention to the effect of adsorbates -- hydrogen and oxygen -- on the electronic structure of Pt/\( \gamma \)-Al\(_2\)O\(_3\) nanoclusters. The spectral changes shown in Figure 5.18c, and reported by others, include a red shift of the absorption edge, decrease in white line intensity, and peak narrowing on the high energy side at elevated temperatures. Such changes have been explained variously as being due to the creation of Pt-H antibonding states, Pt-H scattering, induced changes in Pt-Pt scattering and changes in the atomic background scattering potential (i.e. the atomic x-ray absorption fine structure (AXAFS)).\textsuperscript{51,90-93} The relative importance of these contributions remains controversial and a subject of much debate.\textsuperscript{51,91,92} The present data demonstrate an
important caveat, that such changes are not solely a characteristic of hydrogen on the Pt/γ-Al₂O₃ nanoclusters, given their absence in data for the Pt/C samples (Figure 5.18 and Table 5.2) that clearly show very similar relaxation effects of hydrogen viz. the Pt-Pt bond distances. Ultimately, the data convey the crucial role of the bonding occurring at the particle/support interface. These inferences are further reinforced by the oxygen data, which reflect conditions that cannot accommodate hydrogen bound at an ambient cluster interface. Important consequences for structure do attend the bonding of these adsorbates, however, as discussed below.

H₂ adsorption lifts the surface relaxation of the Pt-Pt bond distances. The sharing of electron density with antibonding states weakens the bonding character of the M-M bonds in the cluster.⁵⁰,⁶⁹,⁹⁰ It is not surprising then that H₂ adsorption also affects the magnitude of the NTE. This trend is particularly evident in the data for the 0.9-nm Pt/γ-Al₂O₃ nanoclusters, for which $\alpha = (-1.3 \pm 0.3) \times 10^{-5} \text{ K}^{-1}$ under H₂ and $(-2.4 \pm 0.4) \times 10^{-5} \text{ K}^{-1}$ under He (Table 5.1). We believe the overall weakening of the Pt-Pt bonds likely diminishes the dissimilarities between the differentiated forms of Pt-Pt bonding (Ptₘ and Ptₒ) revealed by recent DFT/MD calculations. Hydrogen acting as a weak electron donor, one expects it to diminish the $\sigma_s^2$, while increasing its temperature dependence via the weakening of the M-M bonding structure in the cluster. The effects are in fact observed experimentally with the latter manifesting more bulk-like behavior and improved descriptive competency of the correlated Einstein model (Figure 5.16).

The impact of oxygen atom coordination on the nanoclusters has very different effects, notably inducing significant Pt-Pt bond contractions by withdrawing electron density from the cluster. The particle size dependence aspects of this data clearly reveal
the significant consequence that oxygen bound at surface sites result in a stiffer M-M
bonding network (Figure 5.16 and Table 5.3). The smallest (0.9-nm) Pt/γ-Al₂O₃
nanoclusters are impacted most dramatically by coordinated O adatoms. The Pt-Pt bond
lengths in this case contract substantially, the observed NTE is larger in magnitude, and
the σ² is the largest found in any of the experiments (Table 5.3). These oxidized sub-
nanometer clusters exhibit structural and electronic properties that markedly differ from
those of the bulk metal.

We close with a final consideration of broader trends revealed in the size-
dependent emergence of mesoscopic behaviors in the Pt/γ-Al₂O₃ system and the
consequences that such factors may hold with respect to their catalytic properties. The
static contractions of the Pt-Pt bond lengths (due to surface relaxation) correlate strongly
with cluster size and are neither unprecedented nor unexpected. These
bond strains, ones akin to surface relaxation in a bulk crystal, serve to compensate for the
low average Pt-Pt coordination numbers. The present work, however,
demonstrates a somewhat more surprising trend, namely that the perturbations that come
from atoms experiencing metal-support interactions can in fact rival, or possibly exceed,
those due to M-M bonds involving atoms lying at the cluster’s ambient interface (the
latter region being where the influences of adsorbate must be most strongly weighted.
The ensemble-average picture of atomic and electronic structure offered by XAS has
served to mask the strong, and materials-dependent, influences of the metal-support
interactions. Such bonding can be richly diverse even for samples comprised of limited
distributions of atomic mass. It remains, however, that specific dynamical sensitivities
are expressed differently in the XAS data. The long-period, large amplitude librations
that MD/DFT suggests are critically important for Pt/γ-Al₂O₃, provide a notable case in point. Vila et. al.⁷⁷ show that the latter low frequency motion of the cluster center of mass follows a form analogous to that of a 2-dimensional Brownian-like motion (center of mass speed, \( v = \sqrt{\frac{2k_BT}{m}} \) where m is the cluster mass). This motion, given its explicit dependence on \( \frac{1}{\sqrt{m}} \), will be much more significant for small clusters.

The present data, while extensive, leave a critical feature of the Pt/γ-Al₂O₃ systems unsatisfactorily defined -- the atomistic architecture of the metal-support interactions that are central to the properties of this prototypical catalyst system. Part of the deficiency results directly from the considerable uncertainty regarding the atomic structure of the particle-support interface.³⁰-³³,³⁵,⁵² For example, any truncation of the supports bulk structure must present considerable chemical complexity -- including strongly perturbing defects such as oxygen atom vacancies -- at a terminating boundary. The XAS data tells us little of utility vis-à-vis the bonding arrangements that a supported Pt cluster adopts at these latter interfaces. The most likely inference to draw is that these interactions are both fluxional and subject to heterogeneity (supporting the presumption of significant disorder).⁷⁷ All the same, it remains likely that the substantial electronic perturbations are also the result of other contributing factors which strongly weight the compositional morphology of the support. We believe strong cluster interactions with O-atom vacancies on the support may critically contribute to the dynamic behavior of the supported cluster, an inference supported by theoretical study.⁷⁷ Future work will be needed to characterize such aspects more definitively given the critical role that γ-Al₂O₃ appears to play as a support that improves the properties of Pt catalysts. Studies using atomic resolution STEM are currently in progress towards this end.
5.6 Conclusions

We describe the systematic analysis of the complex thermal behaviors of well-defined supported Pt catalysts, by measuring their structural and electronic properties in-situ. These temperature-dependent measurements revealed non bulk-like behavior (NTE, anomalous electronic properties and large static disorder) in the smallest Pt/γ-Al₂O₃ nanocluster samples under O₂, He and H₂ atmospheres. The coincidence of temperature-mediated changes to the electronic structure (observed by XANES) and atomic structure point to the inadequacy of cluster models described only by vibrational dynamics. Our results reveal that mesoscopic phenomena originate from the complex interactions occurring between the Pt clusters and the support under the mediating influences of adsorbates. Adsorption of hydrogen on the Pt/γ-Al₂O₃ nanoclusters reduces the cluster-support interaction by lifting contraction due to surface relaxation of the Pt-Pt bonds while oxidation of the particles increases the support-mediated impacts by increasing the strain and decreasing the electron density in the cluster. Similar measurements made on Pt nanoclusters supported on a carbon black reveal much weaker support effects than are seen for the γ-Al₂O₃ supported samples. Systematic interpretation of EXAFS and XANES measurements of such supported clusters offers an innovative methodology for elucidating support- and adsorbate-mediated changes to the electronic and atomic structures of the nanoparticles. Such insights into the structure and dynamics of nanoscale materials is required to enable the rational design of systems with desired properties, a goal particularly relevant to improving the performance of catalysts and other functional nanomaterials.
5.7 Acknowledgements

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Figure 5.1. HAADF-STEM images and atom-count histograms shown for the (a, b) 0.9-nm (c, d) 1.1-nm and (e, f) 2.9-nm Pt nanoparticles supported on $\gamma$-Al$_2$O$_3$, respectively. The insets in b, d, and f are the corresponding size distribution histograms for the Pt/$\gamma$-Al$_2$O$_3$ depicted in a, c, and e.
Figure 5.2. Quantitative determination of geometric structure of the nanoparticles determined by the integrated areal intensity obtained from HAADF-STEM images. Representative particle diameters are plotted with respect to their integrated intensities (filled circles) for the (a) 0.9±0.2 (b) 1.1±0.3 and (c) 2.9±0.9 nm Pt/γ-Al₂O₃. The curves represent guides correlated with integrated areal intensities for monolayer, cuboctahedral and truncated cuboctahedral nanoparticle structures. The average number of atoms found for the clusters in each sample is shown as Nₐᵥg with ± values representing the average of the calculated standard deviations.
Figure 5.3. Representative data showing the temperature reversibility of the 2.9 and 0.9 nm Pt/γ-Al₂O₃ samples as depicted by their k-space data (a and b), their subsequent Fourier transform (c and d) and the XANES data (e and f) (2.9 and 0.9 nm respectively). The temperatures experienced during the heating procedure were a high temperature of 573 K (573 K) and a low temperature of 185 K (165 K) for the O₂ (H₂) environment.
Figure 5.4. k-space data (a), the subsequent Fourier transform (b) and the XANES data (c) showing reversibility of cluster structure and electronic state are shown for the 2.9 nm Pt/γ-Al₂O₃ sample investigated. The temperature of the reduction and oxidation was 573 K.
Figure 5.5. Pt-Pt Coordination numbers as a function of temperature, for the smallest (0.9nm) and the largest (2.9nm) samples in He and H$_2$ on $\gamma$-Al$_2$O$_3$ support. The trend shows very weak dependence on temperature (same effect was also observed in Pt foil when its coordination number was allowed to vary, which is, evidently, an artifact of the analysis) and thus can be ignored by fixing the coordination number to be constant in the fit.
Figure 5.6. Data for 2.9-nm Pt/γ-Al₂O₃ sample plotted with best fits in reduced states under inert (He) and reducing (H₂) atmospheres analyzed for a series of temperatures.
Figure 5.7. Data for 1.1-nm Pt/γ-Al₂O₃ sample plotted with best fits in reduced states under inert (He) and reducing (H₂) atmospheres analyzed for a series of temperatures.
Figure 5.8. Data for 0.9-nm Pt/γ-Al₂O₃ sample plotted with best fits in reduced its reduced state under inert (He) and reducing (H₂) atmospheres analyzed for a series of temperatures.
Figure 5.9. Examples of the difference file technique used to isolate and fit the low-Z contributors shown here for the low (186 K) and high (573 K) temperature measurements made for the oxidized (O$_2$) 2.9 nm Pt/γ-Al$_2$O$_3$ samples. (a) and (c) show the Fourier transform magnitudes of the raw data and fitting of the Pt-Pt first-nearest-neighbor (~2.1-3 Å) at 186 and 573 K, respectively. Subtraction of the theoretical fit from the experimental data and fitting (~1.4-2 Å) of the remaining low-Z scattering contributions at 186 and 573 K, shown for (b) and (d) respectively.
Figure 5.10. Examples of the difference file technique used to isolate and fit the low-Z contributors shown here for the low (170 K) and high (573 K) temperature measurements made for the 1.8 nm Pt/C samples under He flow. (a) and (b) show the Fourier transform magnitudes of the raw data plotted with the corresponding fits for the Pt-Pt first-nearest-neighbor (~2.1-3 Å) at 170 and 573 K, respectively. Subtraction of the theoretical fit from the experimental data and fitting of the remaining low-Z scattering contributions (~1.4-2 Å) at 170 and 573 K shown for (c) and (f), respectively.
Figure 5.11. HAADF-STEM images of (a) 1.0-nm and (b) 1.8-nm Pt nanoparticles supported on carbon black with the associated size distribution histograms (c) and (d).
Figure 5.12. (a) EXAFS data in k-space illustrating the effect of cluster size on the oscillatory pattern of different Pt/γ-Al₂O₃ samples and a bulk foil standard (k-weight = 0; k-range = 2 – 14 Å⁻¹) with corresponding (b) Fourier transform magnitudes. (c) Progressive changes in intensity of the EXAFS data in k-space for a 2.9 nm Pt/γ-Al₂O₃ sample (k-weight = 0; k-range = 2 – 14 Å⁻¹) in response to temperature variation and (d) corresponding Fourier transform magnitudes with gradual changes in real space.
Figure 5.13. Room temperature Fourier transform magnitudes for the 1.0 and 1.8 nm Pt/C samples plotted with the Pt foil standard.
Figure 5.14. Comparison of the Fourier transform magnitudes \((k^2, k=2-13 \text{ Å}^{-1})\) of Pt/\(\gamma\)-Al\(_2\)O\(_3\) samples in their oxidized and reduced states. The spectra shown were collected at room temperature for reduced (H\(_2\)) or oxidized (O\(_2\)) nanoclusters. (a) 2.9-nm Pt/\(\gamma\)-Al\(_2\)O\(_3\), (b) 1.1-nm Pt/\(\gamma\)-Al\(_2\)O\(_3\), and (c) 0.9-nm Pt/\(\gamma\)-Al\(_2\)O\(_3\) nanocluster samples.
Table 5.1. Fit results and calculated thermal parameters of Pt\(/\gamma\)-Al\(_2\)O\(_3\) nanoclusters measured in reducing and inert environments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>N</th>
<th>Pt-Pt (\gamma^2_{\text{adj}}(\AA^2))</th>
<th>(\gamma_{\text{fit}}(\text{K}))</th>
<th>average (\gamma^2 10^5) (K(^{-1}))</th>
<th>(R_{\text{fit}}(\AA))</th>
<th>(?E_\text{a}(\text{eV}))</th>
<th>reduced (\gamma^2)</th>
<th>average (\gamma^2 10^5) (K(^{-1}))</th>
<th>(R_{\text{fit}}(\AA))</th>
<th>(?E_\text{a}(\text{eV}))</th>
<th>reduced (\gamma^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.9 nm</td>
<td></td>
<td>5.5(2)</td>
<td>0.0069(3)</td>
<td>300(24)</td>
<td>-24(4)</td>
<td>2.686(8)</td>
<td>5.4(5)</td>
<td>14.6</td>
<td>5.9(2)</td>
<td>0.0052(2)</td>
<td>207(6)</td>
</tr>
<tr>
<td>1.1 nm</td>
<td></td>
<td>6.3(3)</td>
<td>0.0045(2)</td>
<td>226(7)</td>
<td>-14(5)</td>
<td>2.704(6)</td>
<td>6.4(4)</td>
<td>7.5</td>
<td>6.8(2)</td>
<td>0.0037(2)</td>
<td>204(5)</td>
</tr>
<tr>
<td>2.9 nm</td>
<td></td>
<td>9.7(1)</td>
<td>0.0021(1)</td>
<td>203(2)</td>
<td>2(1)</td>
<td>2.747(2)</td>
<td>7.9(2)</td>
<td>7.5</td>
<td>9.8(1)</td>
<td>0.0015(8)</td>
<td>200(2)</td>
</tr>
<tr>
<td>Foil</td>
<td></td>
<td>12.1(2)</td>
<td>0.00017(8)</td>
<td>178(2)</td>
<td>11(1)</td>
<td>2.747(2)</td>
<td>8.6(3)</td>
<td>15.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4% H(_2) (balanced by He)</td>
<td></td>
<td></td>
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<td></td>
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</tr>
</tbody>
</table>

Table 5.2. Fit results and thermal parameters of Pt/C nanoclusters

<table>
<thead>
<tr>
<th>Sample</th>
<th>N</th>
<th>Pt-Pt (\gamma^2_{\text{adj}}(\AA^2))</th>
<th>(\gamma_{\text{fit}}(\text{K}))</th>
<th>average (\gamma^2 10^5) (K(^{-1}))</th>
<th>(R_{\text{fit}}(\AA))</th>
<th>(?E_\text{a}(\text{eV}))</th>
<th>reduced (\gamma^2)</th>
<th>average (\gamma^2 10^5) (K(^{-1}))</th>
<th>(R_{\text{fit}}(\AA))</th>
<th>(?E_\text{a}(\text{eV}))</th>
<th>reduced (\gamma^2)</th>
</tr>
</thead>
</table>
| Under He   |    |                                  |                 |                        |                |                 |                 |                        |                |                 |                 |\
| 1.0 nm Pt/C|    | 5.4(2)                           | 0.0029(2)       | 193(4)                 | 2(4)          | 2.735(7)       | 0.9(2)          | 2.16(3)                 | 0.000(4)      | 7.4(8)          | 3.0             | 324.4          |
| 1.8 nm Pt/C|    | 7.7(1)                           | 0.0023(1)       | 195(3)                 | 10(2)         | 2.755(4)       | 0.7(2)          | 2.17(4)                 | 0.000(6)      | 7.6(4)          | 5.3             | 633.4          |
| Under H    |    |                                  |                 |                        |                |                 |                 |                        |                |                 |                 |\
| 1.0 nm Pt/C|    | 5.6(2)                           | 0.0024(2)       | 189(4)                 | 1(3)          | 2.747(7)       | 0.9(2)          | 2.13(4)                 | 0.000(5)      | 7.7(8)          | 5.3             | 681.4          |
| 1.8 nm Pt/C|    | 7.6(2)                           | 0.0023(1)       | 196(3)                 | 10(2)         | 2.755(3)       | 0.7(2)          | 2.17(4)                 | 0.000(5)      | 7.8(5)          | 9.4             | 633.1          |

* Value at 293 K. Uncertainties exceed best fit values.

Table 5.3. Fit results and thermal parameters of oxidized Pt/\(\gamma\)-Al\(_2\)O\(_3\) nanoclusters

<table>
<thead>
<tr>
<th>Sample</th>
<th>N</th>
<th>Pt-Pt (\gamma^2_{\text{adj}}(\AA^2))</th>
<th>(\gamma_{\text{fit}}(\text{K}))</th>
<th>average (\gamma^2 10^5) (K(^{-1}))</th>
<th>(R_{\text{fit}}(\AA))</th>
<th>(?E_\text{a}(\text{eV}))</th>
<th>reduced (\gamma^2)</th>
<th>average (\gamma^2 10^5) (K(^{-1}))</th>
<th>(R_{\text{fit}}(\AA))</th>
<th>(?E_\text{a}(\text{eV}))</th>
<th>reduced (\gamma^2)</th>
</tr>
</thead>
</table>
| O\(_2\)    |    |                                  |                 |                        |                |                 |                 |                        |                |                 |                 |\
| 0.9 nm     |    | 4.7(2)                           | 0.0082(4)       | 350(43)                | -29(4)        | 2.671(1)       | 0.8(2)          | 1.99(2)                 | 0.0006(3)     | 4.5(9)          | 3.7             | 74.1           |
| 1.1 nm     |    | 5.8(3)                           | 0.0040(3)       | 199(7)                 | -14(7)        | 2.689(8)       | 0.6(2)          | 2.01(4)                 | 0.008(4)      | 6.1(5)          | 10.9            | 43.1           |
| 2.9 nm     |    | 8.2(2)                           | 0.0020(1)       | 192(4)                 | 1(3)          | 2.747(8)       | 1.0(1)          | 1.99(1)                 | 0.004(1)      | 8.9(6)          | 18.5            | 44.0           |

* Value at 293K.
Figure 5.15. The role of nanoparticle size on structural dynamics is shown for the 0.9, 1.1 and 2.9-nm Pt/γ-Al2O3 samples. (a) Thermal dependence of the 1NN Pt-Pt bond distances for the different sized Pt/γ-Al2O3 nanoparticles compared to a Pt foil standard illustrating the effect of particle size on NTE. (b) Temperature dependence of the Debye-Waller factors (symbols), $\sigma^2$, for the various sized Pt/γ-Al2O3 nanoparticles and Pt foil plotted with their respective Einstein models (lines). (c) XANES behavior of the Pt/γ-Al2O3 nanoparticles for a given temperature range showing increasing sensitivity to temperature with respect to nanoparticle size. Note: the curves (solid lines) were inserted as aids to guide the eye.
Figure 5.16. The observed adsorbate effect is shown for samples exposed to reactive \((H_2, O_2)\) and inert \((He)\) gas phase environments. (a) Shows the result of particle-adsorbate interactions for the 0.9 nm Pt/\(\gamma\)-Al\(_2\)O\(_3\) sample examined by measuring the temperature dependence of the 1NN Pt-Pt interatomic distances. (b) Dependence of the \(\sigma^2\) (symbols) on temperature for a 0.9 nm Pt/\(\gamma\)-Al\(_2\)O\(_3\) and Pt foil with the Einstein models (lines) included for the different ambient conditions studied. (c) Fluctuations in the XANES spectra of the 0.9 nm Pt/\(\gamma\)-Al\(_2\)O\(_3\) sample for a series of temperatures as influenced by the absence/presence of adsorbate.
Figure 5.17. Control experiment showing behavior of the 1st neighbor distance of the Pt-Pt bonds under 5% H₂ gas mixture (balance He) and ultra-high purity hydrogen gas for the 2.9 nm Pt/γ-Al₂O₃ sample. Both data sets plotted simultaneously with Pt foil data.
Figure 5.18. Effects of the support examined in terms of (a) temperature dependence of the 1NN Pt-Pt distances for 0.9 nm Pt/γ-Al₂O₃ and 1.0 nm Pt/C samples compared simultaneously with a Pt foil standard. (b) Contrasting behaviors of σ² with respect to temperature for the γ-Al₂O₃/C supported Pt particles and Pt foil plotted with their respective Einstein models (lines). (c) Monitored changes to XANES spectra for the 0.9 nm Pt/γ-Al₂O₃ and 1.0 nm Pt/C samples over a temperature range of 165 – 573 K and 170 – 573 K, respectively.
Figure 5.19. (a) Room temperature measurements of 1NN Pt-Pt bond distances, (b) the static component of the Debye-Waller factor, $\sigma_s^2$ and (c) the Einstein temperature, $\Theta_E$, as a function of size for Pt samples (0.9, 1.1 and 2.9-nm Pt/$\gamma$-Al$_2$O$_3$ and Pt foil) measured in reduced (He and H$_2$) and oxidized states. Cluster size is denoted by coordination number and the associated errors are tabulated (See Tables 5.1 and 5.3).
**Figure 5.20.** The top view of an idealized 2.9 nm Pt nanoparticle containing 500 atoms arranged with a truncated cuboctahedral structure is shown in the center image. The structure on the left shows surface relaxation of the cluster atoms as computed using a molecular dynamics simulation. The structure on the right follows from a qualitative relaxation restricted to specific low coordination site atoms. In this latter cluster, atoms that are localized at their perfect lattice positions are shown in grey and atoms in red-scale indicate areas with increasing strain as compared to the idealized structure.
References


For systems with moderate bond length disorder to which EXAFS analysis is applicable, anharmonicity of bond vibration introduces a relatively small correction to the effective pair potential. To extract the lowest cumulants of the pair distribution function of a given pair, it thus required that the EXAFS peak be well isolated from overlap with neighboring single- and multiple-scattering contributions. When a Pt-low Z contribution becomes significant, Pt-Pt coordination becomes a second nearest neighbor (2NN). It is then expected that its analysis by the third cumulant may be unstable, due to the interference with Pt-low Z contribution, and special caution is needed, as shown in our work where the difference file technique was used, to reliably isolate the third cumulants of Pt-Pt bonds in these situations.


(89) Theoretical experiments, then, show a highly consistent picture, with the former establishing the essential underpinnings of dynamics in the mediation of thermal influences on the metal-support and Pt-Pt bonding.


6.1 Abstract

This study describes a prototypical, bimetallic heterogeneous catalyst: compositionally well-defined Ir-Pt nanoclusters with sizes in the range of 1-2 nm supported on $\gamma$-Al$_2$O$_3$. Deposition of the molecular bimetallic cluster $[\text{Ir}_3\text{Pt}_3(\mu-\text{CO})_3(\text{CO})_3(\eta-\text{C}_5\text{Me}_5)_3]$ on $\gamma$-Al$_2$O$_3$, and its subsequent reduction with hydrogen, provides highly-dispersed supported bimetallic Ir-Pt nanoparticles. Using spherical aberration-corrected scanning transmission electron microscopy ($C_s$-STEM) and theoretical modeling of synchrotron-based X-ray absorption spectroscopy (XAS) measurements, our studies provide unambiguous structural assignments for this model catalytic system. The atomic resolution $C_s$-STEM images reveal strong and specific lattice directed strains in the clusters that follow local bonding configurations of the $\gamma$-Al$_2$O$_3$ support. Combined nanobeam diffraction (NBD) and high-resolution transmission electron microscopy
(HRTEM) data suggest the polycrystalline $\gamma$-Al$_2$O$_3$ support material predominantly exposes (001) and (011) surface planes – ones commensurate with the zone axis orientations frequently exhibited by the bimetallic clusters. The data reveal that the supported bimetallic clusters exhibit complex pattern of structural dynamics, ones evidencing perturbations of an underlying oblate/hemispherical cuboctahedral cluster-core geometry with cores that are enriched in Ir (a result consistent with models based on surface energetics, which favor an ambient cluster termination by Pt) due to the dynamical responses of the M-M bonding to the specifics of the adsorbate and metal-support interactions. Taken together, the data demonstrate strong temperature-dependent charge-transfer effects occur that are likely mediated variably by the cluster-support, cluster-adsorbate, and intermetallic bonding interactions.

### 6.2 Introduction

In recent years, the characterization of nanoscale catalysts in basic energy-related research, especially as it regards their structural dynamics under operating conditions, has proven to be a frontier challenge.\(^1\)\(^-\)\(^4\) Significant research efforts have established important, but incomplete, guidance as to the nature of atomistically rationalized structure-rate relationships for several important classes of heterogeneously catalyzed reactions.\(^3\)\(^,\)\(^5\)\(^,\)\(^6\) These findings in some regards follow those developed in the more extensive literature on catalysis carried out on single-crystal surfaces.\(^3\)\(^,\)\(^7\)\(^,\)\(^8\) It has been shown, for example, that the nature of an exposed crystal facet (i.e. (111), (011), etc.) on a nanoparticle can bias the chemistry that occurs at the surface and give rise to varying products.\(^9\)\(^-\)\(^11\) The oxidation of styrene by Ag nanoparticles, as a specific example,
proceeds on the (001) facets at a rate that is significantly higher than that seen on the 
(011) or (111) facets.\textsuperscript{11} This notable example illustrates the larger requirement of 
understanding a nanoparticle’s atomic scale features that might in turn serve to rationalize 
aspects of its catalytic properties.

In most important commercial processes, the catalytic materials present in 
supported form can be chemically quite complex – multi-metallic compositions, complex 
structural and chemical promoters, alloying components, and multifunctional supports 
being some examples.\textsuperscript{3,6,12-15} The modification of supported metallic heterogeneous 
catalysts with secondary metals is especially important as it provides a common strategy 
for improving catalytic activity, selectivity, and stability.\textsuperscript{15-23} The performance 
improvements obtained over supported monometallic catalysts have been attributed 
variously to such features as the alteration of the particle’s structural and electronic 
properties that occurs upon alloying with a second metal.\textsuperscript{22,24,25} Though catalytic 
applications of such materials has garnered considerable attention in research,\textsuperscript{5,16-21,23,26-34} 
much of our mechanistic understanding of enhanced performance remains qualitative at 
best.

A variety of techniques have been used to characterize supported nanoparticle 
catalysts of this type.\textsuperscript{35,36} Electron microscopy, when used in conjunction with energy 
dispersive X-ray spectroscopy (EDX), is particularly useful and provides means through 
which to establish such attributes as catalyst particle size, dispersion, and elemental 
composition.\textsuperscript{35,36} Electron diffraction has been intensively exploited to assess the nature 
of the crystalline habits that are present in nanostructures, doing so with facility in 
systems with metal clusters as small as 2-3 nm.\textsuperscript{37,38} More recently however, C\textsubscript{s}-STEM
has offered stunning results in the characterization of nanocrystal morphologies – measurements providing the most explicit depictions of the atomic structural attributes of heterogeneous catalytic materials.\textsuperscript{39-41} As we and others have shown\textsuperscript{1,42,43} the latter data are complimented by characterizations developed using XAS, which provides quantitative information about electronic structure and the local atomic bonding environments surrounding specific elements in a cluster, as well as a more qualitative description of its geometry.\textsuperscript{44-46} Measurements of the X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) regions of these spectra, more explicitly reveal the nature of specific oxidation states, coordination environments, bond distances, and structural coherency that are present in an ensemble of catalytic clusters.\textsuperscript{44-46} The literature now richly demonstrates the synergies that develop when direct structural probes, such as electron microscopy, are used in tandem with such spectroscopic capabilities.\textsuperscript{2,16,47-49} The present report extends this synergistic coupling to a detailed investigation of the structural dynamics evidenced in an exemplary heterogeneous catalytic system, Ir-Pt bimetallic nanoclusters supported on $\gamma$-Al$_2$O$_3$.

In an earlier report, we described the synthesis and atomic level structural characterization of polymer stabilized Pt and Pd nanoparticles, including clusters with alloy and core/shell motifs, using C$_s$-STEM and theoretical simulations.\textsuperscript{40} In that work it was determined that monometallic nanoparticles of Pt and Pd adopt diverging 3-D crystalline morphologies at the smallest size regime studied (~1-3 nm). The significance of that work is that it demonstrated the exceptional capacities for structural characterization afforded by quantitative analytical electron microscopy measurements made at atomic resolution. For the materials considered in that study, Z-contrast
microscopy provides a means for imaging, counting, and speciating atoms in a nanocluster with single atom precision. Crystal truncations, defects, shape anisotropies, facet systems, and atomic segregation in the binary phases are among the different classes of information that measurements of this type can provide. These materials – systems of interest for electrocatalysis\textsuperscript{17,18,27} – have several advantages that favor C\textsubscript{s}-STEM studies, not the least of which are the significant Z-contrasts afforded by binary Pt-Pd cluster compositions and their distinction from the relatively low-Z scattering background provided by the thin stabilizing polymer layers. In this respect, these compositionally, and morphologically, well defined (essentially homogeneous) cluster catalysts provide a number of important contrasts to the more complex heterogeneous catalysts studied here. Most notable of these complexities are the absence of a Z-contrast between the Ir and Pt constituents as well as the more significant backgrounds contributed by the alumina support.

Here we examine the atomic and electronic structures of a supported bimetallic catalyst that closely models systems broadly used in hydrocarbon reforming processes – Ir-Pt particles supported on $\gamma$-Al\textsubscript{2}O\textsubscript{3}.\textsuperscript{20,33} The incorporation of Ir into Pt/$\gamma$-Al\textsubscript{2}O\textsubscript{3} petroleum refining catalysts has been shown to enhance the stability of the catalyst. In part, this is a result of the hydrogenolytic activity of Ir, which lowers the rate of coke deposition on the Pt metal catalysts.\textsuperscript{24,33,50} It has also been suggested that specific support interactions can lead to improvements in catalyst regeneration.\textsuperscript{6} In general terms, the diverse form of the impacts that have been found in systems like this are ones that are difficult to explain through a mere additive combination of each metal’s attributes. The collaborative interplay of geometric and electronic effects must arise as a consequence of
specific forms of atomic bonding.\textsuperscript{40,51} Their effects, in turn, would be further impacted by the interactions of the metal cluster surfaces with both adsorbates and the support.\textsuperscript{42,52,53} In almost every respect, the atomic-level bonding important in these contexts remains poorly understood.

To aid the characterization efforts of this work we adopted a synthetic approach to the Ir-Pt system that yields supported binary clusters – one based on the use of molecular precursors to prepare Ir-Pt heterogeneous catalysts with narrow size and compositional distributions.\textsuperscript{54,55} Herein we describe the preparation of compositionally controlled Ir-Pt nanoparticles supported on $\gamma$-Al$_2$O$_3$ using the molecular precursor [Ir$_3$Pt$_3$(μ-CO)$_3$(CO)$_3$(η-C$_5$Me$_5$)$_3$].\textsuperscript{56} The C$_s$-STEM micrographs made of the resultant nanoparticles show that these clusters are dispersed evenly over the support surface even at total metal weight loadings as high as 10\%, and that the individual particles retain the 1:1 Ir to Pt stoichiometry of the precursor. We find that the supported particles exhibit complex, environmentally responsive structural dynamics. Collectively, the data suggest that the clusters adopt quasi-phase-segregated core-shell structures that are further impacted by non-bulk-like, environmentally sensitive atomic relaxations. The broader structural features evidenced in Ir-Pt/$\gamma$-Al$_2$O$_3$, and atomic strains embedded within them, are also found to strongly track specific atomic level structural features of the support, as deduced from quantitative analyses of the C$_s$-STEM data.

6.3 Experimental Methods

\textit{Ir-Pt/$\gamma$-Al$_2$O$_3$ Nanoparticle Preparation:} The molecular cluster [Ir$_3$Pt$_3$(μ-CO)$_3$(CO)$_3$(η-C$_5$Me$_5$)$_3$] was synthesized in a manner previously described in literature.\textsuperscript{57}
The precursor cluster has a very strong affinity for the $\gamma$-Al$_2$O$_3$ support and rapidly adsorbs from a toluene solution. In order to achieve a more controlled deposition for a sample with a total metal loading of 10% by weight, the precursor was deposited by four successive treatments from dilute cluster solutions. To a stirred suspension of 500 mg of $\gamma$-Al$_2$O$_3$ (220 m$^2$/g, Alfa-Aesar) in 10 mL of toluene was added 21.5 mg of the Ir$_3$Pt$_3$ cluster compound (FW=1735.65 g/mol) dissolved in 30 mL of toluene. After the mixture had been stirred for 3 h, the cluster had qualitatively adsorbed onto the support. The colorless supernatant was decanted, and a fresh solution (21.5 mg cluster in 30 mL toluene) was added to the $\gamma$-Al$_2$O$_3$ and the same procedure followed. Two additional treatments (20 mg cluster in 30 mL toluene) required stirring times of 14 and 20 h, respectively, to achieve the same level of deposition. The supported clusters were collected on a medium glass frit, washed with 30 mL of toluene and dried under vacuum. The supported cluster sample was heated under a reducing atmosphere in an in-situ XAS sample cell in order to generate the supported Ir-Pt nanoparticles (see details below).

**X-ray Absorption Spectroscopy Experimental Technique:** Argonne National Laboratory’s beam line 33-BM at the Advanced Photon Source was used for acquisition of all XAS data. A pellet of the 10 wt% Ir-Pt/$\gamma$-Al$_2$O$_3$ sample was pressed at 4 tons and then mounted in an in situ EXAFS cell. Spectra were collected in transmission mode at the Ir L$_3$ edge (11215 eV) from 200 eV below the edge to 310 eV above the edge and at the Pt L$_3$ edge (11564 eV) from 200 eV below the edge to 1200 eV above the edge. The 310 eV and 1200 eV values for the Ir L$_3$ and Pt L$_3$ spectra were determined by the onset of the Pt L$_3$ and Ir L$_2$ absorption edges, respectively. Despite the presence of the Pt L$_3$ edge in the Ir L$_3$ EXAFS region most of the Ir EXAFS data was recovered by
deconvoluting it from the Pt L$_3$ edge EXAFS as described in Ref. 57. The same procedure was used to separate Pt L$_3$ edge EXAFS from the total signal that contains also Ir L$_3$ edge EXAFS. A three ion chamber setup was used in which the sample was mounted between ion chambers measuring either the incident beam intensity ($I_0$) or the transmitted beam intensity ($I_t$). The appropriate experimental standard (7 µm thick Pt foil or a pressed pellet of Ir black diluted with C black) was mounted between $I_t$ and a reference ion chamber ($I_r$). This three ion chamber configuration allows for the simultaneous acquisition of the standard spectra and absolute energy alignment of the sample spectra. Gaseous mixtures used for the detection chambers were: 100% N$_2$ ($I_0$); 60% Ar, 40% N$_2$ ($I_t$); and 100% Ar ($I_{ref}$). The desired energy range was selected using a Si(111) double-crystal monochromator and focused using Pd-coated mirrors to reject higher harmonics. The storage ring was operated at 7 GeV with a constant ring current of 101.1 ± 0.4 mA (operated in top-up mode). Our final beam size was 1 mm x 8 mm.

The sample cell was purged with H$_2$ (4%, balance He) and the temperature was raised to 673 K. Subsequent reduction of the precursor cluster was monitored by measuring the Pt L$_3$ absorption edge and noting the decrease in the white line intensity to a steady-state. After reduction was complete, the temperature was lowered to 573 K and full EXAFS scans over the energy regions noted above were made at both the Ir L$_3$ and Pt L$_3$ edges. The temperature was then lowered and measurements at both edges were taken at 423, 293 and 215 K. Once this series of measurements under a H$_2$ atmosphere was completed, the sample was heated to 673 K and the feed gas was switched to ultra-high purity He. Desorption of the hydrogen was monitored by measurement of the Pt L$_3$ edge. Once the white line no longer exhibited perturbations in intensity, the temperature was
decreased to 573 K and measurements of the Pt and Ir edges were taken. Spectra were also collected at both edges for temperatures of 423, 293 and 215 K. Three spectra were measured at each edge for a given temperature/atmosphere combination for signal averaging purposes as well as to ensure that no structural changes were occurring during the measurements.

**XAS Data Analysis:** For this work, the interface programs Athena and Artemis,\textsuperscript{58} which implement the FEFF6 and IFEFFIT codes,\textsuperscript{59,60} were used to analyze the XAS data. The EXAFS oscillations, $\chi(k)$, were obtained from the absorption edge profiles using the background removal method AUTOBK.\textsuperscript{61} In the present work, analysis of the EXAFS data is limited to first nearest neighbor (1NN) scattering paths since they are well isolated from longer scattering paths in the Fourier transforms of the function $\chi(k)$. To separately analyze the local environments of Pt and Ir in the nanoparticle, we had to address the issue of the overlapping Ir L$_3$ and Pt L$_3$ edges to make full use of the information contained within the data. Our analysis consists of simultaneously fitting both the Ir L$_3$ and Pt L$_3$ oscillations while taking into account three spectral contributions: (1) the Ir EXAFS in the Ir L$_3$ edge, (2) the Pt EXAFS in the Pt L$_3$ edge, and (3) the Ir EXAFS in the Pt L$_3$ edge. Because (1) and (3) result from the same Ir coordination environment, they are strictly correlated. In this work, we performed simultaneous data analysis of the Pt and Ir edges using a new method recently developed by our group\textsuperscript{57} to extract the data from the overlapping contributions of the absorption edges. The end result of this analysis is that the Ir EXAFS is analyzed over the full acquisition range except for a small gap of $\sim$1.5 Å$^{-1}$ centered on the Pt L$_3$ edge, where the steep rise in the absorption obscures the EXAFS details. The passive electron reduction factors were determined from Pt foil and
diluted Ir black standards. A total of 10 variables were used in the two-edge fit, a value that was well below the 22 relevant, independent data points.

For all of the analyses described in this article, the theoretical photoelectron paths used were calculated by FEFF6 for Pt-Pt and Ir-Ir 1NN scattering in the bulk fcc structures. Since it was not possible to discern between the 1NN Pt and Ir scattering centers using EXAFS (their scattering amplitudes and phase shifts are very similar), we obtained the effective Pt-M and Ir-M (where M = Pt or Ir) structural information: coordination numbers, bond lengths and their disorder parameters. The coordination numbers were determined to be temperature-independent, within their uncertainties (Figure 6.1), thereby indicating that no large structural changes were occurring over the course of the experiments. As a result, it was possible to further refine the fitting analysis by fitting different data sets concurrently, over multiple measurement temperatures and constraining the temperature-independent variables (coordination number ($N$) and shift in edge energy ($\Delta E_0$)) while varying the temperature-dependent variables (bond distance ($R$), mean squared bond length disorder, also known as the EXAFS Debye-Waller factor ($\sigma^2$) and the third cumulant ($\sigma^{(3)}$)). Interested readers will find complete R-space 1NN fits of the data for both Ir and Pt bulk standards as well as the clusters under H$_2$ and He at all temperatures; and calculated EXAFS values in Figures 6.2-6.4 and Tables 6.1-6.2.

**Scanning Transmission Electron Microscopy:** Samples for scanning transmission electron microscopy (STEM) were prepared by depositing supported nanoparticle samples on a holey carbon film supported on a Mo grid (SPI Supplies). No solvent was used, so as to minimize contamination, and a Mo grid was employed because its EDX spectrum is featureless near the Ir and Pt L$_\alpha$ lines used in the quantitative elemental
analysis. Low magnification imaging, HRTEM, NBD and EDX spectroscopy were performed on a JEOL model 2010F electron microscope equipped with an Oxford INCA 30 mm$^2$ ATW detector for EDX spectroscopy. The instrument was operated at 200 keV with an electron probe beam focused to 0.5 nm for EDX analysis. In order to acquire EDX spectra from individual particles, sweeping of the probe beam was stopped while it was incident on a particle. Slight adjustments of the sample position were necessary to counteract drift during the several minutes required to acquire spectra with a satisfactory signal-to-noise ratio. To prevent signal contributions from neighboring particles, only well-isolated particles were selected for EDX analysis. Atomic resolution images were taken in STEM mode using a on a JEOL model 2200FS electron microscope capable of sub-Ångstrom resolution$^{62}$ operated at 200 keV. All micrographs were analyzed using DigitalMicrograph™ (Gatan Inc.) software.

Although radiation damage and elemental restructuring may occur due to irradiation by the electron beam, the particles and support in the acquisition area appeared unchanged after acquisition of a micrograph. Although it is possible that repartitioning of the elements may occur within individual clusters under the 200 keV electron beam, as we explain below, Ir and Pt atoms are indistinguishable from one another due to the support-originated background.

**Atom Counting:** Quantification of the number of atoms contained within a cluster was carried out by calculating an averaged single-atom scattering intensities for free atoms observed on the $\gamma$-Al$_2$O$_3$ support and measuring their background-corrected intensity contribution against the total intensity of an individual cluster (also background corrected). A similar protocol was implemented in a previous work.$^{40}$
6.4 Results

STEM images show that controlled reduction of the precursor cluster, [Ir₃Pt₃(μ-CO)₃(CO)₃(η-C₅Me₅)₃], affords Ir-Pt nanoparticles that are well dispersed on the γ-Al₂O₃ support (Figure 6.5, Figure 6.6) with an average diameter of 1.7 ± 0.5 nm (Figure 6.5b) and free of larger agglomerates. Inspection of Figure 6.5a shows that some particles exhibit crystalline features while others of similar size assume more disordered habits. Examination of multiple images shows that some atomic defects – in the form of a relatively sparse population of supported single atoms – are also present. This latter population is also represented in Figure 6.5a. The most important point of note here is that the mass fraction of these metal species is exceptionally small relative to the mass fraction of metal atoms present in the clusters. They are, therefore, expected to negligibly contribute to the XAS data, since it represents an average over all habits weighted by their mass fraction.

The presence of single, supported metal atoms allows a more precise, quantitative analysis of a typical cluster’s morphology to be made. Here it is assumed that: 1) the background intensities of the region containing the cluster and free atoms are approximately equal; and 2) the elemental ratio of the single atoms used to find an average scattering value is equal to the elemental ratio within the cluster. The results of EDX measurements support the latter assumption, where an examination of the composition of 50 individual nanoparticles (average size of 1.9 ± 0.4 nm, Figure 6.5c) found that the clusters contained an average of 53 ± 5% Ir. This value lies within the limits of uncertainty of the 50% Ir value anticipated on the basis of the cluster precursor’s
stoichiometry and showed no compositional size dependence. Based on this finding we can conclude that individual, free atoms are equally likely to be either Ir or Pt. By calculating a background corrected scattering of individual atoms and clusters, atom quantification was performed (Figure 6.7a) for 33 individual supported Ir-Pt nanoclusters. The visible trend indicates that the clusters likely adopt a hemispherical cuboctahedral habit. This is a structural assignment that is fully supported by the representative micrograph given in Figure 6.7b; which displays several individual particles oriented orthogonal to the optic axis, such that a cross sectional vantage of the particle-support interface can be observed. Several nanoparticles displaying the inferred hemispherical geometries are clearly evidenced (here circled to highlight the prevalence of this structural form).

The C₅-STEM image presented in Figure 6.7b suggests several features of interest that relate to the nature of specific support interactions that might in fact drive correlated patterns of strain/structural relaxations in the supported clusters. These effects appear to be related to specific truncations of the polycrystalline γ-Al₂O₃ lattice – the surfaces on which nucleation and growth of the Ir-Pt metallic clusters proceeds. We found many regions of highly regular corrugations of the background intensity that had spacings well matched to specific d-spacings of the γ-Al₂O₃ bulk lattice. Due to the comparatively low-Z nature of the support atoms (Zₐl = 13 and Zₒ = 8), it is likely that any support ordering evidenced in the micrographs must correlate with highly aligned atomic columns in order to yield a cumulative intensity that is significant enough to discriminate and then usefully compare to the intensity modula seen due to the ordering of atoms present in the Ir-Pt nanoparticles. We have taken from the larger dataset several examples that better
emphasize specific periodic structures of the γ-Al₂O₃ support and the atomic arrangements of clusters bound on/near them. These data are given in Figures 6.8a and 6.8b, where an intensity profile of the boxed region has been inset into each micrograph to better illustrate the structural corrugations of the support that are present within the image field. Figures 6.8c and 6.8d show atomistic models of the γ-Al₂O₃ oriented along the [001] zone axis (i.e. perpendicular to the e-beam). The arrows indicate the direction of the electron beam (i.e. the direction from which the micrograph would have been acquired) while the dashed lines show the atoms giving rise to the corrugations observed in the C₅-STEM images.

Fourier transforms were used to calculate the real space distance between the corrugation planes. Analysis yielded an interplanar spacing of 2.7 ± 0.1 Å for Figure 6.8c and 1.97 ± 0.02 Å for Figure 6.8d. These values compare very favorably with the d-spacings expected for (022) and (004) in γ-Al₂O₃ crystals (2.797 and 1.978 Å, respectively).⁶³ Observation of these planes is not surprising, as the (011) and (001) surfaces were previously identified as those most frequently exposed on the surface of γ-Al₂O₃.⁴³,⁶⁴ While this allows us to identify the type of planes present, the relatively weak scattering of the support does not allow for facet or zone axis identification of the γ-Al₂O₃ with respect to the electron beam.

Although the C₅-STEM-based micrographs provide some structural information, they are limited by the sub-Ångstrom probe’s depth of field. In contrast, HRTEM utilizes phase contrast to simultaneously image large areas of the sample. Captured HRTEM images (e.g., Figure 6.9) reveal that multiple domains of the γ-Al₂O₃ are present. To better characterize the nature of the polycrystalline γ-Al₂O₃ support, we made NBD
measurements on random areas of the sample to identify the predominant zone axes of the support. It should be noted that the sizes of the areas where diffraction patterns were collected were ~20 nm², well surpassing the dimensions of an average 1.7 nm diameter Ir-Pt particle. This rules out the possibility of a single particle dominating the acquired diffraction pattern in a crystalline support containing region. The majority of the NBD data collected for the support evidenced multiple crystallographic orientations and thus could not be indexed uniquely. There were occasions, however, when one orientation dominated and allowed a specific zone axis to be assigned (e.g., Figure 6.10). Within these diffraction patterns, orientations of [002], [022] and [004] were exhibited with corresponding d-spacings of 3.95, 2.80 and 1.97 Å – values also observed frequently in crystalline Ir-Pt clusters (e.g., Figures 6.8a and b).

Figures 6.11a and b display the XANES data collected for the Ir L₃ and Pt L₃ absorption edges, respectively, measured at a series of temperatures. These measurements were carried out first in an atmosphere of a 4% molar mixture of H₂ (balance in He) and, subsequently, in ultra-high purity He. These data show that a red shift in the edge energy occurs with increasing temperature – one that is more pronounced for the Pt than the Ir atoms in the clusters. To better represent and quantify the effects of the surrounding gases, the ∆E₀ from the XANES spectra was plotted for the Ir-edge (Figure 6.11c) and the Pt-edge (Figure 6.11d) where the data at 573 K under He at each respective edge was taken as the reference value. It can be seen that the Pt-edge position is the one more strongly perturbed by exposure to H₂ with a displacement ranging between +0.22 eV and +0.47 eV. Conversely, the Ir displacement under 4% H₂ attains a maximum offset of only +0.15 eV from the data collected under He.
Figure 6.12 shows the temperature-dependence of $\sigma^2$ plotted with respect to bulk standards for both the Ir- (Figure 6.12a) and Pt-edges (Figure 6.12b). Regression lines are plotted through the data points and extrapolated down to 0 K to qualitatively illustrate trends for the $\sigma^2$ values. The latter provide a qualitative means of assessing the disorder exhibited by each metal relative to the bulk standard. A clear similarity of the sample’s temperature-dependent evolution of $\sigma^2$ to the Ir standard – and its dissimilarity to the Pt standard – suggests unique vibrational constraints are present in the heterometallic clusters, ones we will discuss the significance of below.

Lastly, the temperature-dependent 1NN bond length measurements of the Ir-Pt/$\gamma$-Al$_2$O$_3$ system along with those of the corresponding thin, bulk standards are shown in Figure 6.13 (Tables 6.1 and 6.2). EXAFS fitting analyses of the Ir- and Pt-edge data at room temperature indicates that switching the sample’s environment from H$_2$ to He results in a 1.07% contraction (relaxation) of the Pt-M 1NN distances. In comparison, the Ir 1NN distances show a contraction of only 0.64%. The varied (adsorbate mediated) lifting of these contractions, as occurs upon exposure to H$_2$, is also visible in the data presented in Figure 6.13. This effect has been observed previously in studies of supported Pt clusters and ascribed to electron donation from hydrogen adsorbates.$^{65-67}$ We also make note of the temperature mediated changes in $R_{Ir}$ and $R_{Pt}$. It is obvious that the Pt and Ir bulk standards both experience conventional thermal expansion, whereas the Ir-M and Pt-M 1NN bond lengths contract upon heating, a phenomenon that also has been previously observed for Pt/$\gamma$-Al$_2$O$_3$.$^{42,65}$ This striking mesoscopic behavior is one with origins related to specific (and competing) influences of both metal-adsorbate and metal-support bonding interactions, factors that are discussed more fully below.
6.5 Discussion

Several lines of argument drawn from the data strongly suggest that the motif of a typical Ir-Pt cluster on γ-Al₂O₃ is one defined by an oblate/hemispherical shape. Most directly, the representative images in Figure 6.7 show several examples of clusters oriented to provide a profile view. These clearly reveal examples of clusters with hemispherical/oblate shapes, within which atomic order is also evidenced. On a broader and more qualitative inspection of the data given in Figures 6.7 and 6.8, it is also evident that other forms of oblate cluster shapes are present within the ensemble. Taken together, the data demonstrate a significant interaction with the support must be present, one sufficient to elicit non-spherical cluster shapes as well as drive/or inhibit specific forms of atomic ordering.

Perhaps the most striking feature of the data shown in Figure 6.8 is evidence of clusters with atomic orderings that seem to mirror orientations of the support. This is most evident in the micrograph shown in Figure 6.8b wherein the intensity modula seen in the inset (corresponding to (004), 1.97 Å, d-spacings) correlate very strongly with the atomic structure exhibited by the Ir-Pt cluster (displaying a [001] zone axis). Depending on the specifics of the surface termination, growth habits of this nature will involve periodic interactions of the cluster atoms with Al (or O) atoms on the γ-Al₂O₃ surface. Kwak, et al.⁴³ have provided evidence supporting the idea that the particle-support interface involves a topology wherein cluster atoms bond to only one type of support atom through their demonstration that Pt is anchored at pentacoordinate Al sites in Pt/γ-Al₂O₃. Such models do not fully address the role that surface defects (especially
oxygen atom vacancies) might play within this bonding. It should be noted that if heteroepitaxial growth does indeed occur for the Ir-Pt nanoparticles on this orientation of the $\gamma$-Al$_2$O$_3$ support, there will be a ~5% lattice mismatch for its interaction with a (001) facet plane of the cluster.

We propose that an important bonding mode of the Ir-Pt clusters on $\gamma$-Al$_2$O$_3$ is one that is heteroepitaxial in nature for the predominant facet planes (i.e., (001) and (011)) as judged by the frequencies with which these zone axes were observed for both the clusters and the support. An explicit example of this specific bonding habit is clearly demonstrated in Figure 6.8b, which shows an example where both the support and cluster are oriented along the same zone axis. We must caution, though, that the observation of such orientations of particles lying directly above these specific support corrugations does not definitively prove that the interfacial facet of the alumina and the particle are the same (the observation of a given d-spacing only establishes that the direction of observation is perpendicular to that d-spacing). As noted above, a heteroepitaxial bonding arrangement at the (001) facet of $\gamma$-Al$_2$O$_3$ would need to accommodate $\leq 5\%$ mismatch between the support and fcc metal lattice constants. For clusters with an interaction occurring on a (011) facet (Figure 6.50) similar lattice strains would also be present. In the case of the specific orientation shown in Figure 6.8b, the interatomic distances between the terminal O atoms on the $\gamma$-Al$_2$O$_3$ compare favorably with the atomic spacing of the (001) plane of an Ir-Pt cluster. As noted above, however, O-vacancies are expected to represent a significant number of surface defects which, in turn, would lead to heterogeneity in both the bonding environments and energetics for the metal-support interactions. The literature, and our past theoretical studies, indicate that strong anchoring
of the clusters may occur at these vacancy sites. Clusters bound at O-vacancy sites would likely experience more interfacial strain than their heteroepitaxial counterparts. For small clusters, increasing levels of strain typically lead to decreased crystallinity in a manner similar to the introduction of twin boundaries.

In an earlier report on structural habits adopted in Pt/Pd binary clusters we used atom counting techniques to deduce an average cluster morphology. In that case, it was possible to make specific assignments as to the speciation of atoms within the clusters due to the significant Z contrasts these elements provide. Though C_s-STEM has proven to be a powerful technique for the elemental analysis for these latter systems, the similar scattering power of Ir and Pt (Z_{Ir} = 77 and Z_{Pt} = 78) – even without the presence of the interfering background of a support – obviates a C_s-STEM analysis of this system based on contrast variations. However, by adopting a similar average scattering intensity for the Ir and Pt atoms and (assuming a weak variation of the average background scattering interactions around the clusters) using the proximal single atom defects to calibrate the detector response, it is possible to predict and quantify a functional form for the size scaling of different cluster structural forms. The quantitative atom-counting analysis, in this case, best supports a structure resembling an ideal oblate structure, more specifically that of an oblate/hemispherical cuboctahedron (Figure 6.7a).

Although this conclusion agrees with inferences developed from a visual inspection of the micrographs and the generally accepted morphology of supported clusters, we have further substantiated these assignments through the use of XAS. In this case, analytical fitting of the EXAFS data (Tables 6.1 and 6.2) provides average Ir and Pt 1NN coordination numbers, with values for the 1.7 nm average diameter clusters
examined here of 9.4 ± 0.2 and 6.8 ± 0.3, respectively. Several striking features are evident in these results. First, the fact that the coordination numbers of the Ir and Pt atoms are not equal, given that they reside in a sample characterized by a narrow size distribution and a 1:1 elemental composition, explicitly demonstrates atomic, intra-cluster segregation is occurring in these clusters. We return to this point below. We start first, however, with a morphological interpretation of this data following the procedures developed in earlier works\textsuperscript{2,54,55} and more recently reviewed by Frenkel.\textsuperscript{71}

For a cluster containing two atom types with mole fractions \(x_A\) and \(x_B\) (for elements A and B, respectively), the average metal-metal coordination number is simply related to the partial coordination numbers (\(n\)) of \(A-M\) and \(B-M\) such that:

\[
n_M = x_A n_{AM} + x_B n_{BM}.
\] (1)

Because the nanoparticles have a 1:1 composition (\(x_A = x_B = 0.5\)), it follows that \(n_M\) (the average, non-compositionally dependent first shell coordination number) is simply the average of 9.4 and 6.8 (i.e. \(n_M = 8.1\)). This average value provides a parameter to evaluate various models of the particle shape. For a model hemispherical cuboctahedron [assuming a (011) basal plane]\textsuperscript{72} an average coordination number for a 1.7 nm diameter cluster is \(N = 7.9\), a value that is exceptionally close (and within the experimental uncertainty) to that determined by EXAFS (8.1 ± 0.3) and reaffirms the proposed structure.

An explicit model for a 1.7 nm cluster containing a 1:1 composition of each atom type, a 110-atom hemispherical cuboctahedral cluster whose average coordination number (\(n_M \approx 7.9\)) closely matches that found experimentally for the Ir-Pt nanoparticles, was modeled (Figure 6.15). As noted above, the compositionally dependent coordination
numbers for Ir-M and Pt-M are different from this (9.4 and 6.8, respectively). This requires that, on average, the Pt atoms in an Ir-Pt (1:1) cluster must be allocated to lower coordination sites than are the Ir atoms. For a metal particle of this size, this requires a significant partitioning of the Ir to the cluster’s core, as is schematically depicted in Figure 6.15. Here the Pt atoms shroud the Ir core from the ambient/non-support environment. This model yields a cluster core consisting of 30 atoms covered by an outer shell of 80 atoms (including the 31-atom (011) basal plane). If a 1:1 composition is to be maintained for this structural model, it is clear that some Ir atoms must be placed on the surface.

The XAS data also provides evidence that the phase-segregated structure of the Ir-Pt clusters is accompanied by discernable dynamical impacts on their electronic structure. Most notably, Figure 6.11b shows that a marked temperature-dependent red shift in the absorption edge energy occurs for the Pt-edge with increasing temperature independent of the ambient conditions. These trends are also seen for the Ir data as well, albeit significantly smaller in their magnitudes. A quantitative interpretation of the broader trends (e.g., blue shift) evidenced in the XANES data requires deconvolution of the various competing factors involved, namely those due to adsorbate and cluster-support interactions, the varied influences of temperature on bonding as well as the influences due to the presence of an alloying metal. It must be noted that the constant displacement of the Pt edge data under 4% H₂ as compared to He (Figure 6.11d) reveals information about the elemental apportionment of Pt in the supported clusters. Over the temperature range investigated, we estimate the hydrogen coverage will range between ~13% at 573 K to 100% at 212 K for 4% H₂ (Calculation 6.1). The marked change in the Pt XANES
data when any level of adsorbate is present indicates Pt atoms experience direct-contact 
interactions with adsorbate atoms. The fact that the adsorbate effect on Ir-edge data is 
much weaker than on Pt is consistent with a greater tendency for Pt to segregate to the 
surface of the particle and agrees with the conclusions reached based on the EXAFS 
results.

For the specific case of the Ir-Pt bimetallic nanoparticles, the Pt atoms are 
expected to populate the surface of the clusters based on the differences in surface energy 
\( \gamma_{\text{Pt}} = 2.489 \text{ J/m}^2 \) and \( \gamma_{\text{Ir}} = 3.048 \text{ J/m}^2 \). The literature, which reveals other instances 
where surface energetics have been shown to play a pivotal role in elemental segregation, 
supports this inference. In one notable example, the deposition of Au on a single-crystal 
Ni surface was shown to result in the formation of Au-Ni alloys on top of the Ni surface, 
a process in which the specific atomic arrangements adopted are directed by the relative 
energetics of the Au and Ni near-surface bonding interactions. Somorjai et al. have also 
shown that changes in surface energies caused by the presence of reactive species can 
lead to specific forms of elemental rearrangement within bimetallic nanoclusters.

The XAS data provides further insights into the nature of the clusters’ dynamics. 
For example, one notes that the temperature dependence of \( \sigma_{\text{Ir}}^2 \) (Figure 6.12a) behaves 
similarly to its bulk analogue while the corresponding Pt-edge data deviates dramatically 
from its corresponding bulk standard (Figure 6.12b). Because the slope in a plot of \( \sigma^2 \) 
versus temperature over the range investigated has been shown (using an Einstein 
model\(^2,42\)) to be inversely proportional to the force constant, a smaller slope can be 
interpreted as denoting a stiffer bonding environment. In this respect, the \( \sigma_{\text{Ir}}^2 \) values 
follow a path more resembling that of the Ir black standard as might be expected from
their predominant segregation to the particle core. Meanwhile the $\sigma^2_{\text{Pt}}$ values indicate a bonding environment drastically different from fully coordinated Pt atoms present in the bulk state.

As previously noted, a quantitative evaluation of adsorbate coverage effects on the Ir-Pt/$\gamma$-Al$_2$O$_3$ clusters cannot easily be decoupled from effects rising from the support nor the alloying Ir. For example, there is a noticeable contrast seen in the behavior of each metal’s white line intensity, with an increase occurring for Ir and a decrease occurring for Pt with increasing temperatures (Figures 6.11a and b). This is consistent with the occurrence of a temperature-dependent charge transfer from Ir to Pt in the nanoparticles. Similar temperature dependent white line intensity trends have recently been observed, and similarly interpreted, for heterogeneous Au/Pt nanowires, Au/Pt hybrid nanostructures and AuPt alloy nanoparticles.

The 1NN bond lengths, as represented by the data presented in Figure 6.13, reveals an additional convolution of dynamical effects on structure. The bond-length contraction observed with increasing temperature has been seen in studies made on homometallic supported clusters (Pt). This effect has its origins in the electronic interplay due to both the adsorbate bonding and the metal-support interactions. As illustrated in the data presented in Figure 6.13, the Pt-M and Ir-M bond distances both evidence mesoscopic temperature dependencies – relaxed bond lengths that contract as the temperature increases. One notes that the magnitude of the contraction is largest for the Pt-M bonding and further sensitive to the presence of H-atom adsorbates. The former, present at saturation, partially lifts the cluster’s bond-length contraction and results in bond distances converging toward those found in bulk materials. At higher temperatures,
where the H-coverage is lower, the Pt-M bond distances progressively contract. It is also interesting to note that the M-M’ bond lengths seen for both Ir and Pt in an inert atmosphere are always shorter than that found in the presence of H\textsubscript{2}. In the present case, the thermally mediated influences due to the metal-support interactions are less pronounced than was seen in our studies of supported homometallic Pt clusters. We believe this likely reflects in part the predominant placement of the Pt atoms at the ambient cluster surfaces. While attractive from a qualitative perspective, the data clearly demonstrate that the dynamical behaviors in the bimetallic system are intricate and subject to a more complex interplay of interactions. Even so, the major thermal influences on the M-M’ bond lengths seen in the H\textsubscript{2} atmosphere are likely ones attributable to the coverage dependence of H-atom adsorbates. The current data show the highly anisotropic nature of this effect, where the relaxation of surface atoms occurs toward the particle core with a magnitude that depends on the number of unsatisfied bonds each atom experiences.\textsuperscript{38} The features of the bond-length contraction, and their sensitivity to adsorbates are likely common for many supported, high dispersion systems. We expect these dynamical features must also impact catalytic properties and elements of structure present under real operating conditions.

### 6.6 Conclusions

Advanced synthesis and characterization techniques have been combined to show that Ir-Pt nanoparticles supported on γ-Al\textsubscript{2}O\textsubscript{3} containing a 1:1 ratio of Ir:Pt adopt segregated structures in which Ir occupies the core region and suggests a means by which to control the efficacy of catalyst synthesis. Observation of temperature and adsorbate
dependent bond-length contractions, bond rigidity reflective of one element and metal-metal charge transfer indicate that catalysts evolve dynamically through temperature and adsorbate mediated changes. Further comparison of model structures to the atomic structure of $\gamma$-Al$_2$O$_3$ showed that the corrugations in the intensity of the support matched well to spacings expected within the cluster and represent $\leq5\%$ strain if heteroepitaxial growth is occurring. We believe the methods of analysis used in the present work are more generally applicable to the investigation of supported materials and that the structural dynamics seen in the present model Ir-Pt system are ones likely to be found in other highly dispersed, supported metal systems. How these dynamics might come to influence elementary rate processes of catalytic reaction mechanisms remains an important and interesting challenge for future research.

6.7 Acknowledgements

The authors would like to thank A. J. Sealey and G. S. Girolami for synthesizing the organometallic, Ir-Pt precursor complex used in this work. This work was sponsored in part by a grant from the U.S. Department of Energy (DE-FG02-03ER15476). Experiments were carried out in part at the Frederick Seitz Materials Research Laboratory Central Facilities, University of Illinois, which are partially supported by the U.S. Department of Energy under Grants DE-FG02-07ER46453 and DE-FG02-07ER46471. Research was also carried out at the Advanced Photon Source (APS) at Argonne National Laboratory. The use of the APS was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences (DE-AC02-06CH11357).
6.8 Figures, Tables and Example Calculation

**Figure 6.1.** The plot shows the relative consistency in coordination number under (a) He and (b) H₂ for both the Ir-M and Pt-M contributions when the coordination numbers are left unconstrained with respect to temperature during the fitting process. The straight lines (black, Ir-M; and red dashed, Pt-M) represent the fit values obtained for the coordination number of Ir-M (9.4 ± 0.2) and Pt-M (6.7 ± 0.3) when the coordination numbers were constrained to be one value.
Figure 6.2. Comparison of EXAFS data and first shell fits for isolated (a) Ir black and (b) Pt foil standards \([k^2\text{-weighted}, k=2.0-18.0 \, \text{Å}^{-1}, R=1.8-3.0 \, \text{Å}]\). Comparison of EXAFS data and two-edge, three-component fits for stacked Ir and Pt standards at (c) the Ir L\(_3\) edge \([k^2\text{-weighted}, k=2.7-8.7 \, \text{Å}^{-1}, R=1.2-3.1 \, \text{Å}]\) and (d) the Pt L\(_3\) edge \([k^2\text{-weighted}, k=2.7-16.0 \, \text{Å}^{-1}, R=1.2-3.0 \, \text{Å}]\).
Figure 6.3. EXAFS spectra measured at different temperatures for Ir-Pt/Al$_2$O$_3$ under a 4% H$_2$ atmosphere at the (a) Ir L$_3$ and (b) Pt L$_3$ edges. EXAFS spectra measured at different temperatures for Ir-Pt/Al$_2$O$_3$ under a He atmosphere at the (c) Ir L$_3$ and (d) Pt L$_3$ edges. Spectra at the Ir L$_3$ edge are $k^2$-weighted and Fourier transformed over a $k$ range of 2.0-8.7 Å$^{-1}$ while Pt L$_3$ spectra are $k^2$-weighted and Fourier transformed over a $k$ range of 2.0-16.3 Å$^{-1}$.
**Figure 6.4.** (a) Comparison of data and fits for Ir-Pt/Al₂O₃ under a 4% H₂ atmosphere measured at multiple temperatures at the Ir L₃ and Pt L₃ absorption edges. At the Ir L₃ edge the data were transformed over $k=2.7-8.7 \text{ Å}^{-1}$ and fit over $R=1.2-3.1 \text{ Å}$. At the Pt L₃ edge the data were transformed over $k=2.7-17.1 \text{ Å}^{-1}$ and fit over $R=1.3-3.0 \text{ Å}$. All spectra were $k^2$-weighted. (b) Comparison of data and fits for IrPt/Al₂O₃ under a He atmosphere measured at multiple temperatures at the Ir L₃ and Pt L₃ absorption edges. At the Ir L₃ edge the data were transformed over $k=2.7-8.8 \text{ Å}^{-1}$ and fit over $R=1.2-3.1 \text{ Å}$. At the Pt L₃ edge the data were transformed over $k=2.7-16.5 \text{ Å}^{-1}$ and fit over $R=1.3-3.0 \text{ Å}$. All spectra were $k^2$-weighted.
### Table 6.1. EXAFS fitting results for Ir-Pt/Al$_2$O$_3$ nanoparticles under H$_2$.

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*a* indicates a temperature independent parameter.

### Table 6.2. EXAFS fitting results for Ir-Pt/Al$_2$O$_3$ nanoparticles under He.

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*a* indicates a temperature independent parameter.
Figure 6.5. (a) Representative C$_2$-STEM image of 10 wt% IrPt/γ-Al$_2$O$_3$ at 1 M× magnification. (b) Size distribution histogram of nanoparticle diameters obtained from analysis of individual particles in the microscopy images (300 particles analyzed). (c) Compositional distribution histogram of the elemental constituents of 50 individual nanoparticles as obtained using EDX.
Figure 6.6. Representative STEM image showing dispersion of the Ir-Pt nanoparticles on the $\gamma$-Al$_2$O$_3$ support.
Figure 6.7. (a) Plot showing the number of atoms contained in a cluster as a function of the diameter. Lines represent ideal, fcc structures with a diameter taken as the average of the short and long axes (i.e. vertex-to-vertex and face center-to-face center). The circles represent data obtained by measuring individual particles. Total atom count estimates for these particles were obtained by measuring background-corrected, single atom scattering intensities and extrapolating to the background-corrected cluster intensity. (b) Presents a C$_7$-STEM image showing multiple particles (circled for clarity) that appear to present a hemispherical cuboctahedral structure. The inset in the lower right-hand corner shows a magnified view of one of these clusters.
Figure 6.8. C$_s$-STEM images showing Ir-Pt clusters supported on sections of γ-Al$_2$O$_3$ displaying discernable lattice structures. The light blue, boxed regions represent where areal intensity scans were conducted. These inset scans more clearly show the periodic scattering intensity originating from the underlying support. The planar spacings are 2.7 Å for image (a) and 1.97 Å for image (b). These values compare favorably with the values of 2.797 Å and 1.978 Å expected for the (022) and (004) d-spacings of γ-Al$_2$O$_3$, respectively. (c) and (d) are crystal models oriented along the [100] zone axis (i.e. perpendicular to the electron beam) depict how the structure of a γ-Al$_2$O$_3$ crystal could give rise to corrugated intensities in (a) and (b), respectively. The direction of the electron beam is represented by arrows and the dotted line indicates a plane of collimated atoms that would lead to the observed intensity increases. Al atoms are shown in green while O atoms are depicted in red.
Figure 6.9. HRTEM micrograph image showing the presence of many domains on the γ-Al₂O₃ support.
Figure 6.10. NBD pattern showing a [001] zone axis orientation for the $\gamma$-Al$_2$O$_3$ support. Arrows and parenthetical numbers highlight diffraction spots corresponding to specific lattice planes.
Figure 6.11. XANES data of the (a) Ir L$_3$ and (b) Pt L$_3$ absorption edges measured at a series of temperatures under He and 4% H$_2$ atmospheres. (c) and (d) show the shifts in the L$_3$ absorption edge energy (at a normalized intensity of 0.5) for Ir and Pt, respectively, relative to their edge energies under He at 573 K.
**Calculation 6.1.** Based on the work of Savargaonkar, et al., the parameters: $E_{\text{det}} = 66$ kJ/mol, $k_a = 2.3 \times 10^5$ s$^{-1}$, $k_d = 20$ s$^{-1}$ and $T = 333$ K were used to calculate the hydrogen coverage at different temperatures using the Langmuir model for dissociative adsorption:

$$K P_{H_2} = \frac{\theta_H^2}{(1 - \theta_H)^2}$$

(1)

were $K$ is the ratio of the adsorption and desorption coefficients, $P_{H_2}$ is the pressure of H$_2$ and $\theta_H$ is the surface coverage. Theoretical coverages of hydrogen were calculated to be 1.00 at 215 K and 0.13 at 573 K for a 4% H$_2$ atmosphere.
Figure 6.12. The mean square relative displacement of the 1NN distances found for the Ir-Pt/γ-Al₂O₃ as a function of temperature and surrounding gas determined for (a) Ir absorbers and compared to an Ir black standard and for (b) Pt absorbers and compared to a Pt foil standard.
Figure 6.13. The temperature dependence of the 1NN interatomic bond distances for (a) Ir and (b) Pt atoms in Ir-Pt/γ-Al₂O₃ under H₂ and He compared to their respective standards.
Figure 6.14. Model structures showing the (011) and (001) planar truncations for an fcc cluster with atomic spacing equivalent to an Ir-Pt alloy ((a) and (b), respectively) and for γ-Al$_2$O$_3$ ((c) and (d), respectively). Lines and distances show the spacing between rows of atoms in all images.
Figure 6.15. Schematic representation of a 110 atom, 1.7 nm Ir-Pt nanoparticle truncated by a (011) plane and possessing a hemispherical cuboctahedron morphology. From left to right, the images present views of the supported cluster viewed: perpendicular to the support; parallel to the support; and a cross-section (to show the interior) of the cluster viewed parallel to the support. Pt atoms are depicted in white and Ir atoms are shown in green.
References


(44) Teo, B. K. EXAFS: Basic Principles and Data Analysis; Springer-Verlag: Berlin, 1986.


(71) Frenkel, A. I. Solving the 3D structure of metal nanoparticles. Z. Kristallogr. 2007, 222, 605-611.


CHAPTER 7
INFLUENCE OF ADSORBATES ON THE ELECTRONIC STRUCTURE, BOND STRAIN, AND THERMAL PROPERTIES OF AN ALUMINA-SUPPORTED Pt CATALYST


7.1 Abstract

We describe the results of an X-ray absorption spectroscopy (XAS) study of adsorbate and temperature dependent alterations of the atomic level structure of a prototypical, noble metal hydrogenation and reforming catalyst: ~1.0 nm Pt clusters supported on gamma alumina (Pt/γ-Al₂O₃). This work demonstrates that the metal-metal (M-M) bonding in these small clusters is responsive to the presence of adsorbates – exhibiting pronounced coverage dependent strains in the clusters’ M-M bonding, with concomitant modifications of their electronic structures. Hydrogen and CO adsorbates both demonstrate coverage dependent bonding that leads to relaxation of the M-M bond strains within the clusters. These influences are partially compensated, and variably mediated, by the temperature dependent electronic perturbations that arise from cluster-support and adsorbate-support interactions. Taken together, the data reveal a strikingly fluxional system with implications for understanding the energetics of catalysis. We estimate a 9.1 ± 1.1 kJ/mol strain exists for these clusters under H₂ and that this strain
increases to 12.8 ± 1.7 kJ/mol under CO. This change in the energy of the particle is in addition to the different heats of adsorption for each gas (64 ± 3 and 126 ± 2 kJ/mol for H₂ and CO, respectively).

7.2 Introduction

Investigations of heterogeneous catalytic efficacies are commonly made by monitoring changes in catalyst performance resulting from changes made to macroscopic experimental variables. These variables commonly include temperature, pressure, feedstock ratios, support and promoter compositions, and dispersion.¹⁻⁷ Such classical rate/property correlations frequently contain the implicit assumption that the catalyst’s metal-bonding structure remains static despite changing conditions. While a priori this might seem reasonable, recent studies have begun to show that catalysts dynamically evolve by interacting with their environment through unique combinations of bond strain and electronic exchange.⁸⁻¹² The roles of both factors are reflected in several features: the binding strengths of adsorbates; facet dependent turnover rates; and adsorbate driven structural changes.¹⁰,¹²,¹³

Although Pt/γ-Al₂O₃ is perhaps one of the most prototypical examples of an industrially important heterogeneous catalyst, and thus the subject of numerous studies,¹⁴⁻²⁴ many aspects of its atomic structure and dynamical features under operating conditions remain poorly understood. This deficiency derives in part from the complexity of the system under realistic operating conditions and the limitations of experimental and theoretical methods of characterization in accommodating them. Even so, progress in each of the latter has begun to accelerate, albeit along generally independent paths.¹⁹,²⁰,²⁵
There remains, as a result, a general need to provide experimental measurements that probe the limited length and time-scales accessible to theory. This study addresses questions of catalyst structure and dynamics that are motivated by this larger need.

In this study we use the spectroscopic capabilities of XAS to build a deeper understanding of how supported Pt catalysts evolve in high pressure/high temperature environments by examining nanoscale, supported clusters under different partial pressures of H₂ and CO with changing temperature. Changes in the electronic and M-M bonding structures are monitored using the X-ray absorption near-edge structure (XANES) and the extended X-ray absorption fine structure (EXAFS), respectively. These data serve to elucidate underlying features of atomic structure via specific bonding-centric attributes, specifically: the first nearest neighbor (1NN) coordination number (CN); bond distance (R); the dynamical and static contributions to the mean square disorder (the EXAFS Debye-Waller factor, σ²); and the correlated changes in electronic structure revealed by XANES. We examined the response of these features in the Pt/γ-Al₂O₃ system under steady state conditions using isobars and isotherms to explore various adsorbate coverages. In this way we were able to characterize heretofore poorly understood contributions to the Pt clusters bonding – including atomic strains and the system’s electronic structure – that are both coverage and temperature dependent. These data affirm the predictions of a model that accounts for the anisotropic evolution of dynamic and static strains in terms of atomic (quasi-elastic) deformation energies.

7.3 Experimental Methods
**Sample Preparation:** A sample of 1 wt % Pt/γ-Al₂O₃ was prepared by impregnating 220 m²/g γ-Al₂O₃ (Alfa Aesar) with (NH₃)₄Pt(OH)₂ (Sigma Aldrich). The sample was dried in air and 110 mg was formed into a pellet at a pressure of 2.5 tons. The sample was further processed in the *in situ* XAS cell at beamline X19A at the National Synchrotron Light Source (NSLS) in Brookhaven National Laboratory, Upton, NY. Preparation of the sample consisted of equilibrating the pellet with 100% H₂ at room temperature for 30 minutes, raising the temperature to, and holding it at, 573 K for 1 hour followed by cooling to room temperature in flowing H₂. Prior to experiments, the sample was rereduced at the beamline by exposing it to 5% H₂/He at room temperature for 30 minutes and then raising the temperature to 723 K for 1 hour.

**Scanning Transmission Electron Microscopy Characterization:** Scanning transmission electron microscopy (STEM) micrographs were used to characterize the size distribution of the particles. A small amount of the sample was suspended in ethanol and drop cast onto a copper grid coated with holey carbon (SPI Supplies) for analysis using a JEOL model 2010-F electron microscope operated at 200 kV in STEM mode. A survey of 300 particles yielded a particle size of 1.0 ± 0.2 nm (Figure 7.1). Atomic resolution images were acquired using a JEOL 2200-FS operated at 200 kV in STEM mode (Figure 7.2).²⁹

**XAS Experimental Conditions:** The Pt/γ-Al₂O₃ catalyst was examined under various partial pressures of both H₂ and CO at a series of temperatures using an *in situ* XAS cell. The temperatures for both gases were: 673, 550, 488, 423, and 294 K (the 400 ppm H₂ was measured at 393 K instead of 423 K) and adjusted using feedback from a digitally controlled thermocouple. Three partial gas pressures were used for both H₂ and
CO and were obtained by mixing He with 5% standards of the appropriate gas using Brooks flow controllers. The partial pressures reported are: 50,000 ppm; 25,000 ppm; and 400 ppm of H\textsubscript{2} (or CO) in He, with a total pressure of 1 atmosphere. In all cases, measurements proceeded from the highest temperature (673 K) to the lowest temperature (294 K), and were checked for reversibility by returning the system to the highest temperature and comparing the signal to the initial spectrum for that series. For signal averaging purposes, and to ensure attainment of a steady state condition, measurements at each temperature/pressure combination were made until three spectra containing indistinguishable white line intensities were obtained (Figures 7.3-7.10).

**XAS Data Analysis:** Data processing and analysis was conducted using the IFEFFIT package.\textsuperscript{30} Quantitative XANES analysis relies on accurate energy assignment to each data point, and it is important to ensure that the energy scale is the same for all data. For that purpose, the reference Pt foil spectra measured simultaneously with the samples, were aligned for all of the raw data, guaranteeing a consistent energy scale. The data were then merged and normalized by the edge-step for subsequent XANES analysis. To analyze the EXAFS data, we aligned the data together using the first inflection point in their spectra. This procedure was chosen in order to minimize the dependence of the results on the variations in the photoelectron energy origin that changes significantly, depending on the environmental condition used. Following the alignment, the smooth atomic background function was subtracted from the edge-step normalized data. The resultant k\textsuperscript{2}-weighted \(\chi(k)\) function was fit in R-space using the Artemis program\textsuperscript{31} (Figures 7.11-7.12 and Table 7.1). The photoelectron scattering amplitudes and phases used in the fits were calculated with FEFF6\textsuperscript{32} using a model structure of bulk, fcc Pt.
In analyzing the temperature-dependent changes in the Pt clusters under each atmosphere at the highest at lowest temperatures (Figures 7.13-7.15), the CNs, bond lengths and total bond length disorders were obtained using a multiple data-set fitting scheme. In this scheme each parameter was allowed to vary independently and the photoelectron energy origin was constrained to be the same for all clusters. The latter constraint is justifiable because the data are for EXAFS analysis and the first inflection point on the absorption edge is at the same position for all data. A correction for a possible anharmonic term (the third cumulant) in the effective M-M pair potential was included in the model. For the room temperature data the best fit values of the third cumulant were consistent with zero and were subsequently dropped to minimize the number of free parameters used in the fitting. To estimate the dynamic contribution to the total disorder we used data available for similar size clusters (1.1 nm) of Pt/γ-Al₂O₃ measured under He.⁹ This “zero coverage” proxy value was only used for our strain calculations, and we describe the details and consequences of this assumption in the discussion.

ΔXANES data analysis: The data were aligned in absolute energy as described above. We have chosen to use the 400 ppm at 673 K data for each gas as a reference spectrum for subtraction of all other spectra acquired at the same partial pressure (e.g., Figure 7.16). All ΔXANES spectra were calculated by taking the spectra to be compared and interpolating the region of comparison (11523 to 11605 eV) to a uniform grid of 2000 points and then subtracting the temperature-dependent spectra from the reference spectra using OriginPro software (OriginLab, Northampton, MA). Extrapolation to a uniform grid and alignment of the data using the Pt foils was found to be crucial to the
analysis. A slight change in the energy between the spectra analyzed using $\Delta$XANES can result in large errors because of the rapid intensity change that occurs at the absorption edge. For both gases, the $\Delta$XANES spectra were piecewise integrated to determine the area of each of the two resultant peaks (plotted in Figure 7.17). The first peak was integrated over the range 11549 to 11567 eV while the second peak was integrated from 11567 to 11582 eV. These values were chosen based on the average position of the inflection points in the $\Delta$XANES spectra. Other authors have reported using only the second peak to correlate coverage with the integrated intensity.\textsuperscript{33} We, however, found that similar trends were obtained regardless of whether the integrated intensity of one peak or the absolute sum of both integrated peaks was used. We have, therefore, chosen to report the latter as it provides lower statistical uncertainties.

Fitting of the $\Delta$XANES to a theoretical model (Equation 7.5.1, \textit{vide infra}) was done using OriginPro and defining all values except the heat of adsorption and a scaling constant related to the coverage. Defined values were either theoretically or experimentally determined. During the fitting procedure the scaling constant was allowed to vary independent of adsorbate partial pressure while the heat of adsorption was constrained to be identical for the three partial pressures investigated.

7.4 Results

Despite the frequently used, simplifying assumption that catalysts have ideal crystal structures,\textsuperscript{34-37} the representative aberration-corrected scanning transmission electron microscope (C$_s$-STEM) data of Figure 7.2 clearly shows that this is not the case for very small Pt nanoparticles supported on $\gamma$-Al$_2$O$_3$. Although the structure of an ideal,
hemispherical truncated cuboctahedron, is a commonly used model for Pt/γ-Al₂O₃ – and is used for interpreting many experimental observations\(^8,34,38,39\) – such perfect structures in this size range are exceedingly rare. It is interesting to note that clusters in this size range all embed substantial static disorder, whether synthesized by colloidal/wet chemical methods or the impregnation/reduction method used here.\(^{40}\) The supported clusters examined in this work thus accord well in this respect with the properties of nanoparticles of the same average size and distribution in cluster width created using micellar methodologies.\(^{40-42}\)

The disordered structures evidenced in Figure 7.2 indicate that the clusters possess a large amount of embedded M-M bond strain. Observations of intracluster strain are not new, with surface relaxation being one of the best known examples.\(^9,36,43-46\) The importance of the support’s mediating role in developing specific attributes of strain and anisotropies in crystal truncations, however, has only recently begun to be understood.\(^8,47-51\) Based on analogies with the properties of larger single-crystal surfaces,\(^7,52-55\) one expects that many features of catalysts’ M-M bonding structures will be modified under operating conditions. Strain profiles, for example, may be altered by impurities, defects, changing temperature, and the bonding of the cluster to specific support structures and/or adsorbate species. We also note that the strain may change with temperature and thus the assumption, commonly used in EXAFS analysis, that the static disorder contribution to \(\sigma^2\) is constant should be critically examined in each particular case.

The data in Figures 7.13-7.15 demonstrate how the Pt/γ-Al₂O₃ system changes under a variety of conditions. Because there are many factors at play in these experiments, it is helpful to think how a generalized, model system might behave under
similar conditions and use it to help identify the most important factors that might affect the observed results. As more electron density is donated to the cluster at a fixed temperature, the Pt-Pt bond distance will increase\textsuperscript{18,26,56,57} Such effects can be caused by an increase in the number of electron donating species bonded to the Pt and/or an increase in the amount of electron donation coming from interactions with the support. The coverage-dependent case is mediated most directly by both the partial pressure of the adsorbing species and the temperature of the system; while the impacts due to the support interaction will depend (at least for simple cases) almost solely on the temperature\textsuperscript{28}. Similarly, adsorbates are known to induce (re)structuring of metal surfaces\textsuperscript{52-54} and nanoparticle structures\textsuperscript{13,58,59} so a change in the Pt-Pt coordination and cluster order may exist and depend on both the type of adsorbate and its partial pressure. If this (re)structuring indeed exists, it should also decay as the partial pressure decreases and at higher temperatures where thermally induced fluctuations and lower adsorbate coverages act to obscure features related to bond ordering and (atomic) structural relaxation.

The $R_{\text{Pt-Pt}}$ and static component of the $\sigma_{\text{Pt}}^2$ data obtained from EXAFS analysis allows us to monitor both the nature and magnitude of changes in the average intraparticle strains that are present in a sample of Pt/$\gamma$-Al$_2$O$_3$. We note that these strains are inhomogeneously distributed in clusters of this type, with the surfaces and other low CN occupancies being impacted the most profoundly\textsuperscript{36}. Since EXAFS probes all types of bonds, our results are inherently averaged over the entire ensemble of bonds present in a set of clusters and, hence, underestimate the bond length perturbations due to the adsorbate and support interactions. The results plotted in Figure 7.13 show that the Pt-Pt bond lengths, $R_{\text{Pt-Pt}}$, for Pt/$\gamma$-Al$_2$O$_3$ under H$_2$ and CO atmospheres exhibit strong size,
temperature, and partial pressure dependencies. Comparing Figures 7.13a and 7.13b, contractions of $R_{Pt-Pt}$ relative to bulk Pt are evident with increasing temperature and agree with trends described in other reports.\textsuperscript{9,18,56} They are expanded, however, relative to values previously reported\textsuperscript{9} for a similarly sized, adsorbate free Pt/\(\gamma\)-Al\(_2\)O\(_3\) system, indicating the importance of adsorbate interactions as a mechanism for lifting surface relaxations. Of the two gases, CO elicits longer Pt-Pt bond lengths than does H at all comparable partial pressures and temperatures. Although within the uncertainties, each adsorbate also appears to progressively lift the initial bond relaxations with increasing partial pressure at a given temperature. The longer Pt-Pt bond lengths seen under CO make intuitive sense since CO has a larger heat of adsorption\textsuperscript{60,61} and is known to be the more strongly electron donating adsorbate species.\textsuperscript{62,63} Unfortunately this difference is entwined with the possibility that the state of the support is different for each adsorbate (e.g., it is known that heating in a H\(_2\) free environment leads to a so called “dehydroxylation” of the support) and because temperature and coverage effects are intimately convolved.

Changes in the particle structure are also reflected by $\sigma_{Pt}^2$ (Figure 7.14) which is correlated to both the static and dynamic bond disorder present in the system. In the data in Figure 7.14a, for example, we see that the amount of disorder under CO and H\(_2\) exhibit diverging, pressure-dependent trends. For CO, there is a tendency toward increasing disorder (deduced by the increasing magnitude of $\sigma_{Pt}^2$) as the partial pressure of CO increases, whereas the Pt-Pt bonding becomes increasingly ordered with increasing partial pressure of H\(_2\). At higher temperatures (Figure 7.14b) there appears to be only a weak (if any) adsorbate pressure dependence on the ordering of the Pt particles. The CO
data, despite having overlapping uncertainties with the H$_2$ data, consistently exhibits increased disorder for all pressures. The larger body of data strongly indicates that CO is forcing a more disordered state (i.e., a broader distribution of M-M bond distances) even at higher temperatures. Since CO is a stronger electron donor than H$_2$ it should relieve surface relaxation more efficiently; as is evidenced in Figure 7.13. If the bond disorder was completely attributable to surface relaxation, CO should lead to a more ordered state with increasing partial pressure. Since this is not reflected in a simple way in the $\sigma_{\text{Pt}}^2$ data, this behavior must be caused by some other impact that attends its bonding. The data, and discussions that follow, develop this latter aspect more quantitatively by examining aspects of strain and cluster shape.

The most explicit manifestation of bond strain differences between the two adsorbate environments is evident in the measured Pt-Pt CNs of the Pt clusters (Figure 7.15). The CNs found under hydrogen are always lower than those evidenced in a CO environment, and exhibit only weak pressure and temperature dependencies. Carbon monoxide elicits quite different behaviors in these same clusters – impacts that, due to their reversibility, cannot arise as a consequence of sintering. In the presence of CO, the Pt-Pt coordination increases relative to H$_2$ and has an unusual temperature dependence in that the Pt-Pt coordination number is higher for the highest temperature at all partial pressures. We note that application of our model – which allows varying CNs – to bulk Pt measured at various temperatures showed only a minor tendency toward decreasing CNs that was well within experimental uncertainties for bulk Pt. Such a trend is in contrast to the CO data wherein the CNs of the Pt increase appreciably with temperature. Interestingly, and in a way qualitatively similar to H$_2$, only a weak dependence on partial
pressure is found. The dynamical underpinnings of this behavior are established unambiguously by the fact that the system could be cycled with full reversibility over all partial pressures. Despite the uncertainties ascribed to the CN fits, this strongly suggests that complex mechanistic factors are at work here. These may range from shape change phenomena induced by adsorption\textsuperscript{13,64} to more complex changes originating from the amount of support wetting. Other authors have described a cluster-shape-change behavior for CO adsorption on unsupported Au nanoclusters, suggesting that CO adsorption induces a flattening of the particle.\textsuperscript{64} Spreading of the Pt cluster upon CO adsorption also agrees with Campbell’s observation\textsuperscript{65} that if the energy difference between the adsorbate-metal and adsorbate-support bonding is large enough to overcome the difference in the M-M and M-support bonding, particle flattening will occur. The trends evidenced here, though for a supported system, also seem to point toward a structure that flattens and more strongly “wets” the substrate as a consequence of exposure to CO. This is similar to the theoretical predictions of Hu, \textit{et al.} that modeled an increase in electron donation to Pt\textsubscript{13} and Pd\textsubscript{13} clusters on \textgamma-Al\textsubscript{2}O\textsubscript{3} \textit{via} the effects of increasing support hydroxylation.\textsuperscript{39} We discuss the concept of support wetting in more detail below.

While understanding the order and morphological evolution of Pt clusters under different environments is beneficial, a more thorough understanding of how the catalytic activity is affected also requires knowledge of changes to the clusters’ electronic structures. One means of monitoring the relative change in features of electronic structure between conditions is through their near-edge difference spectra (the \textDelta XANES). Such data are shown in Figure 7.16. As expected, increasing the temperature and/or decreasing the partial pressure of the adsorbate gas leads to a smaller change for H\textsubscript{2} relative to the
reference value (400 ppm, 673 K) for both gases. A more quantitative means of
correlation is provided by plotting the absolute, integrated area of each \( \Delta XANES \)
spectrum (Figure 7.17). Interestingly, the resulting curves exhibit the behaviors expected
for generic desorption curves at different partial pressures near the full and zero coverage
limits for CO and H\(_2\), respectively. There are some features that, initially, appear unusual
for the CO data. The first is the presence of a nearly linear change in the integrated
intensity with increasing temperature for all data even well below temperatures where
this adsorbate partial pressure should be sufficient to saturate the Pt surface (i.e.,
coverage ~1.0). The second somewhat odd feature is the offsets present even at the
lowest temperature for the different CO pressures – where the cluster surface should be
saturated with adsorbate. The predictions of a theoretical model (shown here as lines
plotted in Figure 7.17, *vide infra*) explaining the sources of these changes, and their
importance to the system, are discussed below.

7.5 Discussion

The efficacy of a catalyst is generally thought to result as a consequence of the
combined influences of their electronic and atomic structural characteristics.\(^53,54\) When
these factors work synergistically, low energy pathways for a reaction can be engendered.
Many approaches have been used to alter catalysts in the hope of improving their
performance including: changing the support material;\(^10,54,66\) doping;\(^67,68\)
alloying;\(^8,12,58,69,70\) facet/defect modifications;\(^5,35,37\) and crystallographic anisotropy\(^37,54\) to
name a few. Judicious manipulation of these attributes has allowed for some measure of
catalyst tailoring; creating structures that favor reactant adsorption and/or product desorption.

Some forms of the modifications seen in catalyst motifs relative to the bulk metals are innate to nanoscale systems. For example, the cluster structure in many cases can exhibit significant structural relaxation of surface atoms toward the cluster core. This results in an average bond length that is shortened with a weighting based on the population of surface atoms and other low coordination number sites (e.g., vertices at the support interface). Presenting data reported for bulk and 1.1 nm Pt/γ-Al₂O₃ under He in juxtaposition to our data (Figure 7.13) we see that the presence of adsorbates relieves strains experienced in under-coordinated bonding environments. These strains, however, are neither completely dissipated (that would have resulted in bulklike values of R_{Pt-Pt}) nor are they equivalent for CO and H₂ atmospheres. Exposure to CO leads to more bulk-like Pt-Pt bond distances than H₂, even at low partial pressures. This should be expected in light of the more strongly electron donating character of CO and, concomitantly, its ability to relieve surface relaxation.

An important feature of the structural fluxionality of Pt/γ-Al₂O₃ is revealed in the data presented in Figure 7.15, where the Pt-Pt CN under CO and H₂ is plotted at the highest and lowest temperatures tested. Notably, even though these plots show the same material, the Pt-Pt CN found for each gas is different. Thus, both the magnitude of the average bond length expansions seen and the geometric arrangement of atoms – as is required to induce changes in the CN of the magnitude observed – show that the two cases are quite distinct. Aspects of the mechanism(s) involved are clearly subject to the influence of the adsorbate-metal bond strength (which is larger for CO), but it also
remains a distinct prospect that differences in the metal-support interactions in each case (see below) play a significant role. Expansion toward more bulk-like Pt-Pt values, however, remains limited by the need to minimize the surface energy of the cluster and the interfacial strains induced by the γ-Al₂O₃ support.⁸,⁴⁷

The modifications of bond strains induced by adsorbing species are also evidenced in the systematic trends of the σ₂ values under different isobaric and isothermal conditions. At 294 K, Pt/γ-Al₂O₃ under CO and H₂ takes on diverging trends with increasing partial pressures and, thus, coverage. Under CO, the disorder in the system increases with increasing partial pressure whereas the disorder decreases for H₂. Since CO and H are known to have multiple binding sites on Pt,⁵⁴,⁷¹,⁷² one possible explanation for the observed behavior is that the relative occupancy of the binding sites is changing with the partial pressure of each gas. Adsorption of additional hydrogen, for example, would result in increasing electron donation to the Pt clusters and an increase in the number of H atoms binding at bridge, atop and 3-fold sites. Since H₂ adsorption is dissociative on Pt and results in highly mobile H atoms⁷² any changes observed should be primarily from a decrease in the number of unsatisfied Pt bonds. In contrast, CO favors molecular adsorption in an atop configuration.⁷³ Although CO can also bind in different conformations, it also experiences significant lateral repulsions at high surface coverages.⁵²,⁷³ Atomistic attempts to relieve these interactions may impact σ₂ and manifest as increasing disorder. Direct comparison of the data for each gas at higher temperatures is less straightforward because their different desorption rates will lead to very different limiting coverages over the range of partial pressures examined. Furthermore, any temperature-dependent behavior of the strain may be different for each
isobar, and will not allow separation of the static and dynamic contributions to the total bond length disorder. This can, however, be done at lower temperatures where the dynamic contribution is much smaller. As the surface coverage of each gas decreases the thermal vibrations of intracluster bonds become more important to the final system disorder. Indeed, the relatively constant disorder embedded within the clusters across all partial pressures of both gases at 673 K hints that at higher temperatures the dynamic contributions to the bond disorder are weighted to a far greater extent than adsorbate induced restructuring. This raises what is perhaps the most important, albeit complex, question addressed in this work: How can one best characterize the highly fluxional attributes of adsorbate-mediated bond strains using only a local, temporally and spatially averaging tool such as XAS? In the above case, we see limiting behaviors where the qualitative trends suggest a significant weighting of the adsorbate-determined bond strains within the low temperature and high coverage limits. Similarly, higher temperatures progressively overweigh these adsorbate contributions as the magnitude of the dynamical term in $\sigma_{Pt}^2$ increases. The larger data do speak to the nature of the bond strains present more quantitatively, however.

Using the approach of Frenkel, et al.\textsuperscript{74} we estimate strain energies associated with $\sigma_{Pt}^2$. The time and configuration averaged deformation energy ($U$) per metal atom in a metal cluster, assuming only 1NN contributions, can be evaluated as:

$$U = \frac{1}{2} N k \sigma^2. \quad (7.5.1)$$

Here $N$ is the M-M coordination number; $k$ is the force constant of the M-M bond; and $\sigma^2$ is the mean square bond length disorder. In the harmonic approximation, the force
constant is: 
\[ k = \mu \omega^2, \]  
where \( \mu = m/2 \) is the reduced mass of the M-M bond, \( \omega = k_B \Theta_E/\hbar \) is the Einstein frequency, \( \hbar \) is Planck’s constant and \( \Theta_E \) is the Einstein temperature. When static (temperature independent) strain is present, Equation 7.5.1 can be written as the sum of two contributions: 
\[ U = V(T) + W, \]  
where \( V(T) \) arises due to dynamic vibrations, and \( W \) originates from the static disorder present in the system of interatomic bonds. These two terms can be separately evaluated by expressing \( \sigma^2 \) in terms of the dynamic and static terms \( (\sigma_d^2 \text{ and } \sigma_s^2) \), respectively, of the EXAFS Debye-Waller factor:

\[ \sigma^2 = \sigma_d^2 + \sigma_s^2. \]  
(7.5.2)

The residual elastic strain energy due to the static disorder is then identifiable as simply

\[ W = \frac{1}{2} Nk\sigma_s^2. \]  
(7.5.3)

This provides a foundation to evaluate the strain energies associated with the \( \text{H}_2 \) and CO adsorbate systems studied in this work. We limit our analysis to the strain evidenced in the Pt clusters at room temperature because the higher coverage and smaller thermal contributions yielded higher data quality and will result in the largest adsorbate-induced strains. Also, as mentioned above, the separation between the static and dynamic components of the disorder is expected to be more complicated at higher temperatures. In order to separate the static and dynamic terms from the total disorder measured at room temperature for all gas concentrations, we adopted a perturbative approach. In this model, the clusters are described in terms of a perturbation by adsorbates relative to the underlying “zero coverage” cluster. Any adsorbate-specific surface bond relaxation will then be accompanied by a concomitant change in the strain energy, \( W \). Since the typical values of \( W \) obtained here (Table 7.2) are a small fraction of typical cohesive energies
(e.g., the cohesive energy of Pt is ~ 560 kJ/mol), the effect of the adsorbate-induced stress is only weakly related to the elastic constants associated with non-surface atoms. For this reason, the Einstein temperatures and frequencies for both adsorbates (H and CO) and all partial pressures studied in this work are set to the value derived for the zero coverage case. Sticking with idealized cases, this approximation also fixes both $k$ and $\sigma_d^2$ for all samples. Therefore this approximation relies on the internal cluster atoms experiencing similarly shaped, effective potential wells.

The results of these calculations (Table 7.2) are shown graphically in Figure 7.18. Values of the elastic strain energy range from 9.1 to 12.8 kJ/mol, depending on the specific system conditions. Despite the fact that our estimates are derived from results that average over the entire cluster, we can use them as a lower bound for the strain energy of the more disordered surface layer. Even these underestimated strains are quite large and should be included in theories on nanoscale thermodynamics and reaction energetics. We should also note that, besides its influence on the equilibrium configuration of ground state clusters, this static strain will likely play an important role in the thermal properties of particle-support-adsorbate systems.

The quantification of adsorbate-mediated strain energy in the Pt/γ-Al₂O₃ system provides new insights into the fundamental thermodynamic properties of this system that can be monitored using XAS. Figure 7.16 shows that the electronic characteristics of the system (as revealed in the $\Delta$XANES data) actually (and unexpectedly) changes monotonically with temperature and adsorbate concentration. Since the Pt L₃-edge white line intensity changes drawn out by the $\Delta$XANES are directly related to Pt’s d-state occupancy, there is a continuous reduction of the d-state population with increasing
temperature and/or decreasing gas concentration. Plotting the absolute, integrated area of these curves (Figure 7.17), shows that an increasing CO pressure leads to greater electronic changes at higher temperatures; whereas the H\textsubscript{2} data begins to converge with increasing temperature. Part of this differing behavior can be ascribed to near saturation (or zero) coverage of adsorbates present on the cluster surfaces (inset Figures 7.17a,b) under varying conditions, a dependency that is directly correlated with the gas partial pressure, temperature, and adsorbate bonding strength. Simple thermochemical kinetic calculations suggest, for example, that the coverage of H on Pt at 673 K is very low at the partial pressures we have examined.\textsuperscript{81} Minimal changes in the absolute, integrated intensity with varying partial pressure are therefore expected in this regime. In contrast, the stronger bonding of CO on Pt suggests that a significant coverage will still exist at 673 K (slightly above the desorption temperature) for higher partial pressures but not for the lower partial pressures. Consequently the absolute, integrated intensities for high and low partial pressures of CO are expected to diverge in this case. In point of fact, the actual experimental observations embed additional temperature and partial-pressure dependent sensitivities.

The first important observation is that the \(\Delta\text{XANES}\) for CO changes continuously with temperature, doing so even when the surface coverage should be completely saturated under 50,000 ppm CO. Since the coverage should be almost invariant under these conditions, this linear trend cannot be ascribed (as has been done in some cases reported in the literature)\textsuperscript{18,33,82,83} directly to the number of adsorbed molecules. We believe that one mechanism involved here is actually related to the variation of the particle-support interactions with temperature. The sensitivity of the particle-support
interaction to temperature can be attributed, in part, to the increased librational motion of clusters at elevated temperatures. Such factors in the structural dynamics of supported Pt catalysts have been treated both experimentally\(^9,18,56\) and theoretically\(^28,51\) in the recent literature and found to alter both the electronic and strain states present. We also note that, a saturation coverage of the Pt surface with CO should also occur at 294 K for all partial pressures examined. The data of Figure 7.17 show that there exists a partial pressure-dependent vertical shift of the \(\Delta X\)ANES data. We ascribe this shift to the effects of the support-adsorbate interaction, *vide infra*. All of the trends seen in the \(\Delta X\)ANES signal can be empirically modeled in terms of contributions from a weighted composite of adsorbate-particle, particle-support and adsorbate-support electronic interchanges using:

\[
S(T, P) = A \theta(T, P) + BT + C(P) \tag{7.5.4}
\]

Here \(S\) is the integrated intensity of the \(\Delta X\)ANES signal; \(\theta\) is coverage; and \(A, B, C\) are the weighting of each component. In this equation, the first term on the righthand side addresses electron donation from the species adsorbing on Pt and varies directly with coverage. The second term, \(BT\), models the near-linear temperature dependence of the signal that we find in the data and ascribed to the temperature mediated charge transfer between the particle and support. The final term on the right hand side of Equation 7.5.4 is the partial pressure-dependent offset observed in the experiments, which we believe can be attributed to alterations of the support – presumably *via* spillover – by the adsorbing gas molecules.

To provide quantitative analysis of the \(\Delta X\)ANES using Equation 7.5.4, we describe the coverage-dependent contribution using a Langmuirian formalism,
\[ \theta(T, P) = \frac{(KP)^a}{1 + (KP)^a} \quad (7.5.5) \]

where \( P \) is the pressure, \( K \) is the ratio of the adsorption and desorption equilibrium constants, and \( a = 1 \) or \( 0.5 \) for non-dissociative or dissociative absorption, respectively.

By expressing \( K \) as,

\[ K = A_0 e^{b/RT} \quad (7.5.6) \]

where \( A_0 \) is the ratio of exponential prefactors, \( b \) is the difference between the desorption and adsorption energies and \( R \) is the ideal gas constant, we obtain:

\[ \theta(T, P) = \frac{1}{\alpha e^{-n/T} + 1} \quad (7.5.7) \]

where \( \alpha = 1/(A_0 P)^n \) and \( n = ab/R \). Thus Equation 7.5.4 can be rewritten as

\[ S(T, P) = \frac{A}{\alpha e^{-n/T} + 1} + BT + C(P). \quad (7.5.8) \]

Since the adsorption of \( \text{H}_2 \) and \( \text{CO} \) on Pt are both non-activated, the fit value of \( b \) is equivalent to the heat of adsorption, \( \Delta H \). To reduce the number of variables involved in the fit, we note that at full coverage (low \( T \)) Equation 7.5.8 reduces to:

\[ S(T, P) = A + BT + C(P). \quad (7.5.9) \]

Therefore a plot of \( S \) versus \( T \) – while maintaining full coverage (e.g., 50,000 ppm CO) – will provide values for \( B \) and \( F(P) = A + C(P) \) via the slope and y-intercept, respectively.

Rearranging Equation 7.5.9 we obtain

\[ S(T, P) = \frac{A}{\alpha e^{-n/T} + 1} + BT + F(P) - A. \quad (7.5.10) \]
We further assume that $A_0$ can be approximated by

$$A_0 \sim \frac{\hbar^3}{k_b (2\pi m k_b)^{3/2}} \frac{1}{T^{3/2}},$$

where $k_b$ is Boltzmann’s constant, $\hbar$ is Planck’s constant, $m$ is the mass of the adsorbing molecule and $T$ is the temperature. This means that $A_0$ will be on the order of $\sim 10^{-13}$ for CO and $\sim 10^{-11}$ for H$_2$ over the range of temperatures examined. If the system is near full coverage and the particle-support interaction with temperature (described by the coefficient $B$) is assumed independent of gas pressure, $F(P)$ will shift proportionally to the intensity offset observed at 294 K. Equivalently, the linear term will be vertically shifted for different partial pressures. Because we do not have measurements pertaining to a constant coverage of H$_2$ across all temperatures examined, we determined the $B$ value from the CO curves.

Although these assumptions are idealized, and thus approximate, this ansatz leaves only two unknown values after substituting for theoretical and experimental values: $A$ and $n$. Fitting $n$ for all three pressures simultaneously while allowing $A$ to vary permits estimation of $\Delta H$ for H$_2$ and CO adsorption (Example 7.1). Alternatively, if possible changes in the extent of charge transfer caused by a significantly increased coverage/pressure are ignored (e.g., altered occupancy of less favorable binding sites), $A$ can be treated as a common, partial pressure-independent variable for each adsorbate. Indeed, when $A$ is allowed to vary with pressure, it shows a progressive trend toward increasing values for increasing H$_2$ pressure and an opposite trend for CO (Table 7.5.2). The resulting $\Delta H$ values using this fitting method are $64 \pm 3$ kJ/mol for H$_2$ and $126 \pm 2$ kJ/mol for CO. In the more constrained situation, where $A$ is treated as a common variable (Table 7.4), a less satisfactory fit is produced (Figure 7.5.2). Even in this highly
limited case the predicted ΔH values (61 ± 4 for H₂ and 131 ± 2 for CO) change only marginally.

The principle limitation of adopting a Langmuir isotherm to describe the coverage is that it inherently assumes a coverage-invariant ΔH. In general, heats of adsorption for adsorbates show an approximately linear dependence on coverage up to a monolayer.¹⁵,²⁷,⁸⁴ For our system we note that the CO coverage will vary over a maximal range of approximately 60-100%¹⁶ while the hydrogen will vary within an approximate range of 1-99%.⁸⁴ Therefore the heats of adsorption derived by fitting the experimental data will represent average values over the coverage ranges examined. It should further be noted that our choice of reference means that the “coverage values” fit will range between 0% and 100% for both cases and are values based on our reference partial pressure and temperature. Nevertheless, the fitted coverage (Table 7.5 and Figure 7.20) reproduces the behavior expected for constant pressure adsorbate coverage with increasing temperature (inset Figure 7.17). In addition to the coverage behavior, the values calculated for ΔH by fitting our equation fall nicely within the range of values reported in the literature for H₂ (~50-83 kJ/mol)⁶¹ and CO (~100-140 kJ/mol)⁶¹,⁸⁵ on Pt – values that depend, variably, upon the technique used, the system (e.g., (un)supported, bulk, etc.), the exposed facet(s)/CN of the Pt atoms and the adsorbate coverage. This analysis demonstrates that the XAS data – specifically the ΔXANES data – report on the electronic/structural features of these two chemisorption systems and provide a means to explicitly correlate these attributes to global thermodynamic values.

It is now clear that the particle-support interactions in the Pt/γ-Al₂O₃ system are significant and electronically complex but that fundamental aspects associated with charge
exchange are strongly responsive to temperature. The current literature strongly supports the conclusion that these bonding interactions mediate a net charge flow to the Pt clusters from the support, and may further embed an important role for oxygen atom vacancies in the oxide substrate as components of this bonding. Many features of the system – explicitly the anomalous thermal dependencies seen in the Pt-Pt bond lengths and properties of d-state occupancies that are implied by the ΔXANES intensities – argue strongly in support of this conclusion. At present our ability to address these phenomena via quantitative theoretical models remains limited in important ways. Theory demonstrates non-vibrational (e.g., librational) dynamics plays a crucial role in shaping the thermal responses of Pt/γ-Al₂O₃, both in terms of anomalous XANES behaviors (e.g., red shift) and the non-bulk-like temperature dependent evolution of Pt-Pt bond distances. How this complex and markedly mesoscopic behavior might then lead to the systematic, essentially linear, dependencies of the ΔXANES intensities seen with temperature is presently not understood. We believe further work will be needed to assess the mechanism that might be involved.

We also note that the origins of the ΔXANES offsets seen in the isobaric temperature series presented in Figure 7.17 remain poorly understood. Clearly some form of support interaction/modification must be involved. We know with some certainty that the support differs in significant ways in the two adsorbate-based comparisons. In the work conducted in H₂ ambients the formation of support-bonded H – bonding variably described as hydrogen spillover, hydroxylation, etc. which will alter the extent of support wetting by altering the particle-support interfacial energy. The degree of surface hydroxylation is known to impact the binding energy of Pt to γ-Al₂O₃ as well as leading
to structural rearrangements.\textsuperscript{22,39} A changing number of hydroxide groups at the alumina surface should result in changes to the number of bonds to the Pt clusters and, thus, manifest as a shape change. Whatever its form, the high temperature cycle in a CO environment will desorb this hydrogen, and thus engenders a support phase with very different properties. Even so, and the quantitative differences notwithstanding, the pressure dependent offsets seen in Figure 7.17 are consistent with the expected behavior of an electron donating species binding to the support. In such a case, the increasing electron density of the support will allow more electron density to be transferred to the cluster. This will manifest as an electronic shift consistent with increasing coverage even if the coverage remains static. Similarly, an increase in the electron transfer capabilities of the support will favor a greater wetting of the support. Still, the flattening of unsupported particles under CO has theoretically predicted and experimentally observed,\textsuperscript{64} meaning that the reason(s) for an increase in the Pt-Pt CN with increasing temperature under CO but not H\textsubscript{2} remains a marked but poorly understood feature of the current data, one for which some form of theoretical description is urgently needed.

Finally, we note that the data also provides what we believe is the first description of how Pt-Pt bond strains respond to variable temperature and adsorbate partial pressure in Pt/γ-Al\textsubscript{2}O\textsubscript{3} systems. The role of strain on the electronic structure and reactivity of Pt clusters was recently highlighted by Strasser, \textit{et al}.\textsuperscript{12} It is important to note that our estimates of the strain energy are averaged over the cluster – that is to say that the strains experienced by specific atom sites in the Pt clusters surfaces could be significantly larger. Although the literature clearly establishes the validity of this latter hypothesis,\textsuperscript{36} the energy content of this feature across the conditions examined has not yet been addressed.
The present data suggest the impact of these strains is quite large. Indeed, the strain energy of each system can vary by almost 3 kJ/mol by merely changing the adsorbate partial pressure at room temperature. Further studies are in progress to more precisely quantify this latter aspect of the energetics and provide a rigorous set of benchmarks for address by theory.

7.6 Conclusions

Strain driven, electronic and morphological reconstructions of Pt clusters supported on γ-Al₂O₃ exhibit marked adsorbate and temperature dependencies. Monitoring these changes with XAS under steady state conditions, the contributions of adsorbates and temperature can be parsed, allowing for improved understanding and model development of the multicomponent interactions occurring. Our investigation shows how to extract both strain and thermodynamic information from XAS measurements and offers insight into the relative importance of adsorbate-particle, particle-support and adsorbate-support interactions with changing temperature or pressure for Pt/γ-Al₂O₃. This indicates methods of tailoring catalytic activity and the relative magnitude of those changes on the final catalyst structure.

7.7 Acknowledgements

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7.8 Figures, Tables and Example

Figure 7.1. Representative scanning transmission electron microscopy micrograph of the Pt/γ-Al₂O₃ sample and a particle size histogram obtained by analyzing multiple micrographs.

Figure 7.2. Aberration-corrected STEM image of Pt/γ-Al₂O₃.
Figure 7.3. XAS spectra of a) 400 ppm, b) 25,000 ppm and c) 50,000 ppm H$_2$ over the temperatures examined.
Figure 7.4. XAS spectra of a) 400 ppm, b) 25,000 ppm and c) 50,000 ppm CO over the temperatures examined.
Figure 7.5. XAS spectra at temperatures of: a) 294 K, b) 393 (or 423) K, c) 488 K, d) 550 K and e) 673 K for the H₂ pressures examined.
Figure 7.6. XAS spectra at temperatures of: a) 294 K, b) 393 K, c) 488K, d) 550 K and e) 673 K for the CO pressures examined.
Figure 7.7. Plots demonstrating the temperature evolution of the R-space data for a) 400, b) 25,000 and c) 50,000 ppm \( \text{H}_2 \) at different temperatures.
Figure 7.8. Plots demonstrating the temperature evolution of the R-space data for a) 400, b) 25,000 and c) 50,000 ppm CO at different temperatures.
Figure 7.9. FT magnitudes of raw XAS data measured at a fixed temperature for H$_2$ at different pressures.
Figure 7.10. FT magnitudes of raw XAS data measured at a fixed temperature for CO at different pressures.
Figure 7.11. EXAFS fits for the 294 K (a, c, e) and 673 K (b, d, f) H₂ data at pressures of: a,b) 400 ppm, c,d) 25,000 ppm and e,f) 50,000 ppm. The green box indicates the fitting window used.
Figure 7.12. EXAFS fits for the 294 K (a, c, e) and 673 K (b, d, f) CO data at pressures of: a,b) 400 ppm, c,d) 25,000 ppm and e,f) 50,000 ppm. The green box indicates the fitting window used.
Model i:

<table>
<thead>
<tr>
<th>Gas</th>
<th>T = 294 K</th>
<th>T = 673 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>8.27(21)</td>
<td>7.96(23)</td>
</tr>
<tr>
<td>CO</td>
<td>8.70(25)</td>
<td>9.24(29)</td>
</tr>
</tbody>
</table>

Model ii:

<table>
<thead>
<tr>
<th>Concentration of H₂/He (ppm)</th>
<th>Pt-Pt CN</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>294 K</td>
</tr>
<tr>
<td>400</td>
<td>8.26(37)</td>
</tr>
<tr>
<td>25,000</td>
<td>8.25(53)</td>
</tr>
<tr>
<td>50,000</td>
<td>7.94(48)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Concentration of CO/He (ppm)</th>
<th>Pt-Pt CN</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>294 K</td>
</tr>
<tr>
<td>400</td>
<td>8.56(66)</td>
</tr>
<tr>
<td>25,000</td>
<td>9.06(54)</td>
</tr>
<tr>
<td>50,000</td>
<td>7.83(62)</td>
</tr>
</tbody>
</table>

Table 7.1. Pt-Pt coordination numbers calculated for two fitting models. In the first model, the coordination number was fixed for each gas (assumes no shape change with partial pressure of gas). For the second model, the coordination number was allowed to vary with the partial pressure of the gas.
Figure 7.13. Pt-Pt 1NN distances at a) 294 and b) 673 K for different partial pressures of CO and H$_2$. Dashed lines indicate the values expected for bulk Pt (black) and values previously reported$^9$ for 1.1 nm Pt/γ-Al$_2$O$_3$ under He (gray).
Figure 7.14. Pt-Pt bond length disorder ($\sigma_{Pt}^2$) values at a) 294 and b) 673 K for different partial pressures of CO and H$_2$. 
**Figure 7.15.** Pt-Pt 1NN coordination numbers for the lowest and highest temperatures studied, plotted as a function of partial pressure: (a) $\text{H}_2$/He and (b) CO/He.
Figure 7.16. ΔXANES spectra for H$_2$ (a-b) and CO (c-d) using 400 ppm of each gas at 673 K as a reference.
Figure 7.17. Plot of the integrated intensity obtained from the a) CO and b) H₂ ΔXANES. The different partial pressures are: 400 ppm (circles); 25,000 ppm (triangles); and 50,000 ppm (squares). The solid lines are the lines of best fit obtained using Equation 7.5.8. The insets show the general shape of a desorption curve (coverage versus temperature) derived using the Langmuir approximation and indicate (oval) the desorption region circled appropriate for the designated gas.
Table 7.2. Calculated strain energies for Pt/$\gamma$-Al$_2$O$_3$ under different gaseous environments.

<table>
<thead>
<tr>
<th>Gas/pressure</th>
<th>N(Pt-Pt)</th>
<th>$\Theta$ (K)</th>
<th>$\sigma^2$ (Å$^2$)</th>
<th>$\sigma_s^2$ (Å$^2$)</th>
<th>W(kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% He$^a$</td>
<td>6.3(3)</td>
<td>226(7)</td>
<td>0.0075(2)</td>
<td>0.0045(2)</td>
<td>12.1(1.1)</td>
</tr>
<tr>
<td>400 ppm H$_2}$/He</td>
<td>8.3(4)</td>
<td>226</td>
<td>0.0064(3)</td>
<td>0.0034(3)</td>
<td>12.0(1.4)</td>
</tr>
<tr>
<td>25,000 ppm H$_2}$/He</td>
<td>8.2(5)</td>
<td>226</td>
<td>0.0061(3)</td>
<td>0.0031(3)</td>
<td>10.9(1.4)</td>
</tr>
<tr>
<td>50,000 ppm H$_2}$/He</td>
<td>7.9(5)</td>
<td>226</td>
<td>0.0057(2)</td>
<td>0.0027(2)</td>
<td>9.1(1.1)</td>
</tr>
<tr>
<td>400 ppm CO}/He</td>
<td>7.8(6)</td>
<td>226</td>
<td>0.0059(3)</td>
<td>0.0029(3)</td>
<td>9.7(1.4)</td>
</tr>
<tr>
<td>25,000 ppm CO}/He</td>
<td>8.8(5)</td>
<td>226</td>
<td>0.0064(3)</td>
<td>0.0034(3)</td>
<td>12.8(1.6)</td>
</tr>
<tr>
<td>50,000 ppm CO}/He</td>
<td>8.6(7)</td>
<td>226</td>
<td>0.0065(3)</td>
<td>0.0035(3)</td>
<td>12.8(1.7)</td>
</tr>
</tbody>
</table>

$^a$ Derived from a previous report$^9$ of 1.1 nm Pt/$\gamma$-Al$_2$O$_3$ under He.
Figure 7.18. Graphical depiction of the strain data shown in Table 7.2.
Example 7.1. Equation fitted for 50,000 ppm CO. The numerical values used are, 1) 5066.25 is the partial pressure in Pa; 2) $10^{-13}$ is the, approximate, theoretical ratio of the Arrhenius prefactors for CO; 3) -0.001 is the slope of $S$ with respect to $T$ for 50,000 ppm CO (used for all fits); and 4) 0.808 is the offset at 294 K. Here $x$ is inverse temperature. All pressures were simultaneously fit while constraining $k$ to be the same for all partial pressures but allowing $a$ to vary with partial pressure. See Table 7.3 for offsets and fit results.
<table>
<thead>
<tr>
<th>CO T(K)</th>
<th>400</th>
<th>25k</th>
<th>50k</th>
<th>H2 T(K)</th>
<th>400</th>
<th>25k</th>
<th>50k</th>
</tr>
</thead>
<tbody>
<tr>
<td>294</td>
<td>0.659</td>
<td>0.739</td>
<td>0.808</td>
<td>294</td>
<td>0.460</td>
<td>0.553</td>
<td>0.676</td>
</tr>
<tr>
<td>393</td>
<td>0.560</td>
<td>0.640</td>
<td>0.709</td>
<td>393</td>
<td>0.292</td>
<td>0.414</td>
<td>0.537</td>
</tr>
<tr>
<td>488</td>
<td>0.463</td>
<td>0.545</td>
<td>0.614</td>
<td>423</td>
<td>0.249</td>
<td>0.359</td>
<td>0.478</td>
</tr>
<tr>
<td>550</td>
<td>0.343</td>
<td>0.482</td>
<td>0.552</td>
<td>488</td>
<td>0.172</td>
<td>0.245</td>
<td>0.347</td>
</tr>
<tr>
<td>673</td>
<td>0.000</td>
<td>0.303</td>
<td>0.420</td>
<td>550</td>
<td>0.107</td>
<td>0.157</td>
<td>0.244</td>
</tr>
<tr>
<td></td>
<td>673</td>
<td>-0.018</td>
<td>0.017</td>
<td>0.091</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| a        | 0.28682 | 0.14327 | 0.03458 | a        | 0.110 | 0.167 | 0.223 |
| k (shared)| 15159  | +/- 214  |         | k (shared)| 3871  | +/- 169 |       |
| ΔH (kJ/mol)| 126   | +/- 2   |         | ΔH (kJ/mol)| 64    | +/- 3  |       |

**Table 7.3.** Fit results for data obtained using Equation 7.5.10.
<table>
<thead>
<tr>
<th>CO</th>
<th>Pressure (ppm)</th>
<th>H₂</th>
<th>Pressure (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T(K)</td>
<td></td>
<td>T(K)</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>25k</td>
<td>50k</td>
</tr>
<tr>
<td>294</td>
<td>0.659</td>
<td>0.739</td>
<td>0.808</td>
</tr>
<tr>
<td>393</td>
<td>0.560</td>
<td>0.640</td>
<td>0.709</td>
</tr>
<tr>
<td>488</td>
<td>0.464</td>
<td>0.545</td>
<td>0.614</td>
</tr>
<tr>
<td>550</td>
<td>0.380</td>
<td>0.483</td>
<td>0.552</td>
</tr>
<tr>
<td>673</td>
<td>0.001</td>
<td>0.299</td>
<td>0.395</td>
</tr>
<tr>
<td></td>
<td>673 -0.057</td>
<td>0.032</td>
<td>0.158</td>
</tr>
</tbody>
</table>

Table 7.4. Fit results for data obtained using Equation 7.5.10 with \( A \) as a common variable across all pressures for each gas.
Figure 7.19. Plot of Table 7.4 fits and experimental values for a) H$_2$ and b) CO.
<table>
<thead>
<tr>
<th>CO</th>
<th>Pressure (ppm)</th>
<th></th>
<th>H₂</th>
<th>Pressure (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T(K)</td>
<td>400 25k 50k</td>
<td>T(K)</td>
<td>400 25k 50k</td>
<td></td>
</tr>
<tr>
<td>294</td>
<td>100.0% 100.0% 100.0%</td>
<td>294</td>
<td>91.3% 98.8% 99.2%</td>
<td></td>
</tr>
<tr>
<td>393</td>
<td>100.0% 100.0% 100.0%</td>
<td>393</td>
<td>27.6% 75.1% 81.0%</td>
<td></td>
</tr>
<tr>
<td>488</td>
<td>99.2% 100.0% 100.0%</td>
<td>423</td>
<td>15.9% 60.0% 68.0%</td>
<td></td>
</tr>
<tr>
<td>550</td>
<td>79.1% 99.6% 99.8%</td>
<td>488</td>
<td>5.3% 30.7% 38.5%</td>
<td></td>
</tr>
<tr>
<td>673</td>
<td>2.4% 60.5% 75.4%</td>
<td>550</td>
<td>2.2% 15.3% 20.4%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>673</td>
<td>0.6% 4.8% 6.6%</td>
<td></td>
</tr>
</tbody>
</table>

Table 7.5. Coverage predictions based on fit results in Table 7.3.
Figure 7.20. Plot of Table 7.5 coverage values for a) H$_2$ and b) CO.
References


CHAPTER 8
GENERAL CONCLUSIONS AND FUTURE DIRECTIONS

The focus of my graduate work has been on catalysts due to their utility in industry and general benefit to society. Nonetheless, the techniques and approaches used here are capable of being more broadly applied. A large point of focus was discerning how the structure and electronic nature of the materials was altered with changing environments. These in-situ studies were carried out with XAS and, therefore, represent an average across all particles. Because of the indirect means of interpreting structural changes from XAS, knowing exactly where clusters prefer to nucleate and how this alters the behavior is still a difficult question. One means of investigating localized structural changes is in-situ/environmental (S)TEM. A few things that would be interesting to do are to watch individual clusters curing catalytic cycling to observe structural and electronic changes. This has been done with simple adsorbates but not, to my knowledge, for any reaction that may involve multiple mechanisms/adsorbates. A second project would involve creating nanoscale polycrystalline regions and using aberration-corrected microscopy to observe nucleation along either grain boundaries and/or on specific facets.

A particularly useful means of characterizing short range order is the program I wrote (Chapter 3). Some improvements were made since the writing of Chapter 3 (the code in the appendix has been updated), but improved efficiency and additional functionalities could still be added. For example, attempts could be made to identify zone axes, packing structures, different elemental regions, removal of the second threshold requirement, comparing sequential images (partially implemented through
Deformation.m), strain profiles (partially implemented through Deformation.m), analysis of peak broadening, and generation of a 3D structure for simulation with Zmult – just to name a few possible improvements. Nevertheless, its core functionality will still focus on identifying atoms and structural information from individual micrographs. Ideally I would love to see this used to look at single molecules. While I conducted preliminary work on this front, a frequent problem encountered was that the systems suffered severe degradation from beam damage/dissociation. If these problems could be overcome it would enable direct imaging of molecules adsorbed onto surfaces, yielding information on their dispersion, structure and orientation relative to the support. Even so, beam damaged samples might be useful to examine since they would yield information pertinent to nanoparticle formation via electron beam reduction, atomic layer deposition mechanisms and thin film formation – particularly if supports with different affinities are used. It would also be nice to see the RDF data from microscopy directly compared to X-ray data (PDF, XAS, XRD, etc.). There is some indication that these will not be the same and it would be helpful to address how/why they differ. Namely, if the difference is due to instrumental noise or if the electron beam is imparting discernable structural changes. This conclusion will heavily influence how any electronic state information from a catalytic reaction can be interpreted on the basis of microscopy data. One completely different area of investigation would be using in-situ (S)TEM to examine electronics during their operation. Specifically, it should be possible to monitor electric fields and interfacial migration/structure change.
Overall, I have enjoyed my graduate career. Much was accomplished but, like any good research, the answers obtained have raised more questions that I hope the scientific community will seek to answer.
Zmult is a multi-slice (S)TEM simulation program developed by Dr. Jian-Min Zuo (University of Illinois, Urbana-Champaign). The actual Zmult data files/code and tutorial for different types of simulations (e.g., STEM, coherent convergent beam electron diffraction, etc.) can be obtained from Dr. Zuo and run through a Linux/Unix shell. Below is a brief outline of the input files used for STEM simulations and procedure to conduct a simulation.

Once installed, using the program consists of three distinct steps: 1) make a .dat file, 2) assign parameters in the .ms file, 3) run “zmult <filename.ms> –show wi” in a linux/unix environment.

The .dat file structure is given in A.1 while the .ms file structure is given in A.2. For each file type a more thorough description is given by Dr. Zuo’s tutorial and I have only highlighted the sections that should be changed between simulations. To create an image file from the .adf created, run: Adfimage <filename.adf> n x y, where n is the number of the written output to be plotted and x, y are the number of cells along each direction. Generally, only the final slice is what is interesting and you wish to display the region scanned (no periodicity or truncation departed onto the display). So, for the case of A.2, conversion of the .adf would be: adfimage <trial1.adf> 20 1 1. Although the .adf file contains both inelastic and elastic scattering contributions, the total scattering is (by default) plotted.

**A.1 .dat File Structure**

<table>
<thead>
<tr>
<th>Number of atoms in simulation</th>
<th>923</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atom type identifier</td>
<td>50.426041</td>
</tr>
<tr>
<td>(first type, second, etc.)</td>
<td>Dimension of simulation space in Å, may give 1 or 3 values (default is cubic)</td>
</tr>
<tr>
<td>Atomic coordinates (xyz) in angstrom</td>
<td></td>
</tr>
<tr>
<td>Debye-Waller factor</td>
<td></td>
</tr>
<tr>
<td>Occupancy</td>
<td></td>
</tr>
</tbody>
</table>

- 1 95.086922 145.740601 193.502884 0 1
- 1 93.141914 145.740601 190.134018 0 1
- 1 91.196922 145.740601 186.765198 0 1
- 1 89.251900 145.740601 183.396362 0 1
## A.2 .ms File Structure

<table>
<thead>
<tr>
<th>Key</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td># Name of file containing absolute atom positions</td>
<td>trial1.dat</td>
</tr>
<tr>
<td># HV tilt tiltx tilty (in fractions of reciprocal lattice vector)</td>
<td>0.0 0.0 0.0</td>
</tr>
<tr>
<td># Number of sample points in x and y-direction</td>
<td>512 512</td>
</tr>
<tr>
<td># Number of slices for MS calculations</td>
<td>20</td>
</tr>
<tr>
<td># Extinction rule</td>
<td>1 1</td>
</tr>
<tr>
<td># Potential in reciprocal space = 0, in real space = 1</td>
<td>1 1</td>
</tr>
<tr>
<td># Number of inequivalent atoms</td>
<td>1</td>
</tr>
<tr>
<td># Atom types</td>
<td>Pd</td>
</tr>
<tr>
<td># Atomic scattering factors expressed by 5 Gaussian parameters</td>
<td>0.3055 1.3945 2.9617 3.8990 2.0026 0.5827 3.1035 11.9693 47.9106</td>
</tr>
<tr>
<td># Debye-Waller factor</td>
<td>0.4259</td>
</tr>
<tr>
<td>Pt</td>
<td>0.3557</td>
</tr>
<tr>
<td># Objective aperture</td>
<td>7.0</td>
</tr>
<tr>
<td># Output</td>
<td>20 -0.1</td>
</tr>
<tr>
<td># Name of pendelloesung file</td>
<td>PdcorePshell.pl</td>
</tr>
<tr>
<td>1 0 0</td>
<td>STEM control STEM-ADF</td>
</tr>
<tr>
<td>df_nm</td>
<td>-1.582</td>
</tr>
<tr>
<td>c3_nm</td>
<td>0.5658E-02</td>
</tr>
<tr>
<td>c5_nm</td>
<td>-0.8450</td>
</tr>
<tr>
<td>kmax</td>
<td>0.89715</td>
</tr>
<tr>
<td>a1_nm</td>
<td>1.34 5.44</td>
</tr>
<tr>
<td>a2_nm</td>
<td>22.96 2.31</td>
</tr>
<tr>
<td>a3_um</td>
<td>2.76 -16.70</td>
</tr>
<tr>
<td>a4_um</td>
<td>3.65 -84.00</td>
</tr>
<tr>
<td>a5_nm</td>
<td>2.02 -12.70</td>
</tr>
<tr>
<td>b2_nm</td>
<td>15.90 60.42</td>
</tr>
<tr>
<td>b4_um</td>
<td>48.84 -35.00</td>
</tr>
<tr>
<td>d4_um</td>
<td>19.88 82.20</td>
</tr>
<tr>
<td>s3_um</td>
<td>1.19 150.90</td>
</tr>
<tr>
<td>phi</td>
<td>90</td>
</tr>
<tr>
<td>probe</td>
<td>0.45</td>
</tr>
<tr>
<td>end</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>200 20</td>
</tr>
<tr>
<td>1 2 10</td>
<td></td>
</tr>
</tbody>
</table>

- **Input file name**
- **Mesh size of sampling grid (xy resolution)**
- **Slices in calculation (z resolution)**
- **Number of atom types in simulation**
- **Atom type and debye-waller factor, add additional entries after if desired**
  - **Note:** Atom types MUST be in same order as input file
- **Save data after x iterations (here x=20)**
- **Pendelloesung output file name**
- **Percent of input unit cell to scan in the x and y direction as well as the number of points for each scan (%x, %y, resolution x, resolution y)**
  - **Note:** image displayed is as viewed from the detector NOT the top (i.e., will appear as if looking at the back of the model used).
- **Minimum and maximum detection radius (1/Å) and maximum radius of atoms (10 is sufficient)**

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APPENDIX B

BASH PROGRAMS

B.1 General Comments on Visualization Software and Use

These programs were primarily developed to manipulate data from or for the “Geometrical Modeling of Small Particles” (gmsp) and “Visual Molecular Dynamics” (vmd) programs. The first of these was developed by Dr. Jian-Min Zuo’s group and the second was by Dr. Klaus Schulten’s group (both at the University of Illinois, Urbana-Champaign) and both provide convenient means of producing/manipulating desired structures. Since all of the programs given below are coded in the Bash shell, the user should make sure to convert them to executable files (see the “chmod” command) and that all files that they are accessing have been converted to unix format (i.e. type: dos2unix <filename>). As a forewarning, since I never worked to optimize these programs they may be a bit on the slow side for larger files.
B.2 1typepossibilities

# 1typepossibilities
#--------------------------------------------------------------
# This script will calculate the approximate number of atoms in a column
# for a given intensity based on the parameters entered.
#
#--------------------------------------------------------------

echo "What would you like the output file to be called?"
read out

echo "What is the file with the maximum intensities measured?"
read maxs

echo "What is the intensity of atom a?"
read singlea

#--------------------------------------------------------------
# Start calculating the different integer possibilities
#--------------------------------------------------------------

echo "Combined file:" > $out
de=0

for data in $( cat $maxs ); do
de=$((de+1))
echo "(Possible solutions)" > mtemp.$de
echo "----------" >> mtemp.$de

a=$(echo "scale=6; $singlea" | bc )

finish1=$(echo "scale=6; $data/$a + 1" | bc )

ość=0
counta=0

echo "Calculating for intensity =$data... (this could be awhile)"
until [ "$($(echo "scale=6; $counta > $finish1" | bc )) = "$1" ]; do

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total=$one
cHECK=$(echo "scale=6; (($data-$total) > (-($a*0.5))) \&\& \\
((($data-$total) < (0.5*$a)) ) | bc )
if [ $check -eq 1 ]; then
    echo "$counta" >> mtemp.$dec
fi
counta=$((counta+1))
one=$(echo "scale=6; $one+$a" | bc)
done

echo " " >> $out
echo " " >> $out
echo "-------------------------------" >> $out
echo "File #$dec" >> $out
echo "-------------------------------" >> $out
cat mtemp.$dec >> $out

done

rn mtemp*
B.3 1xyz2zmult

# 1xyz2zmult
#---------------------------------------------------------------
# This script will take one .xyz file and create a large zmult file
# The box size is calculated based on the maximum difference between the
# x, y, or z values (ie largest delta direction) and has a user defined base added
# to it to allow for space on the side of the crystal.

echo -n "What do you want to call the output file? "
read out

echo -n "What is the name of the input file? "
read file

echo -n "What spacing did you want on the side of the crystal (angstroms)? "
read space

#---------------------------------------------------------------
function addon
{
flag=0
skip=0
for data in $(cat $file); do
  if [ $skip -eq 0 ]; then
    echo $data > mtempcoords
    echo "" >> mtempcoords
    skip=1
    continue
  fi
  if [ $flag -eq 3 ]; then
    flag=0
    echo "$data 0 1" >> mtempcoords
    continue
  fi
  flag=$(($flag+1))
  echo -n "$data " >> mtempcoords
done
}
#---------------------------------------------------------------
function combine
{
# write the file
total=0

echo $boxx " " $boxy > $out
echo "" >> $out
cat mtempcoords >> $out
}

#---------------------------------------------------------------
function boxfind
{
  boxx=$(echo "$maxx-(minx)" | bc )
  boxy=$(echo "$maxy-(miny)" | bc )
  # boxz=$(echo "$maxz-(minz)" | bc )
  # if [ $(echo "$boxx>$boxy" | bc ) -eq 1 ] && 
  #   [ $(echo "$boxx>$boxz" | bc ) -eq 1 ]; then
  #   boxx=$(echo "$boxx+$space" | bc )
  #   else
  #   if [ $(echo "$boxy>$boxx" | bc ) -eq 1 ] && 
  #     [ $(echo "$boxy>$boxz" | bc ) -eq 1 ]; then
  #     boxy=$(echo "$boxy+$space" | bc )
  #   else
  #     box=$(echo "$boxz+$space" | bc )
  #   fi
  # fi
}

#---------------------------------------------------------------
function maxmin
{
  awk '{print $2}' $file > mtempxcol
  awk '{print $3}' $file > mtempycol
  # awk '{print $4}' $file > mtempzcol
  skip=2
  # Find max and min x
  for look in $(cat mtempxcol); do
    if [ $skip -eq 2 ]; then
      minx=$look
      maxx=$look
      skip=3
      continue
    fi
    if [ $(echo "$minx > $look" | bc ) -eq 1 ]; then
      minx=$look
  # Find max and min y
  for look in $(cat mtempycol); do
    if [ $skip -eq 2 ]; then
      miny=$look
      maxy=$look
      skip=3
      continue
    fi
    if [ $(echo "$miny > $look" | bc ) -eq 1 ]; then
      miny=$look

continue
fi
if [ $(echo "$maxx < $look" | bc) -eq 1 ]; then
    maxx=$look
    continue
fi
done

skip=2

# find max and min y
for look in $(cat mtempycol); do
    if [ $skip -eq 2 ]; then
        miny=$look
        maxy=$look
        skip=3
        continue
    fi
    if [ $(echo "$miny > $look" | bc) -eq 1 ]; then
        miny=$look
        continue
    fi
    if [ $(echo "$maxy < $look" | bc) -eq 1 ]; then
        maxy=$look
        continue
    fi
done

#skip=2

# find max and min z
#for look in $(cat mtempzcol); do
    # if [ $skip -eq 2 ]; then
    #    minz=$look
    #    maxz=$look
    #    skip=3
    #    continue
    # fi
    # if [ $(echo "$minz > $look" | bc) -eq 1 ]; then
    #    minz=$look
    #    continue
    # fi
    # if [ $(echo "$maxz < $look" | bc) -eq 1 ]; then
    #    maxz=$look
    #    continue
    # fi
#done
}

#-------------------------------------------------- --------------------------
# calling sequence
#-------------------------------------------------- --------------------------

echo "" > $out
maxmin
echo "Finding box size..."
boxfind
addon
combine
echo "$out has been written."
rm mtemp*
B.4 Alloy

# ALLOY
#-------------------------------------------------- --------------------------
# This script asks for a .xyz file and the percentage a particle that you
# would like to be made of one element and then creates a .xyz file
# that assumes the element distribution is random
#-------------------------------------------------- --------------------------

# Get information
#-------------------------------------------------- --------------------------

echo -n "What is the name of the input file (.xyz)? "
read file

echo -n "What would you like the output file to be called? "
read out

echo -n "What decimal percentage of the particle did you want to be different? "
read percentage

#-------------------------------------------------- ------------------------
# This function checks to make sure that a random number isn't duplicated
#-------------------------------------------------- ------------------------
function check
{
for f in $(cat mtemprandom); do
  if [ $number -eq $f ]; then
    bad=1
    break
  fi
done
}

#-------------------------------------------------- ------------------------
# This function identifies the random particle
#-------------------------------------------------- ------------------------
function id
{
for f in $(cat mtemprandom2); do
  if [ $f -eq $position ]; then
    mark=1
    break
  else
    mark=0
  fi
}
for f in $(cat $file); do
  atoms=$f
  echo "" > mtemprandom
  break
done

howmany=$(echo "scale=0; ($atoms * $percentage)" | bc)

echo -n "Finding approximately "
echo -n $howmany
echo " random atoms..."

count=1
bad=0
start=0

# note: the while condition means that we'll always round up when determining
# how many atoms to replace

while [ "$(echo "$count < $howmany" |bc)" = "1" ]; do
  number=$((RANDOM%$atoms))  # random number 0 to ($atoms-1)
check
  if [ $bad -eq 1 ]; then
    bad=0
    continue
  else
    if [ $start -eq 1 ]; then
      echo $number >> mtemprandom
      count=$(($count+1))
    else
      start=1
      echo $number > mtemprandom
    fi
  fi
done
sort mtemprandom > mtemprandom2

change=0
position=0
skip=0
flag=0

for spot in $(cat $file); do
    if [ $skip -eq 0 ]; then
        skip=1
        echo $spot > $out
        echo "" >> $out
        continue
    fi

    if [ $flag -eq 0 ]; then
        position=$(($position+1))
id
        if [ $mark -eq 1 ]; then
            echo -n "2 " >> $out
        else
            echo -n "1 " >> $out
        fi
        flag=$(($flag+1))
        continue
    fi

    if [ $flag -le 2 ]; then
        echo -n "$spot " >> $out
        flag=$(($flag+1))
        continue
    fi

    if [ $flag -eq 3 ]; then
        echo $spot >> $out
        flag=0
    fi
done

rm mtemp*
B.5 altergmsp

# This script takes the output file from GMSP and turns it into a position file for zmult.
# This assumes that there is only one type of atom in the structure. A square box
# size is calculated based on the maximum and minimum values of the
# coordinates (regardless if x, y, or z), and a base of 10 is added to
# this (to allow for a small gap to either side of the crystal).
#
# Output file is: "file".new.pos

# Ask the user for the GMSP file
echo -n "What is the name of the file you want to alter? "
read file

# Flags to exclude extraneous information at beginning of output and to keep required
# (ie atom type and position) on same line.
flag=0
count=0

# Remove any output file previously associated with this name to avoid simply
# appending to an existing
# file of the same name.
if [ -f $file.new.pos ] ; then
    rm $file.new.pos
fi

# Check if the file called exists, if not terminate with message, "Not a valid filename."
if [ -f $file ] ; then
{

    # Begin loop to read data in GMSP file one piece at a time
    for f in $( cat $file ); do

        # Avoid writing box size (from GMSP) to output file
        if [ $flag -lt 5 ]; then
            flag=$(($flag+1))
            continue
        fi

        # Write number of atoms and "atom info" header to output file
        if [ $flag -eq 5 ]; then
            echo $f >> $file.new.pos
            echo " " >> $file.new.pos
            echo "# Atom type, Atom Coordinates, Atom occupancy" >> $file.new.pos
    fi

}
flag=$(($flag+1))
continue
fi

# Write "atom info" to output file. This keeps the GMSP information on the same line and
# appends "0 1" (ie same debye-waller factor and atom type)
if [ $count -eq 3 ]; then
  {
    echo $f " 0 1" >> $file.new.pos
    count=0
  }
else
  {
    if [ $flag -gt 5 ]; then
      count=$(($count+1))
      echo -n $f " " >> $file.new.pos
      fi
    fi
  }
fi
done

#-----------------------------------------------
# find box size
#-----------------------------------------------
flag=0
initial=0

# write last 3 columns to a temp file
awk '{print $2 " $3 " $4}' $file > awktemp

for b in $( cat awktemp ); do

  # Avoid writing box size (from GMSP) to output file
  if [ $flag -le 3 ]; then
    flag=$(($flag+1))
    continue
  fi

  if [ $initial -eq 0 ]; then
    max=$b
    min=$b
    initial=1
  else

  fi

done


if [ $(echo "$b < $min" | bc ) -eq 1 ]; then
    min=$b
fi
if [ $(echo "$b > $max" | bc ) -eq 1 ]; then
    max=$b
fi
done

box=$(echo "$max-$min+10" | bc )
cat $file.new.pos > awktemp
echo $box " " $box > $file.new.pos
echo " " >> $file.new.pos
cat awktemp >> $file.new.pos
rm awktemp
echo "Min: $min  Max: $max"

#----------------------------------------------------------------------
}
else
    echo "Not a valid filename. "
fi
B.6 autoinput

# This file will read a file called "dat" one string at a time, and use those
#  strings as input for the program "question" one at a time until all strings
#  in "dat" have been used.

for f in $( cat dat ); do
  echo $f | ./question
done
B.7 crystalsubtraction

# This script will take a crystal structure calculated from the GMSP program
# and subtract the atomic coordinates from a second crystal structure that
# was created using the GMSP program. Output file is .XYZ for visualization.

clear

echo -n "Did you want the surface atom (0) or core atom (1) coordinates? "
read choice

echo -n "What did you want the output file to be named? "
read out

if [ -f $out ]; then
  rm $out
fi

echo -n "What is the filename of crystal you want to start with? "
read crys1

echo -n "What is the filename of the crystal you want to subtract? "
read crys2

echo -n "What did you want your cutoff to be (in Angstroms)? "
read cutoff

box1flag=0
box2flag=0
counter1=0
counter2=0
box1=0
box2=0

#-----------------------------------------------------------------------
function BoxAtoms
{
  awk '{print $2}' $file > temp
  boxflag=0
  for data in $( cat temp ); do
    if [ $boxflag -eq 0 ]; then
      boxflag=$((boxflag+1))
  done
  boxflag=0
  for data in $( cat temp ); do
    if [ $boxflag -eq 0 ]; then
      boxflag=$((boxflag+1))
  done
}

...
```bash
box=$data
continue
fi

if [ $boxflag -eq 1 ]; then
    atoms=$data
    break
fi
done

rm temp
}

#------------------------------------------------------------------------

function Shift
{
    # Finds the distance needed to move the first crystal to the center of
    # the second crystal

    move=$(echo "scale=6; ($box1-$box2)/2" | bc)
}

#------------------------------------------------------------------------

function Xcompare
{
    # Compares the first x, y, and z-coordinates of crys2 with crys1 and creates an XYZ
    # output.

    flag0=0
    flag=0
    count0=0
    count=0
    removed=0

    # start checking coordinates
    for c1 in $( cat $crys1 ); do

        # skip useless information
        if [ $flag0 -le 5 ]; then
            flag0=$(($flag0+1))
            continue
        fi

```
if [ $count0 -eq 0 ]; then
count0=$(($count0+1))
continue
fi

if [ $count0 -eq 1 ]; then
x1=$c1
count0=$(($count0+1))
continue
fi

if [ $count0 -eq 2 ]; then
y1=$c1
count0=$(($count0+1))
continue
fi

if [ $count0 -eq 3 ]; then
z1=$c1
count0=0
fi

flag=0
count=0

#skip useless information
for c2 in $( cat $crys2 ); do
if [ $flag -le 5 ]; then
flag=$(($flag+1))
continue
fi

if [ $count -eq 0 ]; then
count=$(($count+1))
continue
fi

if [ $count -eq 1 ]; then
x2=$c2
count=$(($count+1))
continue
fi

if [ $count -eq 2 ]; then
y2=$c2
count=$(($count+1))
continue
fi

if [ $count -eq 3 ]; then
    z2=${c2}
count=0
fi

# difference=1 if true, 0.001 is a reasonable
difference=$(echo "scale=6; (sqrt(($x1-($move)-($x2))^2+($y1-($move)-($y2))^2+($z1-($move)-($z2))^2) <= $cutoff)" | bc)

if [ $difference -eq 1 ]; then
    removed=$((removed+1))
break
fi
done

# save values to Removed if not within cutoff
if [ $difference -eq $choice ]; then
echo "1 $x1 $y1 $z1" >> temp
fi
done

# Assign box size and atom counts
file=$crys1
BoxAtoms
box1=$box
atom1=$atoms

file=$crys2
BoxAtoms
box2=$box
atom2=$atoms

Shift
Xcompare
if [ $choice -eq 0 ]; then
    echo "Crystal 2 had $atom2 atoms and $removed atoms in Crystal 1 were identified within "
    echo " $cutoff Angstroms of these atoms and removed. Your shell is "
    $(echo "$atom1-$removed" | bc) " atoms."
fi

if [ $choice -eq 1 ]; then
    echo "Your core consists of $removed atoms"
fi

# create output file
if [ $choice -eq 0 ]; then
    echo $(echo "$atom1-$removed" | bc) > $out.xyz
else
    echo $removed > $out.xyz
fi
echo "" >> $out.xyz
cat temp >> $out.xyz
rm temp

echo "done"
B.8 cubic

# This program will create a cubic system in .xyz coordinates based on the
# parameters input.
# ---------------------------------------------------

echo -n "What did you want to call the output file? "
read out

echo -n "What is the lattice constant (in Angstroms) of the system? 
read lattice

echo -n "How big is the crystal in the x direction (nm)? 
read x

echo -n "How big is the crystal in the y direction (nm)? 
read y

echo -n "How big is the crystal in the z direction (nm)? 
read z

echo "Creating crystal..."

flagx=0
flagy=0
flagz=0
coordx=0
coordy=0
coordz=0
count=0
echo " " > cubictemp

#----------------------------------------------------------
# Find coordinates and write to temp file
#----------------------------------------------------------

while [ "$flagx" != "1" ]; do
  if [ $(echo "scale=6; ($coordx/10) > ($x)" | bc) -eq 1 ]; then
    flagx=1
  else
    while [ "$flagy" != "1" ]; do
      if [ $(echo "scale=6; ($coordy/10) > ($y)" | bc) -eq 1 ]; then
        flagy=1
      fi
    done
  fi
done
else
  while [ "$flagz" != "1" ]; do
    if [ $(echo "scale=6; ($coordz/10) > ($z)" | bc) -eq 1 ]; then
      flagz=1
    else
      echo "$coordx $coordy $coordz" >> cubictemp
      coordz=$(echo "$coordz+$lattice" | bc)
      count=$(($count+1))
    fi
  done
  flagz=0
  coordz=0
  coordy=$(echo "$coordy+$lattice" | bc)
  fi

done
flagy=0
flagz=0
coordy=0
coordz=0
coordx=$(echo "$lattice+$coordx" | bc)

fi

done

#---------------------------------
# Write output file
#---------------------------------

echo $count > $out
cat cubictemp >> $out
rm cubictemp
B.9 fcc

# This program will calculate the atomic positions of atoms in a roughly spherical structure which has fcc packing. Required inputs are the lattice parameter, the sphere radius and the name of the output file.

# Parameter initialization
# *note: all distances should be in the same units

#!/bin/bash

radius=0          # radius of the nanoparticle
a=0               # lattice parameter
out=out           # name of output file
count=0           # number of atomic sites
x=0               # x-coordinate of atom
y=0               # y-coordinate of atom
z=0               # z-coordinate of atom
flag1=0           # flag for whether or not to use xloop function
flag2=0           # flag for whether or not to use yloop function
flag3=0           # flag for whether or not to use zloop function
r=0               # variable returned to calling program

# Functions

function xloop
{
    if [ $flag1 != 0 ]; then
        r=$(echo "($a*$x)^2 <= $radius^2" | bc)
# if satisfied continue
        return $r
    else
        flag1=1
        return 1
    fi
}

function yloop
```bash
if [ $flag2 != 0 ]; then
    r=$(echo "($a^2*($x^2 + $y^2)) <= $radius^2" | bc)  # if satisfied continue
    return $r
else
    flag2=1
    return 1
fi

function zloop
{
    if [ $flag3 != 0 ]; then
        r=$(echo "($a^2*($x^2 + $y^2 + $z^2)) <= $radius^2" | bc)    # if satisfied
        continue
        return $r
    else
    flag3=1
    return 1
fi
}

function first
{
    # output values in first octant and include site in count
    count=$(($count+1))
    echo -n "$(echo "$a*$x" | bc), "
    echo -n "$(echo "$a*$y" | bc), "
    echo "$(echo "$a*$z" | bc)"
}

function second
{
    # output values in second octant and include site in count
    if [ $x != 0 ]; then
        count=$(($count+1))
        echo -n "$(echo "-$a*$x" | bc), "
        echo -n "$(echo "$a*$y" | bc), "
        echo "$a*$z" | bc"
    fi
}

function third
{
```
# output values in third octant and include site in count
if [ $x != 0 ]; then
  if [ $y != 0 ]; then
    count=$(($count+1))
    echo -n "$(echo -$a*$x | bc), "
    echo -n "$(echo -$a*$y | bc), "
    echo "$(echo -$a*$z | bc)"
  fi
fi

function fourth
{
  # output values in the fourth octant and include site in count
  if [ $y != 0 ]; then
    count=$(($count+1))
    echo -n "$(echo $a*$x | bc), "
    echo -n "$(echo -$a*$y | bc), "
    echo "$(echo $a*$z | bc)"
  fi
}

function fifth
{
  # output values in the fifth octant and include site in count
  if [ $z != 0 ]; then
    count=$(($count+1))
    echo -n "$(echo $a*$x | bc), "
    echo -n "$(echo $a*$y | bc), "
    echo "$(echo -$a*$z | bc)"
  fi
}

function sixth
{
  # output values in the sixth octant and include site in count
  if [ $z != 0 ]; then
    if [ $x != 0 ]; then
      count=$(($count+1))
      echo -n "$(echo -$a*$x | bc), "
      echo -n "$(echo $a*$y | bc), "
      echo "$(echo -$a*$z | bc)"
    fi
  fi
}

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function seventh
{
  # output values in the seventh octant and include site in count
  if [ $y != 0 ]; then
    if [ $z != 0 ]; then
      if [ $x != 0 ]; then
        count=$(($count+1))
        echo -n "$(echo "-$a*$x" | bc), "
        echo -n "$(echo "-$a*$y" | bc), "
        echo "$a*$z" | bc)"
      fi
    fi
  fi
}

function eighth
{
  # output values in the eigth octant and include site in count
  if [ $z != 0 ]; then
    if [ $y != 0 ]; then
      count=$(($count+1))
      echo -n "$a*$x", 
      echo -n "$a*$y", 
      echo "-$a*$z" | bc)"
    fi
  fi
}

function all
{
  # output atomic coordinates in all octants
  first >> $out
  second >> $out
  third >> $out
  fourth >> $out
  fifth >> $out
  sixth >> $out
  seventh >> $out
  eighth >> $out
}

#-----------------------------------------------------------------------
# Get the input data from the user
#-----------------------------------------------------------------------

echo -n "What would you like the output file to be named? "

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read out

echo -n "What is the radius of the sphere that you are interested in? (arbitrary units) "
read radius

echo -n "What is the fcc lattice parameter? (use same units as the radius) "
read a

clear

echo "The coordinates of the atoms in an fcc structure with a radius, $radius, and a lattice parameter, $a, are (x, y, z)" >> $out

#-------------------------------------------------- ---------------------
# Looping sequence to generate coordinates of corner atoms
#-------------------------------------------------- ---------------------
until xloop
  do
    until yloop
      do
        until zloop
          do
            all
            z=$(echo "$z+1" | bc)
          done
          z=0
          y=$(echo "$y+1" | bc)
        done
        y=0
        z=0
        x=$(echo "$x+1" | bc)
      done
  done
#-------------------------------------------------- ---------------------
# Looping sequence to generate coordinates of face atoms
#-------------------------------------------------- ---------------------
# Find atoms on the xy faces
#-------------------------------------------------- ---------------------
x=0.5
y=0.5
z=0
until xloop
do
till yloop
do
till zloop
do
all
z=$(echo "scale=6; $z + 1" | bc)
done
z=0
y=$(echo "scale=6; $y + 1" | bc)
done
y=0
z=0
x=$(echo "scale=6; $x + 1" | bc)
done

# Find atoms on the xz faces
#-------------------------------------------------- ---------------------
x=0.5
y=0
z=0.5
until xloop
do
till yloop
do
till zloop
do
all
z=$(echo "scale=6; $z + 1" | bc)
done
z=0.5
y=$(echo "scale=6; $y + 1" | bc)
done
y=0
z=0.5
x=$(echo "scale=6; $x + 1" | bc)
done
# Find atoms on the yz faces
#

x=0
y=0.5
z=0.5

until xloop
do
  until yloop
do
    until zloop
do
      all
      z=$(echo "scale=6; $z + 1" | bc)
done
  z=0.5
  y=$(echo "scale=6; $y + 1" | bc)
done
y=0.5
z=0.5
x=$(echo "scale=6; $x + 1" | bc)
done

echo "Total number of atomic sites in your particle: $count" >> $out
B.10 fccvmd

#-------------------------------------------------- ---------------------
# This program will calculate the atomic positions of atoms in a roughly
# spherical structure which has fcc packing and outputs data to a file
# in XYZ format (for visualization). Required inputs are the lattice
# parameter, the sphere radius and the name of the output file.
#-------------------------------------------------- ---------------------

#-------------------------------------------------- ---------------------
# Parameter initialization
# *note: all distances should be in the same units
#-------------------------------------------------- ---------------------

#!/bin/bash

atom=atom         # name of atom type
radius=0          # radius of the nanoparticle
a=0               # lattice parameter
out=out           # name of output file
count=0           # number of atomic sites
x=0               # x-coordinate of atom
y=0               # y-coordinate of atom
z=0               # z-coordinate of atom
flag1=0           # flag for whether or not to use xloop function
flag2=0           # flag for whether or not to use yloop function
flag3=0           # flag for whether or not to use zloop function
r=0               # variable returned to calling program

#-------------------------------------------------- ---------------------
# Functions
#-------------------------------------------------- ---------------------

function xloop
{
    if [ $flag1 != 0 ]; then
        r=$(echo "($a*$x)^2 <= $radius^2" | bc)
        # if satisfied continue
        return $r
    else
        flag1=1
        return 1
    fi
}

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function yloop
{
    if [ $flag2 != 0 ]; then
        r=$(echo "($a^2*($x^2 + $y^2)) <= $radius^2" | bc) # if satisfied continue
        return $r
    else
        flag2=1
        return 1
    fi
}

function zloop
{
    if [ $flag3 != 0 ]; then
        r=$(echo "($a^2*($x^2 + $y^2 + $z^2)) <= $radius^2" | bc) # if satisfied
        continue
        return $r
    else
        flag3=1
        return 1
    fi
}

function first
{
    # output values in first octant and include site in count
    count=$(($count+1))
    echo -n "$atom " "$(echo "$a*$x" | bc) "
    echo -n "$(echo "$a*$y" | bc) "
    echo "$(echo "$a*$z" | bc)"
}

function second
{
    # output values in second octant and include site in count
    if [ $x != 0 ]; then
        count=$(($count+1))
        echo -n "$atom " "$(echo "-$a*$x" | bc) "
        echo -n "$(echo "$a*$y" | bc) "
        echo "$(echo "$a*$z" | bc)"
    fi
}

function third
{
  # output values in third octant and include site in count
  if [ $x != 0 ]; then
    if [ $y != 0 ]; then
      count=$(($count+1))
      echo -n "$atom " "$(echo "-$a*$x" | bc) "
      echo -n "$(echo "-$a*$y" | bc) "
      echo "$(echo "$a*$z" | bc)"
    fi
  fi
}

function fourth
{
  # output values in the fourth octant and include site in count
  if [ $y != 0 ]; then
    count=$(($count+1))
    echo -n "$atom " "$(echo "$a*$x" | bc) "
    echo -n "$(echo "-$a*$y" | bc) "
    echo "$(echo "$a*$z" | bc)"
  fi
}

function fifth
{
  # output values in the fifth octant and include site in count
  if [ $z != 0 ]; then
    count=$(($count+1))
    echo -n "$atom " "$(echo "$a*$x" | bc) "
    echo -n "$(echo "$a*$y" | bc) "
    echo "$(echo "-$a*$z" | bc)"
  fi
}

function sixth
{
  # output values in the sixth octant and include site in count
  if [ $z != 0 ]; then
    if [ $x != 0 ]; then
      count=$(($count+1))
      echo -n "$atom " "$(echo "-$a*$x" | bc) "
      echo -n "$a*$y" | bc) "
      echo "$(echo "-$a*$z" | bc)"
    fi
  fi
}

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function seventh
{
    # output values in the seventh octant and include site in count
    if [ $y != 0 ]; then
        if [ $z != 0 ]; then
            if [ $x != 0 ]; then
                count=$(($count+1))
                echo -n "$atom " "$(echo "-$a*$x" | bc) "
                echo -n "$(echo "-$a*$y" | bc) "
                echo "$(echo "-$a*$z" | bc)"
            fi
        fi
    fi
}

function eighth
{
    # output values in the eigth octant and include site in count
    if [ $z != 0 ]; then
        if [ $y != 0 ]; then
            count=$(($count+1))
            echo -n "$atom " "$(echo "$a*$x" | bc) "
            echo -n "$(echo "-$a*$y" | bc) "
            echo "$(echo "-$a*$z" | bc)"
        fi
    fi
}

function all
{
    # output atomic coordinates in all octants
    first >> $out
    second >> $out
    third >> $out
    fourth >> $out
    fifth >> $out
    sixth >> $out
    seventh >> $out
    eighth >> $out
}

#---------------------------------------------------------------
# Get the input data from the user
#---------------------------------------------------------------
echo -n "What type of atoms are you looking at? "
read atom

echo -n "What would you like the output file to be named? "
read out

echo -n "What is the radius of the sphere that you are interested in? (arbitrary units) "
read radius

echo -n "What is the fcc lattice parameter? (use same units as the radius) "
read a

clear

#-------------------------------------------------- ---------------------
# Looping sequence to generate coordinates of corner atoms
#-------------------------------------------------- ---------------------

until xloop
do
  until yloop
do
    until zloop
do
      all
      z=$(echo "$z+1" | bc)
done
  z=0
  y=$(echo "$y+1" | bc)
done
y=0
z=0
x=$(echo "$x+1" | bc)
done

#-------------------------------------------------- ---------------------
# Looping sequence to generate coordinates of face atoms
#-------------------------------------------------- ---------------------

#-------------------------------------------------- ---------------------
# Find atoms on the xy faces
#-------------------------------------------------- ---------------------
x=0.5
y=0.5
z=0

until xloop
do  
  until yloop
do  
    until zloop
do  
      all
        z=$(echo "scale=6; $z + 1" | bc)
done
    z=0
    y=$(echo "scale=6; $y + 1" | bc)
done
  y=0
  z=0
x=$(echo "scale=6; $x + 1" | bc)
done

#-------------------------------------------------- ---------------------
# Find atoms on the xz faces
#-------------------------------------------------- ---------------------

x=0.5
y=0
z=0.5

until xloop
do  
  until yloop
do  
    until zloop
do
      all
        z=$(echo "scale=6; $z + 1" | bc)
done
    z=0.5
    y=$(echo "scale=6; $y + 1" | bc)
done
  y=0
  z=0.5
x=$(echo "scale=6; $x + 1" | bc)
done
# Find atoms on the yz faces
#
#
x=0
y=0.5
z=0.5
#
until xloop
  do
    until yloop
      do
        until zloop
          do
            all
              z=$(echo "scale=6; $z + 1" | bc)
          done
          z=0.5
        y=$(echo "scale=6; $y + 1" | bc)
      done
      y=0.5
    z=0.5
  x=$(echo "scale=6; $x + 1" | bc)
done
#
# Output the total number of atoms at the top of the file
#
echo $count >> $out.tmp
echo >> $out.tmp
cat $out >> $out.tmp
mv $out.tmp $out
B.11 gmsp2vmd

# This script takes the output file from GMSP and turns it into an input file
# for vmd. This
# assumes that there is only one type of atom in the structure.
#
# Output file is: "file".xyz

# Ask the user for the GMSP file
echo -n "What is the name of the file you want to alter? "
read file

# Flags to exclude extraneous information at beginning of output and to keep required
# (ie atom type and position) on same line.
flag=0
count=0

# Remove any output file previously associated with this name to avoid simply
# appending to an existing
# file of the same name.
if [ -f $file.xyz ]; then
    rm $file.xyz
fi

# Check if the file called exists, if not terminate with message, "Not a valid filename."
if [ -f $file ]; then
    {
        # Begin loop to read data in GMSP file one piece at a time
        for f in $( cat $file ); do

            # Avoid writing box size (from GMSP) to output file
            if [ $flag -lt 5 ]; then
                flag=$(($flag+1))
                continue
            fi

            # Write number of atoms and "atom info" header to output file
            if [ $flag -eq 5 ]; then
                echo $f >> $file.xyz
                echo " " >> $file.xyz
                flag=$(($flag+1))
                continue
            fi

        done
    }
fi
# Write "atom info" to output file. This keeps the GMSP information on the same line and
if [ $count -eq 3 ]; then
  {
    echo $f >> $file.xyz
    count=0
  }
else
  {
    if [ $flag -gt 5 ]; then
      count=$(($count+1))
      echo -n $f ' ' >> $file.xyz
      fi
    }
  fi
done
} else
  echo "Not a valid filename. "
fi
B.12 multipossibilities

# multipossibilities
#---------------------------------------------------------------
# This script will calculate the different possible combinations
# for a given intensity based on the parameters entered.
# I.e. number of each type of atom.
#---------------------------------------------------------------

echo "What would you like the output file to be called?"
read out

echo "What is the file with the maximum intensities measured?"
read maxs

echo "What is the ratio of intensities for atom a:b ?"
read ratio

echo "What is the intensity of atom a?"
read singlea

#---------------------------------------------------------------
# Start calculating the different integer possibilities
#---------------------------------------------------------------

echo "Combined file:" > $out

dec=0

for data in $( cat $maxs ); do
dec=$(($dec+1))
echo "   a         b       (Possible solutions)" > mtemp.$dec
echo "-------  --------" >> mtemp.$dec

a=$(echo "scale=6; $singlea" | bc )
b=$(echo "scale=6; $singlea / $ratio" | bc )

finish1=$(echo "scale=6; $data/$a + 1" | bc )
finish2=$(echo "scale=6; $data/$b + 1" | bc )

one=0
two=0
counta=0
countb=0

if [ $(echo "$a > $b" | bc) -eq 1 ]; then
    min=$b
else
    min=$a
fi

echo "Calculating for intensity =$data... (this could be awhile)"

until [ "$(echo "scale=6; $counta > $finish1" | bc)" = "1" ]; do
two=0
countb=0

until [ "$(echo "scale=6; $countb > $finish2" | bc)" = "1" ]; do
total=$(echo "scale=6; $one+$two" | bc)
check=$(echo "scale=6; (($data-$total) > (-($min*0.5))) && \n((data-$total) < (0.5*$min))" | bc)
if [ $check -eq 1 ]; then
    echo "$counta          $countb" >> mtemp.$dec
fi
two=$(echo "scale=6; $two+$b" | bc)
countb=$(($countb+1))
done
counta=$(($counta+1))
one=$(echo "scale=6; $one+$a" | bc)
done

echo " " >> $out
echo " " >> $out
echo "-----------------------------------------" >> $out
echo "File #$dec" >> $out
echo "-----------------------------------------" >> $out
cat mtemp.$dec >> $out
done

rn mtemp*
B.13 multizmult

# multizmult
#--------------------------------------------------
# This program reads a file which lists all of the input files you have
# and alters the entered .ms file to run all of the files in the list of
# filenames given. It saves the .adf file created using a .dat file
# as the .dat file extension changed to .adf.
#--------------------------------------------------

echo -n "What is the name of the .ms file? "
read msfile

echo -n "File with name of the different position (.dat) files? "
read positionfile

echo -n "Did you want to run adfimage on the files? (y=1, n=0) "
read execute

count=1

# find the current position file name
current=$(awk 'NR==3' $msfile)

# replace the position file name in the .ms file and run zmult
for f in $(cat $positionfile); do
  sed s/$current/$f/ $msfile > mtemp.$count
cat mtemp.$count > $msfile
current=$f
zmult $msfile wi
count=$(($count+1))
cat ${msfile%.ms}.adf > ${f%.dat}.adf

if [ $execute -eq 1 ]; then
  # assumes that the number of the output slice is the same as the
  # number of slices per MS calculation and a single crystal
  sliceoutput=$(awk 'NR==12' $msfile)
adfimage ${f%.dat}.adf $sliceoutput 1 1
fi
done
# let the user know that all files in their input file have been run
echo "The following files have had zmult run on them."
cat $positionfile

cat $positionfile

cat $positionfile

rm mtemp*
B.14 nm2ang

#-------------------------------------------------- ----------------------
# This script will take an .xyz file which has nm units and change the
# units to angstroms.
#-------------------------------------------------- ----------------------

echo -n "What is the filename you wish to convert? "
read filename

if [ -f $filename ]; then
    echo "Converting $filename..."

    skip=0
    flag=0

    for data in $(cat $filename); do
        # skip 1st line after reading once
        if [ $skip -eq 0 ]; then
            echo $data > $filename.ang.xyz
            echo " " >> $filename.ang.xyz
            skip=1
            continue
        fi

        # write coordinates to output file along with atom type
        if [ $flag -eq 0 ]; then
            echo -n "$data " >> $filename.ang.xyz
            flag=$(($flag+1))
            continue
        fi

        if [ $flag -le 2 ]; then
            echo "$(echo "$data*10 " | bc) " >> $filename.ang.xyz
            flag=$(($flag+1))
            continue
        fi

        if [ $flag -le 2 ]; then
            echo "$($(echo "$data*10" | bc)) " >> $filename.ang.xyz
            flag=0
            fi
        done
    else

echo "Input filename does not exist. Aborting."
fi
B.15 possibilities

# possibilities
#--------------------------------------------------------------
# This script will calculate the different possible combinations
# for a given intensity based on the parameters entered.
# I.e. number of each type of atom.
#--------------------------------------------------------------

echo "What would you like the output file to be called?"
read out

echo "What is the maximum intensity measured?"
read max

echo "What is the ratio of intensities for atom a:b ?"
read ratio

echo "What is the intensity of atom a?"
read singlea

#--------------------------------------------------------------
# Start calculating the different integer possibilities
#--------------------------------------------------------------

echo " a     b     (Possible solutions)" > $out
echo "------     ------" >> $out

a=$(echo "scale=6; $singlea" | bc)
b=$(echo "scale=6; $singlea / $ratio" | bc)

finish1=$(echo "scale=6; $max/$a + 1" | bc)
finish2=$(echo "scale=6; $max/$b + 1" | bc)

one=0
two=0
counta=0
countb=0

if [ $(echo "$a > $b" | bc) -eq 1 ]; then
  min=$b
else
  min=$a
fi
fi

echo "Calculating... (this could be awhile)"

until [ "$(echo "scale=6; $counta > $finish1" | bc )" = "1" ]; do
two=0
countb=0

until [ "$(echo "scale=6; $countb > $finish2" | bc )" = "1" ]; do
total=$(echo "scale=6; $one+$two" | bc )
check=$(echo "scale=6; (($max-$total) > ($min*0.5)) && 
        (($max-$total) < (0.5*$min)) " | bc )
if [ $check -eq 1 ]; then
  echo "$counta $countb" >> $out
fi
two=$(echo "scale=6; $two+$b" | bc )
countb=$(($countb+1))
done
counta=$(($counta+1))
one=$(echo "scale=6; $one+$a" | bc )
done
B.16 pw2xsf

# pw2xsf
#--------------------------------------------------------
# This script changes to the directory where XCrySDen is saved, and uses
# XCrySDen's pwo2xsf.sh and pwi2xsf.sh scripts to convert a PWscf output
# file to a .xsf file (readable by VMD).

place=$PWD

echo -n "Did you want to convert a PWscf: input file(1) or output file(2)? "
read choice

if [ "$choice" = "2" ]; then
  echo ""
  echo "What option did you want?"
  echo "(1) Extract the initial (i.e. input) ionic coordinates."
  echo "(2) Extract the latest estimation of ionic coordinates."
  echo "(3) Extract the optimized coordinates."
  echo "(4) Make an AXSF file for animation (i.e. extract all coordinates)."
  read operation
  case $operation in
    2) var="--latestcoor";;
    3) var="--optcoor";;
    4) var="--animxsf";;
    *) var="--inicoor";;
  esac
  echo $var
fi

echo -n "What is the filename you wish to convert? "
read file

cp $file $XCRYSDEN_TOPDIR/scripts/

cd $XCRYSDEN_TOPDIR/scripts/

if [ "$choice" = "2" ]; then
  ./pwo2xsf.sh $var $file > $file.xsf
else
  ./pwi2xsf.sh $file > $file.xsf
fi

mv $file.xsf $place
rm $XCRYSDEN_TOPDIR/scripts/$file

#cd $place

./xc_cleanscratch
B.17 vmd2xyz

# vmd2xyz
#-------------------------------------------------- --------------------------
# This program takes the .xyz output from vmd and removes the "created by
# VMD" header as well as replaces the atom type with "1". For batch convert
# use: ls *.xyz > file  to create a file with all .xyz files in it which
# will then be read by this script to do replacements on.
#-------------------------------------------------- --------------------------

echo -n "What string (e.g. H, Pd, etc) did you want to replace? "
read replace

echo -n "What string (e.g. 1, Pt, etc) would you like to replace it with? "
read new

echo "File with name of all inputs? "
read file

count=0

for f in $(cat $file); do
  count=$(($count+1))
  sed "s/generated by VMD/ /" $f > mtemp
  sed "s/$replace/$new/" mtemp > mtemp.$count
  cat mtemp.$count > $f
done
rm mtemp* dos2unix *
B.18 xyz2zmult

# xyz2zmult
#-------------------------------------------------- ---------------------
# This script will take the given number of .xyz files and create a large zmult file
# which assumes all of the atoms in the different .xyz files were different.
# The box size is calculated based on the maximum difference between the
# x, y, or z values (ie largest delta direction) and has a user defined base added
# to it to allow for space on the side of the crystal.

echo -n "What do you want to call the output file? "
read out

echo -n "How many .xyz files do you wish to combine? "
read howmany

echo -n "What spacing did you want on the side of the crystal (angstroms)? "
read space

#-------------------------------------------------- -----------------------------------
function get
{
# get the input files

count=0
until [ "$count" = "$howmany" ]; do
count=$(($count+1))
echo -n "Name of file $count? "
read file
cat $file > mtemp.$count
done
}

#-------------------------------------------------- -----------------------------------
function combine
{
# combine the input files

total=0
count2=0

# get the total number of atoms
until [ "$count2" = "$count" ]; do
count2=$(($count2+1))


for atom in $(cat mtemp.$count2); do
total=$(($total+$atomin))
    break
done
done
cat $out > mtempcoord
echo $boxx " " $boxy > $out
echo "" >> $out
echo $total >> $out
cat mtempcoord >> $out
}

# add all coordinates to output file, changing atom type from one file to the next

count3=0
tuntil [ "$count3" = "$count" ]; do
count3=$(($count3+1))
flag=0
skip=0
for coords in $(cat mtemp.$count3); do
    # skip 1st 1 line
    if [ $skip -eq 0 ]; then
        skip=1
        continue
    fi

    # write coordinates to output file along with atom type
    if [ $flag -eq 0 ]; then
        echo -n "$count3 " >> $out
        flag=$(($flag+1))
        continue
    fi

    # write coordinates to output file along with atom type
    if [ $flag -le 2 ]; then
        echo -n "$coords " >> $out
        flag=$(($flag+1))
        continue
    fi

    if [ $flag -le 2 ]; then
        echo -n "$coords " >> $out
        flag=$(($flag+1))
        continue
    fi
if [ $flag -eq 3 ]; then
echo "$coords 0 1" >> $out
flag=0
fi
done
done

#----------------------------------------------------------------------------------------

function boxfind
{
  boxx=$(echo "$maxx-(\$minx)" | bc )
  boxy=$(echo "$maxy-(\$miny)" | bc )
  # boxz=$(echo "$maxz-(\$minz)" | bc )
  # if [ $(echo "$boxx>$boxy" | bc ) -eq 1 ] && \n    # [ $(echo "$boxx>$boxz" | bc ) -eq 1 ]; then
    boxx=$(echo "$boxx+$space" | bc )
  # else
  # if [ $(echo "$boxy>$boxx" | bc ) -eq 1 ] && \n    # [ $(echo "$boxy>$boxz" | bc ) -eq 1 ]; then
    boxy=$(echo "$boxy+$space" | bc )
  # else
  box=$(echo "$boxz+$space" | bc )
  # fi
  # fi
}

#----------------------------------------------------------------------------------------

function maxmin
{
  awk '{print $2}' $out > mtempxcol
  awk '{print $3}' $out > mtempycol
  # awk '{print $4}' $out > mtempzcol
  skip=1

  # Find max and min x
  for look in $(cat mtempxcol); do
    if [ $skip -eq 1 ]; then
      skip=2
      continue
    fi
    if [ $skip -eq 2 ]; then
      minx=$look
      maxx=$look
      skip=3
    fi

    awk '{print $2}' $out > mtempxcol
    awk '{print $3}' $out > mtempycol
    # awk '{print $4}' $out > mtempzcol
    skip=1
  done
}

#----------------------------------------------------------------------------------------
continue
fi
if [ $(echo "$minx > $look" | bc) -eq 1 ]; then
    minx=$look
    continue
fi
if [ $(echo "$maxx < $look" | bc) -eq 1 ]; then
    maxx=$look
    continue
fi
done

skip=2

# find max and min y
for look in $(cat mtempycol); do
    if [ $skip -eq 2 ]; then
        miny=$look
        maxy=$look
        skip=3
        continue
    fi
    if [ $(echo "$miny > $look" | bc) -eq 1 ]; then
        miny=$look
        continue
    fi
    if [ $(echo "$maxy < $look" | bc) -eq 1 ]; then
        maxy=$look
        continue
    fi
done

#skip=2

# find max and min z
#for look in $(cat mtempzcol); do
#    if [ $skip -eq 2 ]; then
#        minz=$look
#        maxz=$look
#        skip=3
#        continue
#    fi
#    if [ $(echo "$minz > $look" | bc) -eq 1 ]; then
#        minz=$look
#        continue
#    fi
#    if [ $(echo "$maxz < $look" | bc) -eq 1 ]; then
#        maxz=$look
#        continue
#    fi
#done
# if [ $(echo "$maxz < $look" | bc) -eq 1 ]; then
#   maxz=$look
#   continue
# fi
#done

#----------------------------------------------------------------------------
# calling sequence
#----------------------------------------------------------------------------

echo "" > $out
get
echo "combining coordinates..."
coordinates
maxmin
echo "Finding box size..."
boxfind
combine
echo "$out has been written."
B.19 xyzcombine

# This script will take the given number of .xyz files and create a large .xyz file
# which assumes all of the atoms in the different .xyz files were different.

echo -n "What do you want to call the output file? "
read out

echo -n "How many .xyz files do you wish to combine? "
read howmany

# --------------------------------------------------------------
# get the input files

count=0
test ["$count" = "$howmany"]; do
  count=$(($count+1))
echo -n "Name of file $count? "
read file
cat $file > temp.$count
done

# --------------------------------------------------------------
# combine the input files

total=0
count2=0

# get the total number of atoms
until ["$count2" = "$count"]; do
  count2=$(($count2+1))
  for atomin in $(cat temp.$count2); do
    total=$(($total+$atomin))
    break
  done
done
echo $total > $out.xyz
echo "" >> $out.xyz

# --------------------------------------------------------------
# add all coordinates to output file, changing atom type from one file to the next

count3=0

until ["$count3" = "$count"]; do
  count3=$(($count3+1))

flag=0
skip=0
for coords in $(cat temp.$count3); do

  # skip 1st 1 line
  if [ $skip -eq 0 ]; then
    skip=1
    continue
  fi

  # write coordinates to output file along with atom type
  if [ $flag -eq 0 ]; then
    echo -n "$count3 " >> $out.xyz
    flag=$(($flag+1))
    continue
  fi

  if [ $flag -le 2 ]; then
    echo -n "$coords " >> $out.xyz
    flag=$(($flag+1))
    continue
  fi

  if [ $flag -eq 3 ]; then
    echo "$coords" >> $out.xyz
    flag=0
  fi
done
done

rm temp.*
B.20 xyzcrystalsubtraction

# This script will take an xyz crystal structure
# and subtract the atomic coordinates from a second xyz crystal structure.
# Output file is .XYZ for visualization. This script does NOT alter/move
# the coordinate centers to match - it assumes that you have positioned
# the input data as necessary.

echo -n "Did you want the surface atom (0) or core atom (1) coordinates? "
read choice

echo -n "What did you want the output file to be named? "
read out

if [ -f $out ]; then
  rm $out
fi

echo -n "What is the filename of crystal you want to start with? "
read crys1

echo -n "What is the filename of the crystal you want to subtract? "
read crys2

echo -n "What did you want your cutoff to be (in Angstroms)? "
read cutoff

counter1=0
counter2=0

#-----------------------------------------------------------------------
function BoxAtoms
{
  boxflag=1

  for data in $( cat $file ); do
    if [ $boxflag -eq 1 ]; then
      atoms=$data
      break
    fi
  done

}
function Xcompare
{
    # Compares the first x, y, and z-coordinates of crys2 with crys1 and creates an XYZ output.

    flag0=0
    flag=0
    count0=0
    count=0
    removed=0

    # start checking coordinates
    for c1 in $( cat $crys1 ); do

        # skip useless information
        if [ $flag0 -le 0 ]; then
            flag0=$(($flag0+1))
            continue
        fi

        if [ $count0 -eq 0 ]; then
            count0=$(($count0+1))
            continue
        fi

        if [ $count0 -eq 1 ]; then
            x1=$c1
            count0=$(($count0+1))
            continue
        fi

        if [ $count0 -eq 2 ]; then
            y1=$c1
            count0=$(($count0+1))
            continue
        fi

        if [ $count0 -eq 3 ]; then
            z1=$c1
            count0=0
            fi

    flag=0
}
count=0

#skip useless information
for c2 in $( cat $crys2 ); do
  if [ $flag -le 0 ]; then
    flag=$(($flag+1))
    continue
  fi

  if [ $count -eq 0 ]; then
    count=$(($count+1))
    continue
  fi

  if [ $count -eq 1 ]; then
    x2=$c2
    count=$(($count+1))
    continue
  fi

  if [ $count -eq 2 ]; then
    y2=$c2
    count=$(($count+1))
    continue
  fi

  if [ $count -eq 3 ]; then
    z2=$c2
    count=0
  fi

  # difference=1 if true, 0.001 is a reasonable start/guess
  difference=$(echo "scale=6; (sqrt(((x1)-(x2))^2+((y1)-(y2))^2+((z1)-(z2))^2)) <= $cutoff" | bc)

  if [ $difference -eq 1 ]; then
    removed=$(($removed+1))
    break
  fi

done

# save values to Removed if not within cutoff
if [ $difference -eq $choice ]; then
  echo "1 $x1 $y1 $z1" >> temp
fi

done

}

# Assign box size and atom counts
file=$crys1
BoxAtoms
atom1=$atoms

file=$crys2
BoxAtoms
atom2=$atoms

Xcompare

if [ $choice -eq 0 ]; then
  echo "Crystal 2 had $atom2 atoms and $removed atoms in Crystal 1 were identified within "
  echo "$cutoff" Angstroms of these atoms and removed. Your shell is "
  $(echo "$atom1-$removed" | bc) " atoms."
fi

if [ $choice -eq 1 ]; then
  echo "Your core consists of $removed atoms"
fi

# create output file
if [ $choice -eq 0 ]; then
  echo $(echo "$atom1-$removed" | bc) > $out.xyz
else
  echo $removed > $out.xyz
fi

echo "" >> $out.xyz
cat temp >> $out.xyz
rm temp

echo "done"
B.21 zdir

echo "Name the directory in which you would like to run zmult on all *.ms files."
read directory
if cd ~/$directory; then
cd ~/$directory
for f in *.ms; do
    zmult $f
done
else
    echo "Not a valid directory from your home directory."
fi
C.1. General Comments

These programs were developed with the goal of analyzing/manipulating different input data. In some cases it was for microscopy images, while other times it was meant to deal with the .xyz files for model structures. While the programs are designed to be run separately, many are interlinked in one way or another. For example, Multicall.m repeatedly calls AtomFinderCircular.m (it is implemented as a function) and combines the data. Similarly, AngleFinder.m uses the centroids found using one of the AtomFinder* programs. The best way to figure out what is needed is to look at what files the program is trying to read and which ones are produced. Since I was the only one using the programs, I did not implement a GUI for the various programs – meaning that the various parameters must be set in either the program code or as an input (when prompted), depending on the program.
C.2 AngleFinder.m

function [] = AngleFinder(x)

%-----------------------------------------------
% AngleFinder
%-----------------------------------------------
% This program attempts to find the angles between the centroids of
% species identified in the "Centroids_*" file.
% NOTE: This does NOT account for area swept out during search for
% particles at a given distance.
% Input variables:
% 1) image (centroids filename)
% 2) pixel size (nm)
% 3) desired cutoff distance for finding neighboring atom angles
%
% Outputs:
% 1) binned distribution of angles between centroids (image)
% 2) txt file containing angles found (in degrees)
%
% Possible future improvements:
% 1) Normalize histogram and rose plot
%
%-----------------------------------------------

% Get input data
imagein=imread(x);
calib=0.00664557;
cutoff=0.3; %cutoff distance in nm
radius=(round(cutoff/(calib))); %convert desired cutoff distance to pixels

% find centroids and mark on image
center = regionprops(imagein, 'centroid');
centroid = cat(1, center.Centroid);
figure, imshow(imagein,'DisplayRange',[])
hold on
plot(centroid(:,1), centroid(:,2), 'b*')
hold off

% display the number of atoms/centroids found
NumAtoms=size(centroid,1)

% convert to 3D vector for computational reasons (see below)
centroids=zeros(NumAtoms,3);
centroids(:,1)=centroid(:,1);
centroids(:,2)=centroid(:,2);

% create matrix to store angle values in
Angles=0;
count=0;

for (i=1:NumAtoms)
    for (j=1:NumAtoms)
        if ((i~=j) && (norm(centroids(i,:)-centroids(j,:))<radius))
            for (k=1:NumAtoms)
                if ((i~=k) && (j~=k) && (norm(centroids(i,:)-centroids(k,:))<radius))
                    count=count+1;
                    vector1=centroids(i,:)-centroids(j,:);
                    vector2=centroids(i,:)-centroids(k,:);
                    Angles(count)=(atan2(norm(cross(vector1,vector2)),dot(vector1,vector2)));
                    % find the angle between vectors
                    % Note: using atan2 is supposed to be better able to
                    % handle small angles but will only work with 3D
                    % vectors.
                end
            end
        end
    end
end

Angles1=Angles*180/pi; % convert angles from radians to degrees

% Plot histogram of angles
l=0; % define lower angle of histogram
u=180; % define upper angle of histogram
s=5; % define angle step size
r=l:s:u;
nbins=(u-l)/(s); % find the number of bins used
y(1,:)=hist(Angles1,r); % identify number of elements in each bin
y(2,:)=r;

% Create histogram and Rose plot of angles observed
figure
a=rose(Angles,36) % rose plot
b=get(a,'Xdata');
c=get(a,'Ydata');
d=patch(b,c,'b');
figure
hold on
hist(Angles1,r) \text{%histogram}
hold off

\text{% Create file names}
Name=regexp(x,'\.','split'); \text{%split input file name at the period to remove .tif}
AngleFile=sprintf('Angles\_%s.txt',Name{1}); \text{% txt file to store angles}

\text{% Open files for writing}
foutAngle=fopen(AngleFile,'w');

\text{% Write the information above to the output files}
fprintf(foutAngle, 'Angle (degrees):
');
fprintf(foutAngle, '%.4f
', Angles1);

\text{% Close files being written}
fclose(foutAngle);

end
C.3 AtomFinder3.m

%-------------------------------------------------- -----------------------
% Atom Finder3
%-------------------------------------------------- -----------------------
%
% This program attempts to find atoms by integrating over a (boxed)
% region that approximates the size of an atom (user input). I
%
%
% Input variables:
% 1) image
% 2) pixel size calibration (nm)
% 3) size an atom should appear (nm)
% 4) percentage above neighboring regions to qualify as an atom
%
% Future improvements:
% 1) change search to a circular area
% 2) color identified atom
% 3) include all the way to the edge in comparisons
%-------------------------------------------------- -----------------------
clc;
clear all;

% Get input data
imagein=input('What is the image that you would like to analyze? ', 's');
calib=0.0137791%0.00673645 %0.0137791; %calib1=input('How many nm is a pixel? ',
's'); %input('How many nm is a pixel? ', 's');
%calib=str2num(calib1);
atomsize=0.12; %input('Approximately how big should an atom be (nm)? ',
's');
%atomsize=str2num(atomsize1);
numstdevs=.75; %input('How many standard deviations from the background intensity is
an "atom"? (e.g. 10% = 0.1)', 's');
RangeThreshold=0.0; %input('What percentage of the maximum intensity do you wish to
exclude? (e.g. 10% of highest and lowest = 0.1)', 's');
FinalThreshold=0.0; %input('What percentage of the average intensity is the threshold?
(e.g. 10% = 0.1)', 's');
%threshold1=str2num(threshold1);
disp('Removing background...

%Set up parameters and matrices
image1=imread(imagein);
length=max(size(image1)); %find image size
boxlength=round(atomsize/calib); %find approximate box size of an atom
found=(zeros(length)); %matrix to store new image in
image(found);
for (i=1:length) %fill 'image' and 'found' matrices (eliminates color notations)
    for (j=1:length)
        image(i,j)=image1(i,j);
    end
end

%imageR1=(image>RangeThreshold*max(max(image))); %imageR2=(imageR1<(1-RangeThreshold)*max(max(image)));
%imageR3=imageR1.*imageR2;
%image=image.*imageR1;

%found=image;

%initialize values
boxsum=0;
above=0;
below=0;
right=0;
left=0;
scale=0;
stdmatrix=zeros(2,5); %matrix to hold mean of box, above, below, right, left, and their stdevs
surrounding=zeros(4,boxlength,boxlength);

%Start searching
for (i=1:length-boxlength+1) %scan image from top to bottom
    %initialize values
    boxsum=sum(sum(image(i:i+boxlength-1,boxlength:2*boxlength-1))); stdmatrix(1,1)=mean2(image(i:i+boxlength-1,boxlength:2*boxlength-1));
    stdmatrix(2,1)=std2(image(i:i+boxlength-1,boxlength:2*boxlength-1));
    if (i>boxlength)
        above=sum(sum(image(i-boxlength:i-1,boxlength:2*boxlength-1))); stdmatrix(1,2)=mean2(image(i:i+boxlength-1,boxlength:2*boxlength-1));
        stdmatrix(2,2)=std2(image(i:i+boxlength-1,boxlength:2*boxlength-1));
        surrounding(1,:,:)=image(i-boxlength:i-1,boxlength:2*boxlength-1);
    end
    if (i+2*boxlength-1<=length)
        below=sum(sum(image(i+boxlength:i+2*boxlength-1,boxlength:2*boxlength-1))); stdmatrix(1,3)=mean2(image(i+boxlength:i+2*boxlength-1,boxlength:2*boxlength-1));
        stdmatrix(2,3)=std2(image(i+boxlength:i+2*boxlength-1,boxlength:2*boxlength-1));
        surrounding(2,:,:)=image(i+boxlength:i+2*boxlength-1,boxlength:2*boxlength-1);
    end
    if (3*boxlength<=length)
        right=sum(sum(image(i:i+boxlength-1,2*boxlength:3*boxlength-1))); stdmatrix(1,4)=mean2(image(i:i+boxlength-1,2*boxlength:3*boxlength-1));
        stdmatrix(2,4)=std2(image(i:i+boxlength-1,2*boxlength:3*boxlength-1));
    end
end
stdmatrix(2,4)=std2(image(i:i+boxlength-1,2*boxlength:3*boxlength-1));
surrounding(3,:,:)=image(i:i+boxlength-1,2*boxlength:3*boxlength-1);
end
left=sum(sum(image(i:i+boxlength-1,1:boxlength)));  
stdmatrix(1,5)=mean2(image(i:i+boxlength-1,1:boxlength));
stdmatrix(2,5)=std2(image(i:i+boxlength-1,1:boxlength));
surrounding(4,:,:)=image(i:i+boxlength-1,1:boxlength);
for (j=boxlength:length-boxlength-1) %scan image from left to right starting with an offset of one boxlength
    if (j+boxlength-1<=length)
        %shift boxsum by one column to the right (subtract 1st column and %add one column to the end
        boxsum=boxsum+sum(image(i:i+boxlength-1,j+boxlength))-
        sum(image(i:i+boxlength-1,j));
        stdmatrix(1,1)=mean2(image(i:i+boxlength-1,j+1:j+boxlength));
        stdmatrix(2,1)=std2(image(i:i+boxlength-1,j+1:j+boxlength));
surrounding(1,:,:)=image(i-boxlength:i-1,j+1:j+boxlength);
        end
    if (i-boxlength>0 && j+boxlength-1<=length)
        %shift above by one column to the right (subtract 1st column and %add one column to the end, otherwise leave above alone.
        above=above+sum(image(i-boxlength:i-1,j+boxlength))-sum(image(i-boxlength:i-1,j));
        stdmatrix(1,2)=mean2(image(i-boxlength:i-1,j+1:j+boxlength));
        stdmatrix(2,2)=std2(image(i-boxlength:i-1,j+1:j+boxlength));
surrounding(2,:,:)=image(i-boxlength:i-1,j+1:j+boxlength);
        end
    if (i+2*boxlength-1<=length && j+boxlength-1<=length)
        %shift below by one column to the right (subtract 1st column and %add one column to the end, otherwise leave below alone.
        below=below+sum(image(i+boxlength:i+2*boxlength-1,j+boxlength))-sum(image(i+boxlength:i+2*boxlength-1,j));
        stdmatrix(1,3)=mean2(image(i+boxlength:i+2*boxlength-1,j+1:j+boxlength));
        stdmatrix(2,3)=std2(image(i+boxlength:i+2*boxlength-1,j+1:j+boxlength));
surrounding(2,:,:)=image(i+boxlength:i+2*boxlength-1,j+1:j+boxlength);
        end
    if (j+2*boxlength<=length)
        %shift right by one column to the right (subtract 1st column and %add one column to the end, otherwise leave right alone.
        right=right+sum(image(i:i+boxlength-1,j+boxlength))-sum(image(i:i+boxlength-1,j+2*boxlength));
        stdmatrix(1,4)=mean2(image(i:i+boxlength-1,j+boxlength+1:j+2*boxlength));
        stdmatrix(2,4)=std2(image(i:i+boxlength-1,j+boxlength+1:j+2*boxlength));
surrounding(3,:,:)=image(i:i+boxlength-1,j+boxlength+1:j+2*boxlength);
        end
    if (j-boxlength>0)
        %shift left by one column to the right (subtract 1st column and
% add one column to the end, otherwise leave left alone.
left = left + sum(image(i:i+boxlength-1,j:j)) - sum(image(i:i+boxlength-1,j-boxlength));

stdmatrix(1,5) = mean2(image(i:i+boxlength-1,j-boxlength+1:j));
stdmatrix(2,5) = std2(image(i:i+boxlength-1,j-boxlength+1:j));
surrounding(4,:,:)=image(i:i+boxlength-1,j-boxlength+1:j);
end

% amplify the region if its integrated intensity is above the
% 'numstdevs' criterion
maxavg = max(stdmatrix(1,2:5));
surroundingmean = mean(stdmatrix(1,2:5));
maxed = stdmatrix(1,2:5) + stdmatrix(2,2:5);
locate = maxed == max(maxed);
switch logical(true)
case {boxsum < RangeThreshold*max(max(image))*boxlength^2}
    continue; % ignore regional intensities above RangeThreshold
% case {(boxsum-above==0 && boxsum>=below && boxsum>=left &&
boxsum>=right) || ...
    % (boxsum-below==0 && boxsum>=above && boxsum>=left &&
boxsum>=right) || ...
    % (boxsum-left==0 && boxsum>=above && boxsum>=below &&
boxsum>=right) || ...
    % (boxsum-right==0 && boxsum>=above && boxsum>=below &&
left>=left)}
    scale = 1; % keep if >= neighbor(s)
case
    (mean2(surrounding)+numstdevs*std2(surrounding)) < stdmatrix(1,1) 
       & ... 
       & (stdmatrix(1,3)+numstdevs*stdmatrix(2,3))
       & ... 
       & (stdmatrix(1,5)+numstdevs*stdmatrix(2,5))

    scale = 1; % keep if outside numstdevs (check)
otherwise
    scale = 0;
end
for (k=1:boxlength) % scan box from top to bottom
for (l=1:boxlength) % scan box from left to right
    found(i+k-1,j+l) = found(i+k-1,j+l) + (boxsum/(boxlength^2))*scale; % adjust
box pixels to region average
    found(i+k-1,j+l) = found(i+k-1,j+l) + image(i+k-1,j+l)*scale
%le; % assign pixel intensity based on raw image
end
end
end
end
% apply FinalThreshold to "found" matrix
m=max(max(found));
t=found/m>FinalThreshold;
found2=t.*found;

figure, imshow(image, 'DisplayRange', [])
figure, imshow(found, 'DisplayRange', [])
figure, imshow(found2, 'DisplayRange', [])

% find display parameters and scale found for image saving
lowered=found-min(min(found)); % change to 0 to x
NewMax=max(max(lowered)); % find max ("x") value in lowered
ScaledFound=uint16(65535*lowered/(NewMax)); % normalize and convert to 16-bit
imwrite(ScaledFound,'BkgCorrected.tif');

% Find centroids and distances between atoms
%----------------------------------------------------------------------
% convert to black-and-white
found3 = im2bw(found2);

% find centroids and mark on image
location = bwlabel(found3);
center = regionprops(location, 'centroid');
centroids = cat(1, center.Centroid);
imshow(found3)
hold on
plot(centroids(:,1), centroids(:,2), 'b*')
hold off

% save image
imwrite(found3,'BkgCorrected2.tif');

% display the number of atoms/centroids found
NumAtoms=size(centroids,1)

% make a distance matrix
t=size(centroids,1);
z=(t*(t-1))/2;
distances=zeros(z,1);

% populate distance matrix
count=0;
for (i=1:t-1)
    for (j=i+1:t)
        count=count+1;
        distances(count,1)=((centroids(i,1)-centroids(j,1))^2+(centroids(i,2)-
        centroids(j,2))^2)^0.5*calib;
    end
end

% Plot histogram of distances
l=0.04;  %define lower limit of histogram
u=0.90; %define upper limit of histogram
s=0.02; %define histogram step size
x=l:s:u;
nbins=(u-l)/(s); %find the number of bins used
h1=distances(distances<u); %remove values above upper limit
h2=h1(h1>l); %remove values below lower limit
y=hist(h2,x); %identify number of elements in each bin
for (i=1:nbins+1)
    h3(i,1)=(i-1)*s+l;
    h3(i,2)=y(i)/(pi*((i*s+l)^2-((i-1)*s+l)^2)); %normalize number of occurrences to area
examed (arbitrary units)
end
h3(:,2)=h3(:,2)/max(h3(:,2)); %normalized h3 to maximum value
figure, bar(h3(:,1),h3(:,2)) %display histogram
title('Area Normalized Particle Frequency Histogram (PDF)')

% Open file for writing
fout=fopen('PairDistances.txt','w');

% Write the information above to the output file: "PairDistances.txt"
fprintf(fout, 'Pair Distances (nm):
');
fprintf(fout, '%.4f 
', distances);

% Close file being written
fclose(fout);
function [] =
AtomFinderFunctionCircular(x,calib,atomsize,cutoffpercentage,numstdevs,FinalStdev)

%-------------------------------------------------- -----------------------
% AtomFinderFunctionCircular
%-------------------------------------------------- -----------------------
%
% This program attempts to find atoms by integrating over a (circular)
% region that approximates the size of an atom (user input).
%
% Input variables:
% 1) image
% 2) pixel size calibration (nm)
% 3) size an atom should appear (nm)
% 4) standard deviation of final "found atoms" to be classed as an atom
% 5) distance cutoff to around atom for comparison
%
% Outputs:
% 1) .tif file after median filter and background removal
% 2) .tif file after last limiting criteria (for centroids)
% 3) .txt file of the pair distances from 3)
% 4) .txt of the pair distances within the bins defined and the area of
% those bins for each point (accounts for the edge of the image)
% 5) .tif of the structure showing the number of "atoms" in each column
% as determined by the lowest avg intensity found
%
% Possible future improvements:
% 1) remove background contribution from intensities
% 2) include all the way to the edge in comparisons
% 3) change from a function so it asks the user for input (deleted since
% a function)
% 4) implement min/max thresholds
% 5) use a different fitting function besides a gaussian for the atom
% and bkg regions (intensities won't be gaussian because of
% contributions from neighbors)
% 6) allow user to define (in function call)
% a) min/max bins for pdf distances
% 7) method of weighting and/or centroid determination
%
% Last edit: ~10-23-12
%-------------------------------------------------- -----------------------
% Get input data
imagein=x;
calib=0.0183721; %(15M); 0.0344477; %(8M); 0.00725802 %(25M); 0.0137791 (20M);
atomsize=0.11; % apparent size of atom in micrographs (usually ~75% of actual diameter)
cutoffpercentage=1.333; % percentage of atomsize which is considered the cutoff range beyond atomsize (1=100%)
umstdevs=0.75; % initial filter, usually best to go with a very low value to maximize items found
FinalStdev=1.9;%.25; % final filter. Number of stdevs below peak intensity to include.

% Set up parameters and matrices
image1=imread(imagein);
length=max(size(image1)); % find image size
found=(zeros(length)); % matrix to store new image in
image=found;
if (ndims(image1)==2) % fill 'image' matrix (eliminates color notations)
    image(:,:)=image1(:,:);
else
    image(:,:)=.2989.*image1(:,:,1)+.5870.*image1(:,:,2)+.1140.*image1(:,:,3);
end

% Convert given distances into pixel counts
radius=(round(atomsize/(2*calib)));
cutoff=(round(atomsize*(1+cutoffpercentage)/(2*calib))); % distance for cutoff from pixel of interest

% Use a median filter on the image
% image=medfilt2(image);

% Create a cartesian grid for referencing
[xx yy]=meshgrid(1:length);
disp('Removing background...')

% Create masks
RingMskMaster=sqrt((xx-cutoff-2).^2+(yy-cutoff-2).^2)<=cutoff & ...
    sqrt((xx-cutoff-2).^2+(yy-cutoff-2).^2)>radius; % create a mask for background around "atom" ("atom" = location to be compared)
AtomMskMaster=sqrt((xx-cutoff-2).^2+(yy-cutoff-2).^2)<=radius; % create a mask of the "atom"
RingMsk=RingMskMaster(1:2*cutoff+3,1:2*cutoff+3);
AtomMsk=AtomMskMaster(1:2*cutoff+3,1:2*cutoff+3);
Region=RingMskMaster(1:2*cutoff+3,1:2*cutoff+3);
count=0; %number of identifications made
stdvals=0; %initial set value
AtomArea=sum(sum(AtomMsk)); %find area of atom

%Start searching
for (i=cutoff+2:length-cutoff-2) %scan image from top to bottom
    for (j=cutoff+2:length-cutoff-2) %scan image from left to right
        Region=image(i-cutoff-1:i+cutoff+1,j-cutoff-1:j+cutoff+1);
        RingHold=nonzeros(Region.*RingMsk);
        RingMean=mean(RingHold);
        RingStd=std(RingHold);
        AtomHold=nonzeros(Region.*AtomMsk);
        AtomMean=mean(AtomHold);
        AtomStd=std(AtomHold);
        if (AtomMean>(RingMean+numstdevs*RingStd))
            %calculate overlap probability based on gaussian curves
            RingProb=0.5-erf((AtomMean-RingMean)/(RingStd*sqrt(2)))/2;
            AtomProb=0.5-erf((AtomMean-RingMean)/(AtomStd*sqrt(2)))/2;

            %record new image using and scale intensity (several options)
            %found(i-cutoff-1:i+cutoff+1,j-cutoff-1:j+cutoff+1)=...
            %    found(i-cutoff-1:i+cutoff+1,j-cutoff-1:j+cutoff+1)+...
            %    AtomMsk*(AtomProb/(RingProb+AtomProb)); %adjust box pixels
            %found(i-cutoff-1:i+cutoff+1,j-cutoff-1:j+cutoff+1)=...
            %    found(i-cutoff-1:i+cutoff+1,j-cutoff-1:j+cutoff+1)+...
            %    AtomMsk*(1-RingProb.^AtomArea);
            count=count+1; %number of identifications
            stdvals(count)=RingStd;
        end
    end
end

value=mean(stdvals);

% Find approximate gaussian profile for found intensities
UniqueFound=unique(found(found>0));
tempUnique=flipud(UniqueFound);
ToFit=cat(1,UniqueFound,tempUnique); %make intensity profile symmetric
p=polyfit((1:size(ToFit,1))', log(ToFit), 2); %fit ln of data to x^2 (since
gaussian~exp(x^2))
stddev=sqrt(-1/(2*p(1))); %stdev of data in terms of matrix cells
FitCenter=-(p(2)/(2*p(1))); %center of data in terms of matrix cells
%apply FinalStdev to "found" matrix
if ((FitCenter-stdev*FinalStdev)<1) %if the number of standard deviations would
   encompass all the data, do so (avoid negative cell references)
   range=1:round(FitCenter);
else
   range=round((FitCenter-stdev*FinalStdev)):round(FitCenter);
end

t=found>=min(ToFit(range));
found2=t.*found;

%figure, imshow(image, 'DisplayRange', [])
%figure, imshow(found, 'DisplayRange', [])
%figure, imshow(found2, 'DisplayRange', [])

%find display parameters and scale found for image saving
lowered=found-min(min(found)); %change to 0 to x
NewMax=max(max(lowered)); %find max ("x") value in lowered
ScaledFound=uint16(65535*lowered/(NewMax)); %normalize and convert to 16-bit

%-------------------------------------------------------------
% Find centroids and distances between atoms
%-------------------------------------------------------------

% convert to black-and-white and threshold to desired confidence level
found3 = im2bw(found2,0);

% find centroids
% %location = logical(found3); % shouldn't be needed
% center = regionprops(location, 'centroid');
% centroids = cat(1, center.Centroid);

% find the weighted centroids, weighting based on found2 intensities
center=regionprops(found3,found2,'WeightedCentroid');
centroids=cat(1,center.WeightedCentroid);

%figure, imshow(image,'DisplayRange',[])
%hold on
%plot(centroids(:,1), centroids(:,2), 'b*')
%hold off
%figure, imshow(found,'displayrange',[])
%figure, imshow(found2,'displayrange',[])
%figure, imshow(found3,'displayrange',[])

% display the number of atoms/centroids found
NumAtoms=size(centroids,1)

% make a matrix of pair distances
distances=pdist(centroids)*calib;

% Plot histogram of distances
l=0.05; %define lower limit of histogram
u=3.92; %define upper limit of histogram
s=0.03; %define histogram step size
x=l:s:u;
nbins=(u-l)/(s); %find the number of bins used
h1=distances(distances<u); %remove values above upper limit
h2=h1(h1>l); %remove values below lower limit
y(2,:)=hist(h2,x); %identify number of elements in each bin
y(1,:)=0; %initialize areas to zero

% Account for area examined (Pair distribution function)
for (i=1:size(centroids,1))
    BinEdge=0;
    for (j=1:nbins+1)
        BinEdge=BinEdge+s;
        Msk=sqrt((xx-centroids(i,1)).^2+(yy-centroids(i,2)).^2)<(BinEdge+s)/calib & ...
            sqrt((xx-centroids(i,1)).^2+(yy-centroids(i,2)).^2)>=(BinEdge/calib; %create mask
            y(1,j)=y(1,j)+nnz(Msk)*calib^2; %add area of ring to previous rings at same
distance
            % if i==30
            %   figure, imshow(Msk*max(max(image))/3+image,'DisplayRange',[])
            % end
    end
end

%for (i=1:nbins+1)
%    h3(i,1)=(i-1)*s+l; %start value in of each bin
%    h3(i,2)=y(2,i)/y(1,i); %normalize number of occurrences to area examined (arbitrary units)
%end

%h3(:,2)=h3(:,2)/max(h3(:,2)); %normalized h3 to maximum value
%figure, bar(h3(:,1),h3(:,2)) %display histogram
%title('Area Normalized Particle Frequency Histogram (PDF)')

%--------------------------------------------------
% Find approximate # of atoms in each column based on lowest intensity in
% image ("single" atom).
% Project original intensities onto locations identified
PrjIntensity = double(found3).*image;
ScaledIntensity = double(found3);

% Find Average intensity of each region and set region to that value
Regions = regionprops(bwlabel(PrjIntensity),PrjIntensity,'MeanIntensity','PixelIdxList');
for i=1:size(Regions,1)
    spots=Regions(i).PixelIdxList;
    meanI=Regions(i).MeanIntensity;
    ScaledIntensity(spots) = ScaledIntensity(spots).*meanI;
end

% Identify lowest mean intensity (i.e., find intensity of "single" atom)
% and normalize ScaledIntensity to this value (and round)
Single=min(Regions.MeanIntensity);
ScaledIntensity(:,:)=round(ScaledIntensity(:,:)/Single);
ScaledIntensity=uint16(ScaledIntensity); %convert to 16-bit for saving

% Create file names
Name=regexp(imagein,'.\','split'); %split input file name at the period to remove .tif
PairDists=sprintf('PairDist_%s.txt',Name{1}); % Pair distance txt file
BinAreas=sprintf('BinArea_%s.txt',Name{1}); % Bin area txt file
CentsLoc=sprintf('Centroids_Locations_%s.txt',Name{1}); %coordinates of centroids
Filtered=sprintf('Filtered_%s.tif',Name{1}); % Filtered image
Cents=sprintf('Centroids_%s.tif',Name{1}); %Centroid image
NumInCol=sprintf('Number_in_column_%s.tif',Name{1}); %ScaledIntensity image

% Save .tif files
imwrite(ScaledFound,Filtered);
imwrite(found3,Cents);
imwrite(ScaledIntensity,NumInCol);

% Open files for writing
foutPair=fopen(PairDists,'w');
foutAreas=fopen(BinAreas,'w');
foutCentsLoc=fopen(CentsLoc,'w');

% Write the information above to the output files
fprintf(foutPair, 'Pair Distances (nm):
');
fprintf(foutPair, '%.4fn', distances);

fprintf(foutAreas, 'Bin size (nm^2) \t Atoms in bin\n');
fprintf(foutAreas, '%.4f \t %.4f\n', y); %note matrix format allows this to save correctly

fprintf(foutCentsLoc, 'xy location of centroids\n');
c=centroids'; %change to a 2xn matrix to speed up storing
fprintf(foutCentsLoc, '%.6f \t %.6f\n', c); % matrix format allows correct saving

figure, imshow(image,'DisplayRange',[])
hold on
plot(centroids(:,1),centroids(:,2),'r.'
hold off
figure, imshow(found2);
figure, imshow(found);

end
C.5 AtomicCoordination.m

% ------------------------------------------------- ------------------------
% Atomic Coordination
% ------------------------------------------------- ------------------------
% This program will ask the user for an .xyz input file (note: this requires an .xyz file in
% the format: # # # #)
% and the desired cut-off radius to be considered coordinated.
% 
% 
% Mass output includes:
% 1) Average coordination
% 2) Number of atoms for each element
% 3) Variance in the bond distances <input cutoff for each element
% i.e. ~ the static Debye-Waller factor for the first nearest
% neighbor distance (note: holds a max of 12 coordinates.)
% 
% Individual output includes:
% 1) Atom type
% 2) xyz coordinates
% 4) Number of atoms coordinated
% 3) Number of same-type atoms coordinated

clear;

% Get input data
file = input('What is the name of the .xyz file that you wish to examine? ', 's');
radius = input ('What is the cut-off radius for something to be considered coordinated? ');

% Open file for writing
fout=fopen('AtomicCoordination.txt','w');

% Read in file and store into array
fin = fopen ( file, 'r' );
atoms = fscanf(fin, '%d', [1]);
data = fscanf(fin,'%d %f %f %f',[4 atoms]);
data=data';

% Close the file.
fclose ( fin );

%loop through all coordinates
%identify the element
%element: [atom type, # of atoms of same type in file, total atoms coordinated, like atoms coordinated]
temp= sort(data,'descend');
tempelement(1,1)=temp(1,1);

%Count the number of elements
n=1;
for (i=2:1:atoms)
    hold=n;
    if (tempelement(hold,1)~=temp(i,1))
        n=n+1;
        tempelement(n,1)=temp(i,1);
    end
end

%Initialize data storage array
element=zeros(atoms,6);
for (i=1:atoms)
    for (j=1:4)
        element(i,j)=data(i,j);
    end
end

%Find the how many of each element there are
howmany=zeros(n);
for (i=1:n)
    for (j=1:atoms)
        if (tempelement(i,1)==element(j,1))
            howmany(i)=(howmany(i)+1);
        end
    end
end

%Initialize arrays to store the variance (12 neighbors max) and R data
% variance(element, distance to <=13 atoms less than given cutoff)
% vardata(number of atoms of each type of element, sum(R), and sum(R^2)
variance=zeros(atoms,14);
vardata=zeros(n,3);

for (position=1:1:atoms)
    variance(position,1)=element(position,1);
    connection=1; % flag for number of elements bonded used in variance
    for (i=1:1:atoms)
%displacements (x, y, z) - note: this counts the atom too.
x2=(element(i,2)-element(position,2))^2;
y2=(element(i,3)-element(position,3))^2;
z2=(element(i,4)-element(position,4))^2;
%check distance
if ((x2+y2+z2)^.5<=radius)
  connection=connection+1;
  variance(position,connection)=(x2+y2+z2)^.5;
  element(position,5)=(element(position,5)+1);
  %identify and increment if it's the same type of element
  if (element(i,1)==element(position,1))
    element(position,6)=(element(position,6)+1);
  end
end
%remove self-counting
element(position,5)=(element(position,5)-1);
end
%identify and increment if it's the same type of element
if (element(i,1)==element(position,1))
  element(position,6)=(element(position,6)+1);
end
end
%remove self-counting
end
end
%populate vardata array with appropriate information
for(i=1:n)
  for (j=1:atoms)
    if (variance(j,1)==tempelement(i))
      for (k=1:13)
        if (variance(j,k+1)==0)
          vardata(i,1)=vardata(i,1)+1;
          vardata(i,2)=vardata(i,2)+variance(j,k+1);
          vardata(i,3)=vardata(i,3)+((variance(j,k+1))^2);
        end
      end
    end
  end
end
%Find average coordination number
tot=0;
for (i=1:atoms)
  tot=tot+element(i,5);
end
avg=tot/atoms;

% Output results
disp('See output file: AtomicCoordination.txt');

% Write the information above to the output file: "AtomicCoordination.txt"
fprintf(fout, 'Number of each atom type:
');
for (i=1:n)
    fprintf(fout, 'Element %d', tempelement(i));
    fprintf(fout, ': %d
', howmany(i));
end
fprintf(fout, 'Average coordination number in cluster: ');
fprintf(fout, '%.2f', avg);
fprintf(fout, 'Atom type, average bond length and variance in bond length
');
for (i=1:n)
    v=((vardata(i,3)/vardata(i,1))-(vardata(i,2)/vardata(i,1))^2); %find the variance
    r=(vardata(i,2)/vardata(i,1)); %find the average bond length
    fprintf(fout, 'Element: %d
', tempelement(i));
    fprintf(fout, 'Average bond length: %.6f
', r);
    fprintf(fout, 'variance: %.6f
', v);
end
fprintf(fout, 'Format:
Atom type; x y z coords; total coordination; same-element
coordination
');
for x=1:atoms
    fprintf(fout, '%d %.6f %.6f %.6f %d %d
', elemen t(x,1), element(x,2), element(x,3),
        element(x,4), element(x,5), element(x,6));
end
% Close output file
fclose(fout);
C.6 AverageCoordination.m

% This program will ask the user for an .xyz input file (note: this requires an .xyz file in the format: # # # #)
% and the desired cut-off radius to be considered coordinated.
%
% The output includes:
% 1) Number of atoms in the cluster
% 2) Average coordination of atoms in the cluster (if it was monometallic)
% 3) Element specific information:
%    a) Number of atoms of element type
%    b) Number of atom-atom coordinations between atoms of this element
%       (lower value => the element is more secluded)
%    c) Average coordination between atoms of this element
%    d) Number of atom-atom coordinations between this element type and other element types
%    e) Average coordination between this atoms of this element and atoms of different elements
%    f) Average coordination of this element to any type of element
%       (lower value => the element is more likely to reside on the surface/at low coordination sites)

clear;

% Get input data
file = input('What is the name of the .xyz file that you wish to examine? ', 's');
radius = input ('What is the cut-off radius for something to be considered coordinated? ');

% Open file for writing
fout=fopen('coordination.txt','w');

% Read in file and store into array
fin = fopen ( file, 'r' );
atoms = fscanf(fin, '%d', [1]);
[data, count] = fscanf(fin,'%d %f %f %f',[4 atoms]);
data=data';

% Close the file.
fclose ( fin );

%loop through all coordinates
%identify the element
%element: [atom type, # of atoms of same type in file, total atoms coordinated, like atoms coordinated]
temp= sort(data,'descend');
tempelement(1,1)=temp(1,1);
n=1;
for (i=2:1:atoms)
     hold=n;
     if (tempelement(hold,1)~=temp(i,1))
         n=n+1;
         tempelement(n,1)=temp(i,1);
     end
end

element=zeros(n,4);

for (i=1:n)
    %set first cell of element to element type
    element(i,1)=tempelement(i,1);
    for (j=1:atoms)
        %set second cell of element to the number of atoms of that type present
        %within the .xyz file
        if(element(i,1)==data(j,1))
            element(i,2)=element(i,2)+1;
        end
    end
end

for (c=1:n)
    %total number of atoms coordinated to atom type
    coordination=0;
    %total number of atoms
    tatoms=0;
    for (position=1:1:atoms)
        %if same element, identify atoms within specified cutoff that haven't
        %been checked yet
        flag=0;
        for (i=1:1:atoms)
            %displacements (x, y, z) - note: this counts the atom too.
            x2=(data(i,2)-data(position,2))^2;
            y2=(data(i,3)-data(position,3))^2;
            z2=(data(i,4)-data(position,4))^2;
            %check distance
            if(x2+y2+z2<=cutoff^2)
                flag=1;
            end
        end
        if(flag==0)
            nº
        end
    end
end
if ((x2+y2+z2)^.5<=radius)
    coordination=coordination+1;
% identify if it's the same type of element
if (data(i,1)==data(position,1))
    flag=flag+1;
end
end
% get total coordination for element of given type
if (((x2+y2+z2)^.5<=radius) && (data(position,1)==element(c,1)))
    element(c,3)=element(c,3)+1;
end
end
% number of like atoms coordinated, removing self-counting
if (data(position,1)==element(c,1))
    element(c,4)=element(c,4)+flag-1;
end
position=position+1;
tatoms=tatoms+1;
end

% correct for self-counting
coordination=coordination-tatoms;
element(c,3)=element(c,3)-element(c,2);
snumber=element(c,4);
dnumber=element(c,3)-snumber;

% output results
a1='';
a2=['Total number of atoms in cluster: ', num2str(tatoms)];
a3=['Average coordination of an atom in the cluster (ie as if monometallic): ', num2str(coordination/tatoms)];
b1='';
b2='Specific information...';
b3='';
c1=['Element: ', num2str(element(c,1))];
c2=['Number of atoms matching element type: ', num2str(element(c,2))];
c3=['Number of (like) atom-atom coordinations: ', num2str(snumber)];
c4=['The average coordination between like atoms of this type is: ', num2str(snumber/element(c,2))];
c5=['Number of other (unlike) atom-atom coordinations: ', num2str(dnumber)];
c6=['The average coordination of your element to unlike atoms is: ', num2str(dnumber/element(c,2))];
c7=['Average coordination of this element to any atom type: ', num2str(element(c,3)/element(c,2))];

% Display above information on screen
disp(a1)
disp(a2)
disp(a3)
disp(b1)
disp(b2)
disp(b3)
disp(c1)
disp(c2)
disp(c3)
disp(c4)
disp(c5)
disp(c6)
disp(c7)

% Write the information above to the output file: "coordination.txt"
fprintf(fout,'\n');
    fprintf(fout,a2);
    fprintf(fout,'\n');
    fprintf(fout,a3);
    fprintf(fout,'\n');
    fprintf(fout,b2);
    fprintf(fout,'\n');
    fprintf(fout,b3);
    fprintf(fout,'\n');
    fprintf(fout,c1);
    fprintf(fout,'\n');
    fprintf(fout,c2);
    fprintf(fout,'\n');
    fprintf(fout,c3);
    fprintf(fout,'\n');
    fprintf(fout,c4);
    fprintf(fout,'\n');
    fprintf(fout,c5);
    fprintf(fout,'\n');
    fprintf(fout,c6);
    fprintf(fout,'\n');
    fprintf(fout,c7);
    fprintf(fout,'\n');
end

% Close output file
fclose(fout);
function [] = Deformation(RefLocations,TestLocations,MinDistance,MaxDistance,calib)

% Deformation.m
%-------------------------------------------------- -----------------------
% This program takes 2 "Centroids_Locations_**" files produced by
% AtomFinderFunctionCircular.m and compares their locations based on the
% maximum and minimum pair distance values within the Distance range
% given. It also examines the coordination of each location based on these
% distances.
% Output:
% The "TestLocations" input is plotted with colors indicating the
% distance (maximum-minimum) for the distances between MinDistance and
% MaxDistance.
%
% Notes:
% 1) This implementation means that the user must define what are
% considered the cutoff distances.

%calib=0.0183721; %(15M); 0.0344477; %(8M); 0.00725802 %(25M); %0.0137791
%(20M);

% import files
RefIn=importdata(RefLocations);
TestIn=importdata(TestLocations);

if size(TestIn.data,2)==3 %if 3 columns, create matrix accordingly
    Test=TestIn.data;
    Test(:,2)=Test(:,3); %move y coordinates to second column
    Test(:,3)=0; %zero third column for difference storage
    Ref=RefIn.data;
    Ref(:,2)=Ref(:,3); %move y coordinates to second column
    Ref(:,3)=0; %zero third column
elseif size(TestIn.data,2)==2 %if 2 columns create matrix accordingly
    Test=zeros(size(TestIn.data,1),3);
    Test(:,1)=TestIn.data(:,1); %set x values
    Test(:,2)=TestIn.data(:,2); %set y values

Ref=zeros(size(RefIn.data,1),3);
Ref(:,1)=RefIn.data(:,1); %set x values
Ref(:,2)=RefIn.data(:,2); %set y values
else
disp('Error in input file format.');
return;
end

%Determine 2D distance matrix for Ref and Test matrices
StrainDistance=pdist2(Ref,Test);
TestStrain=Test;
for i=1:size(Test,1)
temp=StrainDistance(find((MinDistance/calib)<=StrainDistance(:,i) & StrainDistance(:,i)<=(MaxDistance/calib)),i);
if (isempty(temp))
    TestStrain(i,3)=0; %if no species within distance, set strain to zero
elseif (max(temp)==min(temp))
    TestStrain(i,3)=max(temp); %if only 1 strain value, set equal to that
else
    TestStrain(i,3)=max(temp)-min(temp);
end
end

%Determine 2D distance matrix for elements of Test matrix
CoordDistance=pdist2(Test,Test);
TestCoord=Test;
for j=1:size(Test,1)
temp=(find((MinDistance/calib)<=CoordDistance(:,j) & CoordDistance(:,j)<=(MaxDistance/calib)));
if (isempty(temp))
    TestCoord(j,3)=0; %in no species within cutoff distance, set equal to zero
else
    TestCoord(j,3)=size(find(temp>0),1);
end
end

%Save data
Name=regexp(TestLocations,'\.','split'); %split input file name at the period to remove .tif
StrainFile=sprintf('Strain_%s.txt',Name{1}); % Strain txt file
CoordFile=sprintf('Coordination_%s.txt',Name{1}); % Coordination txt file

% Open files for writing
foutStrain=fopen(StrainFile,'w');
foutCoord=fopen(CoordFile,'w');

% Write the information above to the output files
fprintf(foutStrain, sprintf('Strain between limits:  %.6f \t %.6f \n', MinDistance, MaxDistance));
fprintf(foutStrain, 'X-coord \t Y-coord \t Distance from ref \n');
for c=1:size(TestStrain,1)
    fprintf(foutStrain, '%.6f \t %.6f \t %.6f \n', TestStrain(c,:));
end

fprintf(foutCoord, sprintf('Coordination between limits:  %.6f \t %.6f \n', MinDistance, MaxDistance));
fprintf(foutCoord, 'X-coord \t Y-coord \t Coord \n');
for c=1:size(TestCoord,1)
    fprintf(foutCoord, '%.6f \t %.6f \t %.6f \n', TestCoord(c,:));
end
fclose('all');

% Plot data (assumes a 512x512 grid was used for raw image analyzed
StrainFig=zeros(512);
CoordFig=zeros(512);
for k=1:size(Test,1)
    x=TestStrain(k,1); %note x and y coordinates for strain and coord will be the same
    y=TestStrain(k,2); %note x and y coordinates for strain and coord will be the same
    zStrain=TestStrain(k,3);
    zCoord=TestCoord(k,3);
    StrainFig(round(x),round(y))=zStrain;
    CoordFig(round(x),round(y))=zCoord;
end

%orient image correctly
StrainFig=flipud(StrainFig');
CoordFig=flipud(CoordFig');

%make atoms locations bigger for viewing
StrainDilate=imdilate(StrainFig,strel('disk',4,4));
CoordDilate=imdilate(CoordFig,strel('disk',4,4));

figure, contourf(StrainDilate,'LineStyle','none');
title('Strain Figure');
colorbar;
figure, contourf(CoordDilate,'LineStyle','none');
title('Coordinate Figure');
colorbar;
end
C.8 Lineblur.m

% Program: lineblur.m
%---------------------------------------------------------------
% This program will take an input of a linescan and perform a gaussian
% convolution blur on it. Specifically, it will add the previous and next
% pixel to 2 times the current pixel and divide by 3. The user specifies
% the number of times to perform this convolution.
%---------------------------------------------------------------

% Get input file

file = input('What is the name of the file with the line scan data to be blurred? ', 's');
times = input('How many times did you want to perform this convolution? ');

data=load(file, 'v1');
temp=data;
length=size(temp,1);

for i=1:times
    % special treatment for first entry
    temp(1)=(1/3)*(2*temp(1)+temp(2));

    % convolute the main spectra
    for j=2:(length-1)
        temp(j)=(1/3)*(temp(j-1)+2*temp(j)+temp(j+1));
    end

    % special treatment for last entry
    temp(length)=(1/3)*(temp(length-1)+2*temp(length));
end

%save data
save('blur.txt','-ascii','-double','temp');
C.9 Multicall.m

% Multicall
%-------------------------------------------------- ------------------
% This program uses the user defined function on all .tif files. Both the
% function and files must be in the current folder.
%
% ------------------------------------------------- ------------------

% Find the .tif files in the folder
List=dir('Gewirth*.tif');
NumFiles=size(List,1); % count the number of .tif files found

% Run the function
%FunctName=input('What function would you like to use on the .tifs? ','s');
%hold=regexp(FunctName,'\','.','split'); % split function name at the period
%CallFunct=sprintf(hold{1}); % define the function name
for (i=1:NumFiles)
    FileName=List(i).name; % find the next file name
    eval('AtomFinderFunction(FileName)'); % run AtomFinderFunction.m function
end

% Find all 'BinArea*.txt' files
List2=dir('BinArea*.txt');
NumFiles2=size(List2,1); % count the number of BinArea*.txt files

% State the binning used in AtomFinderFunction.m
l=0.05; %lower bound
s=0.03; %step/increment size
u=0.92; %upper bound

% Create a compiled matrix of all bins and counts
Compiled=zeros((u-l)/s+1,3);

% Populated Compiled matrix
for (i=1:(u-l)/s+1)
    Compiled(i,1)=l+s*(i-1);
end
for (j=1:NumFiles2)
    CurrentFile=dlmread(List2(j).name,'%d', 1,0); % read BinArea*.txt into matrix (without header)
    Compiled(:,2)=Compiled(:,2)+CurrentFile(:,1);
    Compiled(:,3)=Compiled(:,3)+CurrentFile(:,2);
end
% Save final matrix to file
fout=fopen('Compiled Data.txt', 'w');
fprintf(fout, 'Bin (nm) \t Total Area (nm) \t Total counts \n');
fprintf(fout, ' %.4f \t %.4f \t %.4f', Compiled'); % Note: needed to transpose the
matrix to save properly
fclose('all'); % close all open files that might be hanging around
C.10 MulticallAngles.m

% Multicall Angles
%-------------------------------------------------- ------------------
% This program uses the user defined function on all 'Centroid.*' files. Both the
% function and files must be in the current folder.
% %
% % -----------------------------------------------

% Find the .tif files in the folder
List=dir('Centroid*.tif');
NumFiles=size(List,1); % count the number of 'Centroid*.tif' files found

% Run the function
for (i=1:NumFiles)
    FileName=List(i).name; % find the next file name
    eval('AngleFinder(FileName)'); % run AngleFinder.m function
end

% Find all 'Angles*.txt' files
List2=dir('Angles*.txt');
NumFiles2=size(List2,1); % count the number of Angles*.txt files

% State the binning used in AngleFinder.m
l=0; %lower bound
s=5; %step/increment size
u=180; %upper bound

% Populated Compiled matrix
Compiled=dlmread(List2(1).name,'%d',1,0);
Temp=Compiled;
for (j=2:NumFiles2)
    CurrentFile=dlmread(List2(j).name,'%d', 1,0); % read Angles*.txt into matrix (without
    % header)
    Temp=[Temp(:)' CurrentFile(:)'
end
Compiled=Temp';

% Save final matrix to file
fout=fopen('Compiled Angles.txt', 'w');
fprintf(fout, 'Angles 
');
fprintf(fout, '%.4f
', Compiled'); %Note: needed to transpose the matrix to save properly
fclose('all'); % close all open files that might be hanging around
% Final plots
% Create histogram and Rose plot of angles observed
figure
a=rose(Compiled*pi/180,36) %rose plot
b=get(a,'Xdata');
c=get(a,'Ydata');
d=patch(b,c,'b');
figure
hold on
hist(Compiled,1:s:u) %histogram
hold off
C.11 PairDistances.m

% This program will ask the user for an image input file, the pixel size in
% nm and the number of points to be selected. The resulting output file
% (PairDistances.txt) is the pair distances between all points selected.
%

clear;

% Get input information
file=input('What is the name of the file/image you want to analyze? ', 's');
pshold=input('What is the pixel size in nm? (ie calibration factor) ', 's');
%pthold=input('How many points will you be selecting? (Press "Enter" to terminate
early) ', 's');
%pt=str2num(pthold);
ps=str2num(pshold);

% Open file for writing
fout=fopen('PairDistances.txt','w');

% Open/show image for point selection
pic=imread(file);
image(pic);

% Get point coordinates and mark them as user selects them
disp('Left mouse button picks points.')
disp('Right mouse button picks last point and terminates analysis.')

b=1; % sets b to left mouse button click value.
pt=0;
hold on; % allows circles to be drawn on image so saving shows selected points

while b==1
    pt=pt+1;
    [x,y,b] = ginput(1);
    rectangle('Position',[x-1,y-1,3,3], 'Curvature', [1,1], 'FaceColor', 'r'); % draws a red circle
    around select point
    location(pt,1)=x;
    location(pt,2)=y;
end

hold off;
% Create storage array
distance=zeros((pt*(pt-1))/2,1);

% Find pair distances (in nm) and store them
position=0;
for i=1:pt-1
    for j=i+1:pt
        position=position+1;
        distance(position,1)=((location(i,1)-location(j,1))^2+(location(i,2)-location(j,2))^2)^0.5*ps;
    end
end

% Write the information above to the output file: "PairDistances.txt"
fprintf(fout, '
Pair Distances (nm):
');
fprintf(fout, '%.4f 
', distance);

% Close file being written
fclose(fout);
C.12 RIXSfunction.m

function RIXSfunction(file, contours)

%---------------------------------------------------------------
% RIXSfunction.m
%---------------------------------------------------------------
%
% Program to read in RIXS scans from ESRF and plot them.
%
% Input: Start of RIXS scan names.
% Number of contour lines to be drawn on RIXS plots
%
% Note: Data must all be of the same length, otherwise you may get a
% "dimension mismatch" type of error
%
% Plots:
% 1) Raw data
% 2) HERFD (only shows the result if max emission is monitored)
% 3) Data interpolated to a square grid and plotted with the elastic peak
% 4) RIXS plotted as energy transfer vs. incident energy
% 5) Integrated Energy Transfer
% 6) Integrated Incident Energy
% 7) HERFD (in progress)
%
%---------------------------------------------------------------

% Get data
%file = input('What do the files names all start with? ',s);
list = dir(fullfile(file,'*'));
number = size(list,1);

% Find out energy range scanned (by checking number of scans in scan 2)
fid = importdata(list(2).name);
rows = size(fid.data,1);

RIXS = zeros(3,rows,number-1);
y1 = zeros(1,number-1);

for (i = 1:number-1) % Ignore first entry (It didn't have a any results when this was made)
    readfile = importdata(list(i+1).name); % since default import, stores data (after header)
in 'data' field
    RIXS(1,:,i) = readfile.data(:,2); % record energies scanned per scan
RIXS(2,:,i) = readfile.data(:,4)./readfile.data(:,9); % normalize data (3rd channel value divided by 8th channel)
y1(i) = readfile.data(1,13); % record emission energy being monitored during scan
RIXS(3,:,i) = y1(i); % dE RIXS
end

% Find/Plot HERFD
[scanval scanrow]=max(sum(RIXS(2,:,i)));
HERFD=RIXS(2,:,scanrow);
figure();
plot(RIXS(1,:,scanrow),HERFD);
title(['HERFD along max emission energy: ' num2str(y1(scanrow)) ' keV']);
xlabel('Incident Energy (keV)');
ylabel('Intensity (arbitrary)');

% Plot RIXS
z1(:,:)=RIXS(2,:,i); % stores intensities in a matrix with rows=(# of Energy scans) and columns = (# of Emissions monitored) (not technically right, since E's aren't the same)
figure();
contour(RIXS(1,:,1),y1,z1',contours); % assumes little/no change in incident E for changing emission E
title('Data: Emission E vs. Incident E and HERFD Line');
xlabel('Energy (keV)');
ylabel('Emission Energy (keV)');
hold on
plot(RIXS(1,:,scanrow),y1(scanrow),'-k','LineWidth',10);
hold off

% Put all energies of scans into 1 matrix
tempx(1,:) = RIXS(1,:);
x = tempx(1,:);

% Put all measured intensities into 1 matrix
tempz(1,:) = RIXS(2,:);
z = tempz(1,:);

% Put all emissions monitored into 1 matrix
tempy(1,:) = RIXS(3,:);
y = tempy(1,:);

% Interpolate data to a uniform grid
xmin=min(x);
xmax=max(x);
ymin=min(y);
ymax=max(y);
xresolution=rows; % grid spacing
yresolution=xresolution; %grid spacing
xv=linspace(xmin, xmax, xresolution);
yv=linspace(ymin, ymax, yresolution);
[Xinterp, Yinterp]=meshgrid(xv,yv);
Zinterp=griddata(x,y,z,Xinterp,Yinterp);
% Record data for energy spacing of grid and start value
Xstep=(max(xv)-min(xv))/xresolution;
Ystep=(max(yv)-min(yv))/yresolution;
Xoffset=min(xv);
Yoffset=min(yv);

% Find (approximate) elastic peak
[MaxVals, MaxLoc]=max(Zinterp);
RowHold=(1:xresolution);
Fit=polyfit(RowHold,MaxLoc,1); % Fit xy grid location of max intensities to a second
order regression (y=m*x+b)
line=polyval(Fit,RowHold); % Find points to plot
figure();
plot(RowHold*Xstep+Xoffset,MaxLoc*Ystep+Yoffset,'.',RowHold*Xstep+Xoffset,line*
Ystep+Yoffset,'-r'); % Plot linear fit
title('Maximum Emission E vs. Incident E and Linear Fit');
xlabel('Energy (keV)');
ylabel('Emission Energy (keV)');
hold on
contour(Xinterp,Yinterp,Zinterp);
hold off

% Create RIXS graph with emission at zero
RIXS2=zeros(xresolution, yresolution);

RIXS2=RIXS2';

for (i=1:xresolution)
    for (j=1:yresolution)
        if (j<(round(Fit(1)*i+Fit(2))))
            RIXS2(j+(yresolution-(round(Fit(1)*i+Fit(2)))),i)=Zinterp(j,i)'
        end
    end
end

% Remove background using a linear fit across the emission data
%BkgRIXS2=zeros(xresolution);
%for (i=1:yresolution)
%    fitNan=RIXS2(i,find(~isnan(RIXS2(i,:)))); % make a matrix without Nan values
%    fity=fitNan(find(fitNan)); % remove all zero values from the matrix

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% fitx=size(fity,2);
% Bkg=polyfit(1:fitx,fity,1);
% BkgRIXS2(i,:)=RIXS2(i,:)-Bkg(2);
%end
%plot(flipud(BkgRIXS2),50);

% Plot spectra with decreased energy facing upward
figure();
contour((0:xresolution-1)*Xstep+Xoffset, (0:yresolution-1)*Ystep*1000, flipud(RIXS2), contours);
title('RIXS: E Transfer vs. Incident E');
xlabel('Energy (keV)');
ylabel('Energy Transfer (eV)');

% Integrate/sum energy transfer values for each incident energy
IET=zeros(1,xresolution);
for (i=1:xresolution) %edit subtracted value to exclude data
    IET(i)=sum(RIXS2(RIXS2(1:yresolution-20,i)>=0,i)); %specify range and cutoff values to sum
    IET(i)=IET(i)/(sum(RIXS2(1:yresolution-20,i)>0)); %normalize to the number of elements>0
end
%IET=smooth(IET,5);
figure();
plot((0:xresolution-1)*Xstep+Xoffset, IET);
title(['Constant Incident Energy ' num2str(Ystep*20*1000) ' eV above zero energy transfer']);
xlabel('Incident Energy (keV)');
ylabel('Intensity (arbitrary)');

% Integrate/sum incident energy values for each transfer energy
IIE=zeros(1,yresolution);
for (i=1:yresolution-20) %edit subtracted value to exclude data
    IIE(i)=sum(RIXS2(i,RIXS2(i,1:xresolution)<1)); %specify range and cutoff values to sum
    IIE(i)=IIE(i)/(sum(RIXS2(i,1:xresolution)>0)); %normalize to the number of elements>0
end
%IIE=smooth(IIE,5);
figure();
plot((0:yresolution-1)*Ystep*1000, fliplr(IIE));
title(['Constant Energy Transfer truncated at ' num2str(Ystep*20*1000) ' eV above zero energy transfer']);
xlabel('Energy Transfer (eV)');
ylabel('Intensity (arbitrary)');
% Save files
dlmwrite('Raw_RIXS.txt', flipud(z1'), 'delimiter', '\t', 'precision', 6);
dlmwrite('Shifted_RIXS.txt', RIXS2, 'delimiter', '\t', 'precision', 6);

% Combine all line scans into 1 matrix and save
Combined=[RIXS(1,:,scanrow); HERFD; ((0:xresolution-1)*Xstep+Xoffset); IET;
((0:yresolution-1)*Ystep*1000); fliplr(IIE)];
fid = fopen('Select_RIXS_Scans.txt','w');
fprintf(fid, 'HERFD E \t HERFD Intensity \t Constant Incident Energy \t CIE Intensity \t Constant Energy Transfer \t CET Intensity \n
')
fprintf(fid, '%.6f \t %.6f \t %.6f \t %.6f \t %.6f \t %.6f \n', Combined);
fclose(fid);

end
C.13 StructureDisorder.m

% This program will ask the user for an .xyz input file (note: this requires an .xyz file in the format: # # #), the desired level of disorder and the cutoff distance (min and max) for bonds.
% Currently only implemented for monometallic systems.
% Note, the basis of this is "AtomicCoordination.m" so some of the matricies have not been changed so as to allow for later integration of multimetallic systems.
%
%
% Mass output includes:
% 1) Structure
% 2) Variance in the bond distances <input cutoff for each element i.e. ~ the static Debye-Waller factor for the first nearest neighbor distance (note: holds a max of 30 coordinates.)
% 3) Histogram of distances
% 4) Average bond distance
%

clear all;

% Get input data
file = input('What is the name of the .xyz file that you wish to examine? ', 's');
radiusMin = input('What is the minimum cutoff distance for bonding? ');
radiusMax = input('What is the maximum cutoff distance for bonding? ');
disorder = input('What is the level of disorder you are trying to simulate? ');

% Set initial step size for atom movement
step=sqrt(disorder);

% Read in file and store into array
fin = fopen ( file, 'r' );
atoms = fscanf(fin, '%d', [1]);
[data, count] = fscanf(fin,'%d %f %f %f',[4 atoms]);
data=data';

% Close the file.

fclose ( fin );

element=zeros(6);
element(:,1:4)=data(:,1:4);

%Initialize data storage array
%Initialize arrays to store the variance (12 neighbors max) and R data
%   variance(element, distance to <=13 atoms less than given cutoff)
%   vardata(number of atoms of each type of element, sum(R), and sum(R^2)
variance=zeros(32);
vardata=zeros(1,3);

%Initialize flags to determine level of completion
finish=0;

%---------------------------------------------------------------------------
% Move atoms and find variance
%---------------------------------------------------------------------------

while (finish==0)

%Create random spherical displacements for all atoms centered on themselves
moveR(:,1)=random('Uniform',0,step,atoms,1);
movePhi(:,1)=random('Uniform',0,2*pi,atoms,1);
moveTheta(:,1)=random('Uniform',-pi/2,pi/2,atoms,1);

[x y z]=sph2cart(movePhi(:),moveTheta(:),moveR(:));

%Find variance of atoms
for (position=1:1:atoms)
    variance(position,1)=element(position,1);
    connection=1; % flag for number of elements bonded used in variance
    for (i=1:1:atoms)
        %displacements (x, y, z) - note: this counts the atom too.
        %check distance
        d = sqrt((element(i,2)-element(position,2))^2+...
            (element(i,3)-element(position,3))^2+...
            (element(i,4)-element(position,4))^2);
        if (d<=radiusMax && d>radiusMin)
            connection=connection+1;
        end
    end
end

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variance(position,connection)=d;
element(position,5)=(element(position,5)+1);
end
end

%remove self-counting - not included since any r>0 will remove self
%counting
%element(position,5)=(element(position,5)-1);
end

%populate vardata array with appropriate information
for (j=1:atoms)
  for (k=1:31)
    if (variance(j,k+1)~=0)
      vardata(1,1)=vardata(1,1)+1;
      vardata(1,2)=vardata(1,2)+variance(j,k+1);
      vardata(1,3)=vardata(1,3)+(variance(j,k+1))^2;
    end
  end
end

%Find average coordination number
tot=0;
for (i=1:atoms)
  tot=tot+element(i,5);
end
avg=tot/atoms;

% Find variance and average bond length
v=((vardata(1,3)/vardata(1,1))-(vardata(1,2)/vardata(1,1))^2)  %find the variance and
display on screen
r=(vardata(1,2)/vardata(1,1));  %find the average bond length

% Determine whether to continue (variance = disorder to 4 decimal places)
% and change step size if needed. This part can be made much more efficient by
% changing the convergence speed based on earlier runs.
if ((round(v*10^4))==round(disorder*10^4))
  finish=1;
elseif (round(v*10^4)>round(disorder*10^4))
  step = step/2;  %reduce step size
  element(:,1:4)=data(:,1:4);  %reset to initial coordinates and values
  element(:,5:6)=0;
  variance(:,2:14)=0;  % zero variance
  vardata(:,::)=0;  % zero vardata
elseif (round(v*10^4)<round(disorder*10^4))
  %increase step size by random amount to avoid infinite loop between
  %increasing and decreasing the step

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step = step*20*rand();
element(:,1:4)=data(:,1:4); %reset to initial coordinates and values
element(:,5:6)=0;
variance(:,2:14)=0; % zero variance
vardata(:,:,)=0; % zero vardata
end
end

%-----------------------------------------------------------------------------------------------
%-----------------------------------------------------------------------------------------------

% Output results

% Make histogram
x=radiusMin:0.1:radiusMax;
temp=variance(:,2:32);
y=sort(temp(find(temp)));
hist(y,x)
title(["Bond distances between ' num2str(radiusMin) ' and ' num2str(radiusMax) ' and a
DWF of ', num2str(disorder)]);
xlabel('Bond distance');
ylabel('Frequency');

disp('See output file: DisorderStructure.txt and DisorderVariance.txt');

% Open file for writing
fout=fopen('StructureDisorder.txt','w');

% Write the information above to the output file: "DisorderStructure.txt"
% fprintf(fout, 'Average bond length: ');
fprintf(fout, '%.6f
', r);
fprintf(fout, 'variance: ');
fprintf(fout, '%.6f
', v);

fprintf(fout, '
%d

', atoms);
for x=1:atoms
  fprintf(fout, '%d %.6f %.6f %.6f 
', element(x,1), element(x,2), element(x,3), element(x,4));
end

% Close output file
fclose(fout);
% Write information to "DisorderVariance.txt"
% Output format is the element with the next 31 entries being the bonding
% entries (used and unused) for that element
dlmwrite('DisorderVariance.txt', variance, 'delimiter', 't', 'precision', '%.6f');