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**Simulation Tools for Predicting the Atomic Configuration of Bimetallic
Catalytic Surfaces**

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**Simulation Tools for Predicting the Atomic Configuration of Bimetallic
Catalytic Surfaces**

by

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Simulation Tools for Predicting the Atomic Configuration of Bimetallic Catalytic Surfaces

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Transition metal alloys are an important class of materials in heterogeneous catalysis due in no small part to the often greatly enhanced activity and selectivity they exhibit compared to their monometallic constituents. A host of experimental and theoretical studies have demonstrated that, in many cases, these synergistic effects can be attributed to atomic-scale features of the catalyst surface. Realizing the goal of designing—rather than serendipitously discovering—new alloy catalysts thus depends on our ability to predict their atomic configuration under technologically relevant conditions. This dissertation presents original research into the development and use of computational tools to accomplish this objective.

These tools are all based on a similar strategy: For each of the alloy systems examined, cluster expansion (CE) Hamiltonians were constructed from the results of density functional theory (DFT) calculations, and then used in Metropolis Monte Carlo (MC) simulations to predict properties of interest.

Following a detailed description of the DFT+CE+MC simulation scheme, results for the AuPd/Pd(111) and AuPt/Pt(111) surface alloys are presented. These two systems exhibit considerably different trends in their atomic arrangement, which are explicable in terms of their interatomic interactions. In AuPd, a preference for heteronuclear, Au-Pd

interactions results in the preferential formation of Pd monomers and other small ensembles, while in AuPt, a preference for homonuclear interactions results in the opposite. AuPd/Pd(100) and AuPt/Pt(100) were similarly examined, revealing not only the effects of the same heteronuclear/homonuclear preferences in this facet, but also a propensity for the formation of second nearest-neighbor pairs of Pd monomers, in close agreement with experiment. Subsequent simulations of the AuPd/Pd(100) surface suggest the application of biaxial compressive strain as a means increasing the population of this catalytically important ensemble of atoms. A method to incorporate the effects of subsurface atomic configuration is also presented, using AuPd as an example. This method represents several improvements over others previously reported in the literature, especially in terms of its simplicity. Finally, we introduce the dimensionless scaled pair interaction, whereby the finite-temperature atomic configuration of any bimetallic surface alloy may be predicted from a small number of relatively inexpensive calculations.

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Chapter 1: Introduction

Heterogeneous catalysis is essential to an estimated 20% of all industrial output¹ and also plays a pivotal role in a host of current and emerging energy technologies such as polymer electrolyte membrane fuel cells^{2,3} and photocatalytic water splitting^{4,5}. Despite their prevalence, the mechanistic details of how particular catalysts actually work are frequently unknown, and the process of developing new catalysts remains costly and often owes as much to chance as it does to physical insight. Uncovering the principles that govern the catalytic properties of materials is thus an important research activity and a necessary first step toward the ultimate goal of designing new catalysts.

Transition metal alloys are one class of materials that has garnered enormous attention in this regard. Alloys often exhibit catalytic properties that are remarkably superior to those of their pure constituent metals, suggesting the enticing possibility of improving or even creating entirely new functionality in metal catalysts by purposefully altering their composition.

A combination of experimental and theoretical efforts has shown that in many cases, the enhanced properties of alloys can be attributed to atomic-scale details of their surface structure. For instance, it has been proven experimentally that the addition of gold to palladium catalysts results in dramatically enhanced activity toward the direct synthesis of hydrogen peroxide⁶. Subsequent theoretical calculations demonstrated that surface sites composed of individual Pd atoms surrounded by Au were likely the key to this improvement⁷. At these sites, O-O bond scission, an unwanted side reaction which readily occurs on the pure Pd surface, is suppressed due to the comparatively low adsorption energy of the reaction products on Au.

The role played by surface Pd monomers in improving the activity and selectivity of AuPd catalysts toward H_2O_2 synthesis is an example of an *ensemble effect*⁸⁻¹¹, defined as an improvement in catalytic properties that arises from the presence of a particular geometric arrangement of surface metal atoms. *Ligand effects*—improvements due to modifications to the surface electronic structure of an alloy because of dissimilar metal-metal interactions—have proven to be important in other instances. Clearly, understanding and taking advantage of these kinds of connections between the surface structure and surface chemistry of alloys will require detailed knowledge of their atomic configurations. This is the central motivating concern of the research presented in this dissertation. In each of the following chapters, a different aspect of my inquiry into the atomic configuration of alloy catalysts is reported.

A detailed description of the simulation schemes that were used in this work is offered in Chapter 2. These are in all cases based ultimately on density functional theory (DFT), a quantum mechanical modeling method. Due to the relatively high computational cost of DFT calculations, extensive use was made of Ising-like models of alloy energetics known as cluster expansions (CE), which are many orders of magnitude faster and less memory intensive. The CEs were constructed from the results of DFT calculations, and then incorporated into simulations based on the Metropolis Monte Carlo algorithm in order to predict the finite-temperature, equilibrium properties of alloys.

Chapter 3 reports the use of this scheme to examine and compare the atomic configuration of AuPt/Pt(111) and AuPd/Pd(111) surface alloys. In particular, the MC-predicted size and shape distributions of contiguous Pt and Pd ensembles are presented for a range of compositions and temperatures, and these results are explained in terms of the differing interatomic interactions present in each alloy. Through the use of electronic structure calculations, it was found that in AuPt, homonuclear, Pt-Pt interactions are

avored over heteronuclear, Au-Pt interactions, while in AuPd the opposite is true. Accordingly, the Monte Carlo simulations showed that Pd prefers to form small, isolated ensembles with extended shapes, and Pt prefers to agglomerate and form larger ensembles with compact shapes.

Results from simulations of AuPd and AuPt surface alloys in the (100) crystallographic facet are reported in Chapter 4. As in the (111) surface, a preference for heteronuclear interactions in the AuPd surface led to an increased number of small Pd ensembles, and the reverse occurred in AuPt. A tendency for Pd monomers to form second nearest-neighbor pairs was also identified. Pairs of Pd monomers have been observed experimentally by the Goodman group, and the MC simulation results are in remarkable agreement with statistics derived from their STM images of the bulk AuPd(100) surface. Second nearest-neighbor pairs of Pd monomers have been identified as the active ensemble in vinyl acetate synthesis on the AuPd(100) surface, and soon-to-be published work by the Hwang research group also shows that they may promote the oxygen reduction reaction, as well.

The effects of biaxial strain on the arrangement of atoms in AuPd(100) are presented in Chapter 5. Application of 2% compression was found to heighten the preference for heteronuclear Au-Pd interactions, and 4% tensile strain to reduce it. The tendency toward formation of monomer pairs also increased under compression. One consequence is that $c(2\times 2)$ ordering was found to persist up to significantly higher temperatures in the compressed surface than in either the strain-free or tensile strain cases. An electronic structure analysis that linked strain and atomic arrangement in the AuPd/Pd(100) surface to characteristics of its *d*-band electron density of states is also presented.

Chapter 6 describes the development and application of a methodology for predicting surface segregation and atomic configuration in surface terminated bulk alloys. Once again, the approach is based on DFT, the cluster expansion method, and Monte Carlo simulations; this time, however, in the grand canonical ensemble. Issues pertaining to training set and cluster expansion construction in this system are addressed, and the approach is shown to be an improvement over others reported in the literature, particularly in terms of reduced complexity. In addition, a shortcoming in the Direct Exchange Monte Carlo method of performing simulations in the grand canonical ensemble is identified.

In Chapter 7, the topic of surface alloys is once again taken up, but with a slightly different focus. In the work reported in earlier chapters, cluster expansions were developed with the goal of closely matching DFT predictions. This is what enabled distinguishing between the three strain cases in Chapter 5 and the close correspondence between experiment and the simulation results presented in Chapter 4. Unfortunately, as will be explained in Chapter 2, this approach relies on the iterative construction of a relatively large “training set” of computationally expensive DFT calculations. Predicting the atomic configuration of surface alloys composed of more than a handful of separate transition metal pairs—for a high-throughput theoretical catalysis study, for example—would thus be impractical. To address this concern, a strategy based on first nearest-neighbor pair interactions and a restricted DFT training set is described, as is its application to several bimetallic surface alloys. As will be shown, limiting interactions to first nearest-neighbor pairs provides the additional benefit of reducing the canonical ensemble description of all bimetallic surface alloys to a single dimensionless parameter, termed the scaled pair interaction.

Chapter 2: Methodology

2.1 INTRODUCTION

This chapter describes the methodological approaches used in the remainder of this dissertation. In the first section (2.2), a brief review is given of density functional theory (DFT), which is a means of efficiently solving the Schrödinger equation. While DFT is the tool of choice for a wide variety of theoretical investigations of materials and even chemistry, it remains too computationally expensive to apply to many problems directly. Hence, in the second section (2.3), the cluster expansion (CE) method is described. The CE method is used to construct highly accurate and computationally efficient Hamiltonians for use in substitutional, lattice-based systems. The cluster expansions developed in this work are all based on the results of DFT calculations and in that light can be viewed as “extending” the reach of DFT. The CE method formalism is discussed, as well as its specific application to a few of the systems considered later. In the final section (2.4), the Metropolis Monte Carlo algorithm for estimating finite-temperature, equilibrium properties is reviewed, including the original proof provided by Metropolis *et al.* in their seminal paper.

2.2 DENSITY FUNCTIONAL THEORY

Since Walter Kohn¹² and John Pople¹³ were jointly awarded the Nobel Prize in Chemistry in 1998 for their contributions to the development of density functional theory (DFT), its use has continued to increase rapidly, as shown in Figure 2.1¹⁴. Because the majority of the calculations that will be presented in the following chapters are based ultimately on DFT, a brief overview of its theoretical underpinnings will be provided in this section. For the general outline and many of the references, I am indebted to the

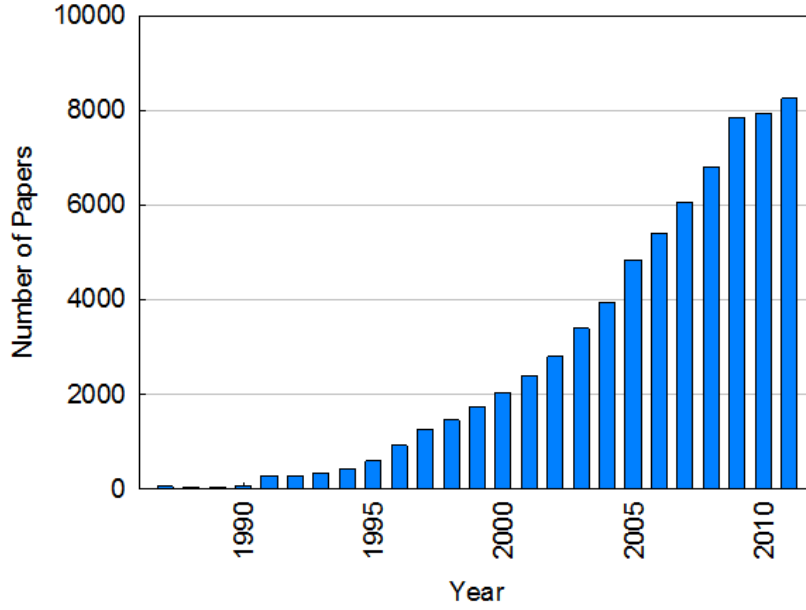


Figure 2.1. The number of papers returned by a Web of Knowledge search for the term DFT by year. Reproduced from Fig. 1 in Ref. 14.

authors of Refs. 15 and 16. Emphasis will be placed on the implementation in the Vienna Ab initio Simulation Package (VASP)¹⁷⁻²⁰, which was used for all calculations.

2.2.1 The Schrödinger equation

The time-independent Schrödinger equation

$$H\psi = E\psi \quad (2.1)$$

is a partial differential equation which relates the stationary states or wavefunctions, ψ , of a system characterized by a Hamiltonian, H , to their corresponding energies, E . In the context of materials science or chemistry, the primary systems of interest are collections of atoms that make up molecules or condensed matter. In systems such as these, ψ depends on the coordinates in three dimensional space of every electron and nucleus. That is, in a collection of M atoms that possess a total of N electrons, $\psi = \psi(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_M, \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$, where $\mathbf{R}$ and $\mathbf{r}$ are position vectors of the atomic nuclei

and electrons, respectively. However, since the mass of a nucleon is approximately 1836 times larger than the mass of the electron²¹, the electrons respond much more rapidly to changes in their surroundings than do the nuclei. This leads to the so-called Born-Oppenheimer approximation^{22,23}, in which the electrons are treated separately from the nuclei, and the ground-state energy is considered a function of nuclear position, $E(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_M)$.

Equation (2.2) shows a still quite general form of the Schrödinger equation which makes more explicit the Hamiltonian for a system of electrons and nuclei interacting under the Born-Oppenheimer approximation.

$$\left[-\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N V(\mathbf{r}_i) + \sum_{i=1}^N \sum_{j=1}^{i-1} U(\mathbf{r}_i, \mathbf{r}_j) \right] \psi = E\psi \quad (2.2)$$

The first term in the brackets is the kinetic energy of each electron, and the second and third terms are the potential energies due to electron-nuclei interactions and electron-electron interactions, respectively. The form of the electron-nuclei interaction term depends on the system in question (in particular, the positions and atomic numbers of the nuclei), but $U(\mathbf{r}_i, \mathbf{r}_j) = \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$, the Coulomb interaction between electrons i and j . It is also this latter term that prevents solution of the Schrödinger equation by separation of variables, making its analytical solution an intractable many-body problem in all but the very simplest cases, such as the hydrogen atom.

2.2.2 Hohenberg, Kohn, and Sham

In 1964, Hohenberg and Kohn²⁴ laid the groundwork for density functional theory by proving two theorems. These theorems are restated in plain language by Sholl and Steckel¹⁵ as:

1. *“The ground-state energy from Schrödinger’s equation is a unique functional of the electron density”*
2. *“The electron density that minimizes the energy of the overall functional is the true electron density corresponding to the full solution of the Schrödinger equation.”*

The first theorem of Hohenberg and Kohn means that the ground-state energy (and other properties) of a system of interacting electrons and nuclei is known if the electron density, $n(\mathbf{r})$, is known. Since $n(\mathbf{r})$ is only a three-dimensional function, this is in principle a vast improvement over attempting to directly calculate E and ψ , a function of $3N$ coordinates.

Although the exact form of the functional $E[n(\mathbf{r})]$ is unknown, the second theorem provides some direction in how to go about finding the true, ground state $n(\mathbf{r})$. Given an assumed, approximate energy functional, successively better (in the sense that they result in lower energy) guesses for $n(\mathbf{r})$ move us closer and closer to the ground state energy. This is known as the variational principle.

The following year, Kohn and Sham²⁵ demonstrated that it is possible to replace the original many-body problem posed by the Schrödinger equation with a system of non-interacting, single-electron equations. Their approach was based on first writing the electron density as a sum over occupied single-electron orbitals

$$n(\mathbf{r}) = \sum_i \psi_i^*(\mathbf{r})\psi_i(\mathbf{r}) \quad (2.3)$$

Then writing the energy in terms of $n(\mathbf{r})$,

$$E_{KS}[n(\mathbf{r})] = T_s[n(\mathbf{r})] + E_H[n(\mathbf{r})] + E_{XC}[n(\mathbf{r})] + \int V(\mathbf{r})n(\mathbf{r})d\mathbf{r} + E_{II} \quad (2.4)$$

In this equation, $T_s[n(\mathbf{r})]$ is the sum of the kinetic energy contributions of each non-interacting electron, which equals $-\frac{\hbar^2}{2m}\sum\int\psi_i^*(\mathbf{r})\nabla^2\psi_i(\mathbf{r})d\mathbf{r}$. The Hartree energy, $E_H[n(\mathbf{r})] = \frac{1}{2}\int\int\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'d\mathbf{r}$, accounts for a portion of electron-electron interactions. The interaction of electrons with the external potential (including the atomic nuclei) is defined by $V(\mathbf{r})$, and the nuclei-nuclei interactions are equal to E_{II} . The final term in eq. (2.4) is the exchange-correlation energy, $E_{XC}[n(\mathbf{r})]$. This term accounts for all the effects not included in the other terms. The formulation of $E_{XC}[n(\mathbf{r})]$ is an ongoing topic of research and will be discussed further in the next section.

Kohn and Sham minimized eq. (2.4) by taking the functional derivative with respect to $n(\mathbf{r})$, in accordance with Hohenberg and Kohn's second theorem. The result is a system of equations of the form

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r}) \quad (2.5)$$

In eq. (2.5), the third term, $V_H(\mathbf{r})$, is the Hartree potential and is equal to $e^2\int\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'$. It describes the Coulomb interaction between electron i and the combined density of all electrons in the system and includes an erroneous self-interaction energy between the electron and itself. $V_{XC}(\mathbf{r})$ is the functional derivative of the exchange-correlation energy.

$$V_{XC} = \frac{\delta E_{XC}}{\delta n} \quad (2.6)$$

The system of equations represented by eq. (2.5) explicitly contains both $n(\mathbf{r})$ and $\psi_i(\mathbf{r})$ and must be solved in a self-consistent fashion using an iterative procedure. A set of $\psi_i(\mathbf{r})$ or, equivalently, $n(\mathbf{r})$ is “guessed.” $V(\mathbf{r})$, $V_H(\mathbf{r})$, and $V_{XC}(\mathbf{r})$ for this density are calculated. Then, the system of Kohn-Sham equations is solved for ε_i and $\psi_i(\mathbf{r})$. These $\psi_i(\mathbf{r})$ are used to compute $n(\mathbf{r})$. If this $n(\mathbf{r})$ is similar enough to the “guessed” $n(\mathbf{r})$, convergence has been achieved. Otherwise, a new $n(\mathbf{r})$ is constructed and the process is repeated. Figure 2.2 shows an outline of this procedure.

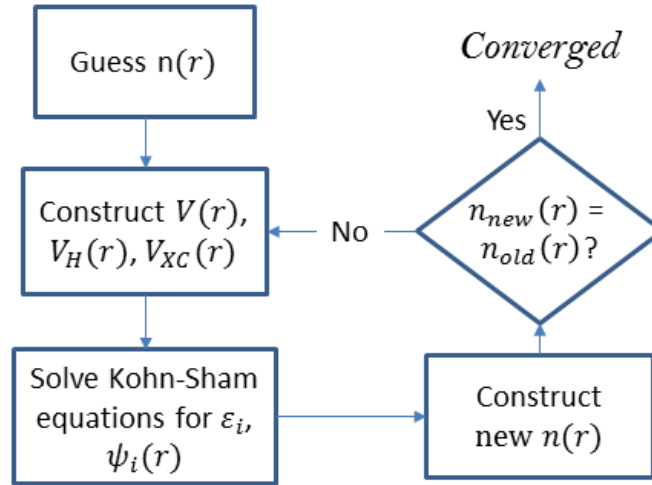


Figure 2.2. Flowchart for iterative solution of the Kohn-Sham equations.

2.2.3 The Exchange-Correlation Functional

As stated above, the exchange-correlation energy comprises all the many-body effects that are not accounted for by the other terms in eq. (2.5). One such effect, the exchange interaction, arises from the Pauli exclusion principle; no two electrons may occupy the same quantum state simultaneously, and so they are forced spatially apart,

lowering their Coulombic repulsion. Problematically, the true form of $E_{XC}(n)$ is unknown, which has led to the development of many competing “functionals.”

The first functionals were based on the local density approximation (LDA). In the LDA, it is assumed that $J_{XC}[n(\mathbf{r})]$ at a point $\mathbf{r}$ in the system of interest can be approximated by its value in a homogeneous electron gas that has the same density $n(\mathbf{r})$. The exchange energy can be rigorously derived in this system^{26,27} as

$$e_X^{hom}(n) = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} n^{4/3} \quad (2.7)$$

On the other hand, the correlation energy of the homogeneous electron gas is known exactly only in the high and low density limits²⁷. The results of quantum Monte Carlo simulations are interpolated at intermediate values.

Functionals based on the generalized-gradient approximation (GGA) incorporate local gradient information, instead of assuming a homogeneous electron gas. That is,

$$E_{XC}[n(\mathbf{r})] = \int d\mathbf{r} f[n(\mathbf{r}), \nabla n(\mathbf{r})] \quad (2.8)$$

The functional used throughout this work is a GGA functional, and was developed by Perdew and Wang in 1991^{28,29}. It is fittingly named PW91.

2.2.4 Basis Set

Solutions of the Schrödinger equation in a periodic system must be in Bloch form³⁰

$$\psi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r}) u_{\mathbf{k}}(\mathbf{r}) \quad (2.9)$$

In eq. (2.9), $u_{\mathbf{k}}(\mathbf{r})$ is a periodic function with the same translational symmetry as the underlying lattice ($u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{T})$, where $\mathbf{T}$ is any lattice vector), and $\mathbf{k}$ is vector with units of reciprocal length that labels $\psi_{\mathbf{k}}(\mathbf{r})$.

In VASP, $u_{\mathbf{k}}(\mathbf{r})$ is expanded in terms of a set of planewaves, which compose the basis set,

$$u_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{G}} \exp(i\mathbf{G} \cdot \mathbf{r}) \quad (2.10)$$

The sum in this expression is over lattice vectors in reciprocal space, $\mathbf{G} = v_1 \mathbf{b}_1 + v_2 \mathbf{b}_2 + v_3 \mathbf{b}_3$, where the basis vectors $\mathbf{b}_i$ are related to the real-space unit cell basis vectors $\mathbf{a}_i$

$$\mathbf{b}_i = 2\pi \frac{\mathbf{a}_j \times \mathbf{a}_k}{\mathbf{a}_i \cdot \mathbf{a}_j \times \mathbf{a}_k} \quad (2.11)$$

Hence,

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{G}+\mathbf{k}} \exp[i(\mathbf{G} + \mathbf{k}) \cdot \mathbf{r}] \quad (2.12)$$

One variable that is crucial to the accuracy and efficiency of the calculation is the number of planewaves in the sum. This is controlled via the cutoff energy³¹,

$$E_{cut} = \frac{\hbar^2}{2m} \mathbf{G}_{cut}^2 \quad (2.13)$$

The planewaves defined by eq. (2.10) must meet the criterion $\mathbf{G} + \mathbf{k} < \mathbf{G}_{cut}$.

2.2.5 Pseudopotentials

Although strictly speaking, pseudopotentials are not formally a part of density functional theory, they are in practice almost always used in DFT calculations, and therefore are worthy of mention.

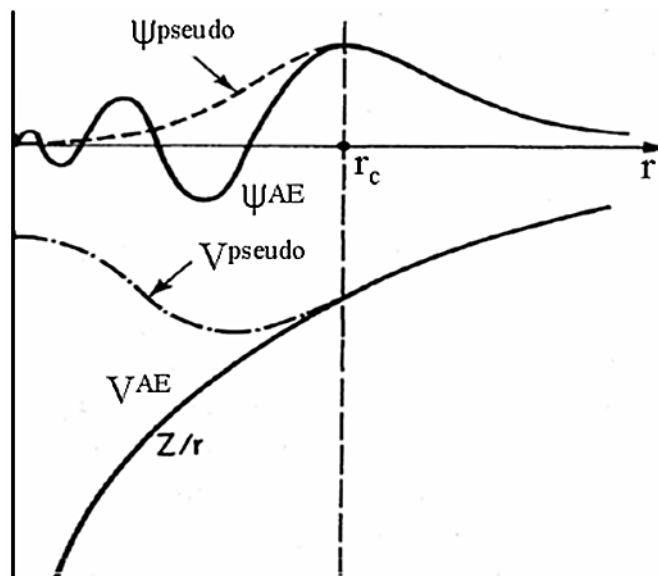


Figure 2.3. Comparison between pseudo and all-electron wavefunction and between pseudopotential and all-electronic potential. Taken from Ref. 32.

Pseudopotentials address two related concerns in quantum chemical calculations. First, it is chiefly the valence electrons that participate directly in chemical bonding, and the core electrons, which are typically much lower lying in energy, are not strongly affected by the environment surrounding the atom. Even so, core electrons must still be explicitly simulated in an “all electron” calculation. Second, the core electron wave functions vary rapidly near the nucleus. Representing these fluctuations correctly requires

a high E_{cut} (that is, use of a larger basis set, or number of planewaves). In both cases, the cost of the DFT calculation is significantly increased, but for questionable benefit.

Sholl and Steckel¹⁵ provide the following definition, the import of which is now easily understood:

Conceptually, a pseudopotential replaces the electron density from a chosen set of core electrons [around a nucleus] with a smooth density chosen to match various important physical and mathematical properties of the true ion core. The properties of the core electrons are then fixed in this approximate fashion in all subsequent calculations; this is the frozen core approximation.

The pseudopotential approach is illustrated schematically in Figure 2.3³². In an all electron (AE) calculation, interaction of the electrons with the true potential $V^{AE} = Z/r$ results in the fluctuating electron wave function Ψ^{AE} . The pseudopotential V^{pseudo} has been carefully designed to result in a wavefunction Ψ^{pseudo} that coincides with Ψ^{AE} beyond the cutoff radius r_c .

2.3 THE CLUSTER EXPANSION METHOD

2.3.1 Introduction

The energetics of a system can provide important insight into its configuration and, consequently, its properties. For example, we may be interested in finding the minimum-energy state of a multicomponent material, or in predicting finite-temperature thermodynamic averages of its properties. This presents a practical difficulty. Even if we stipulate that the systems to be considered are well-represented by crystal lattices, N lattice sites may be occupied by M constituents in M^N unique ways, neglecting symmetry. Any one of these may in principle be the ground state, and all of them contribute to some degree to the system's partition function. Except for small systems that have few components, directly applying DFT or any other quantum-mechanics based approach is out of the question. Indeed, it is somewhat unusual to encounter a DFT-based

study in the literature in which more than a few dozen small configurations have been examined.

One possible alternative is to use an appropriate empirical potential, such as the Stillinger-Weber potential³³ or the Embedded Atom Method³⁴. In a potential, the total energy of an atomic configuration is written as a sum of the interactions between its atoms. The interactions are calculated using relatively simple functional forms which are written in terms of quantities such as interatomic separations and bond angles. They also depend on a set of parameters which are usually determined by fitting to some combination of experimental data and simulation results from higher level methods like DFT.

One of the advantages to using potentials is that they impose few restrictions on the geometry of the atomic configuration; that is to say, potentials may be as readily used to model amorphous materials as crystalline ones. At first glance, this is an attractive feature, since even in lattice-based systems, local relaxations away from exact lattice points can significantly affect the relative stability of a configuration. On the other hand, since potentials “coarse-grain” the physics of bonding, they always involve compromises and tradeoffs between accuracy, simplicity, and transferability. This shortcoming is reflected in the fact that although many researchers have attempted to generate libraries of general purpose potentials and parameters for an assortment of elements³⁵⁻³⁸ would-be users often seem to find it necessary to spend considerable time and effort re-optimizing them prior to use³⁹⁻⁴¹. Another strike against potentials is that while they do allow explicit local relaxation of the lattice, it is just as accurate to say that they require it, and optimizing the geometry of a single configuration can require calculating energies and gradients at dozens of intermediate steps. Moreover, calculating thermodynamic averages

at just a single condition (e.g. constant NVT) typically requires computing the (relaxed) total energies of $\sim 10^4$ configurations per lattice site.

2.3.2 Formalism

The cluster expansion (CE) method is a frequently used technique⁴²⁻⁴⁹ to model the dependence of energy on configuration in lattice-based materials and systems. In most cases, accuracy comparable to DFT can be achieved. CE Hamiltonians also possess many other qualities that recommend their use over potentials for this class of problems, as will be discussed below.

To construct a cluster expansion, every site i in a lattice is assigned an occupation variable σ_i which takes an integer value according to the species at the site. In a binary alloy of species A and B, $\sigma_i = +1$ or -1 , according to whether site i is occupied by A or B. The dependence of any property (usually, but not necessarily, energy) on the occupancy of the lattice may now be expanded⁵⁰ in terms of polynomials of these σ_i . The occupation variables are sometimes also referred to as “spins,” probably in reference to the similarities between the cluster expansion method and the Ising model.

For a two-component system, the polynomials are simply products of the occupation variables themselves. Using the CE method, the total energy of a binary system with N lattice sites $[E(\boldsymbol{\sigma}), \boldsymbol{\sigma} = \{\sigma_1, \sigma_2, \dots, \sigma_N\}]$ may be written

$$E(\boldsymbol{\sigma}) = J_0 \cdot N + \sum_i J_i \sigma_i + \sum_{i < j} J_{ij} \sigma_i \sigma_j + \sum_{i < j < k} J_{ijk} \sigma_i \sigma_j \sigma_k + \dots \quad (2.14)$$

where J_0 , J_i , J_{ij} , and J_{ijk} are expansion coefficients [called *effective cluster interactions* (ECIs)] for empty, point, and all pair, and three body “clusters” of occupation variables. The complete expansion contains all clusters allowed by the symmetry and extent of the lattice, but in practice it can be truncated to just a few of the most important terms

without unacceptable loss of precision. The procedure to choose the clusters and pick parameters is outlined in section 2.2.3.

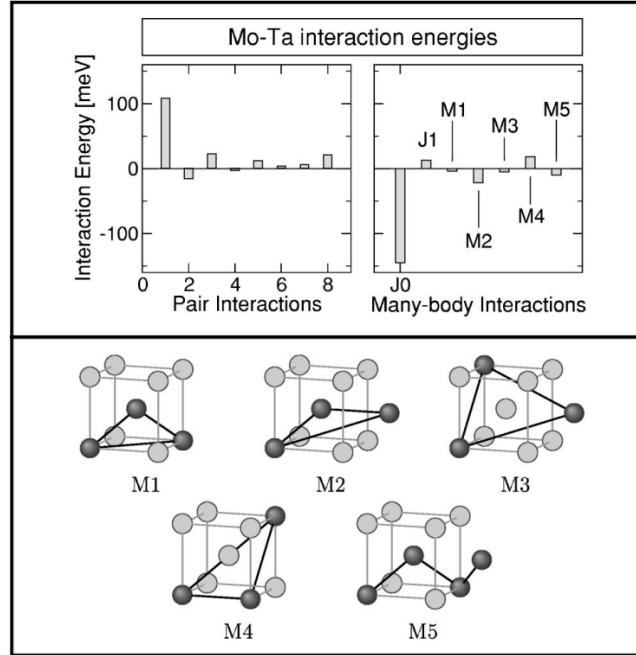


Figure 2.4. Upper panel: Symmetry-weighted pair and many-body interactions obtained in the cluster expansion of Mo-Ta. Lower panel: definition of the figures. From Fig 1 in Ref 46.

Figure 2.4 shows a CE Hamiltonian developed for the body-centered cubic Mo-Ta alloy examined in Ref. 46. The upper part of the figure contains ECIs for the pairs and multi-body clusters included in the expansion, and the lower panel shows the multi-body clusters. Application of this CE requires (1) visiting every site in the lattice in order to (2) add up the products of the σ_i for each pair and multi-body cluster, as in eq. (2.14), while (3) taking care not to “double count” interactions and also (4) properly taking the symmetry of the lattice into consideration. These items will be elaborated in the next section.

Based on the description of potentials and the form of eq. (2.14), some of the computational advantages of cluster expansions may now be apparent. Using CE Hamiltonians mostly involves multiplying and adding integers, while nearly all potentials employ several transcendental functions, which are several orders of magnitude more expensive to compute. Also, when potentials are used, geometry optimization is usually necessary to account for energy changes due to local relaxations. However, there is no reason in principle that this effect cannot be folded into the CE itself by cluster expanding the energies of already-relaxed configurations. Indeed, this is nearly always what is done.

Another advantage of CEs is that, compared to potentials, they make few prior assumptions about the nature of bonding in a material. In this way, the problem posed by unanticipated physical phenomena (for example, coulomb interactions due to charge transfer in metal alloys) which stymies many potentials is side-stepped by cluster expansions.

2.3.3 CE Implementation

2.3.3.1 Introduction

This section will explain, in some detail, several considerations related to implementing a cluster expansion in a particular lattice. It is intended not only to convey the methods used in subsequent chapters, but to be used as a primer by those who may wish to produce their own cluster expansion-based codes.

Particular attention will be given to the fcc(100) and fcc(111) surface facets, shown in Figure 2.5. The (100) surface is a square lattice (space group $p4m$). Its primitive unit cell is defined by the orthonormal basis vectors shown in Figure 2.5(a). The (111) surface, a hexagonal lattice, belongs to one of two space groups, depending on whether the subsurface layer of atoms is taken into consideration. The darkened 3-fold hollow

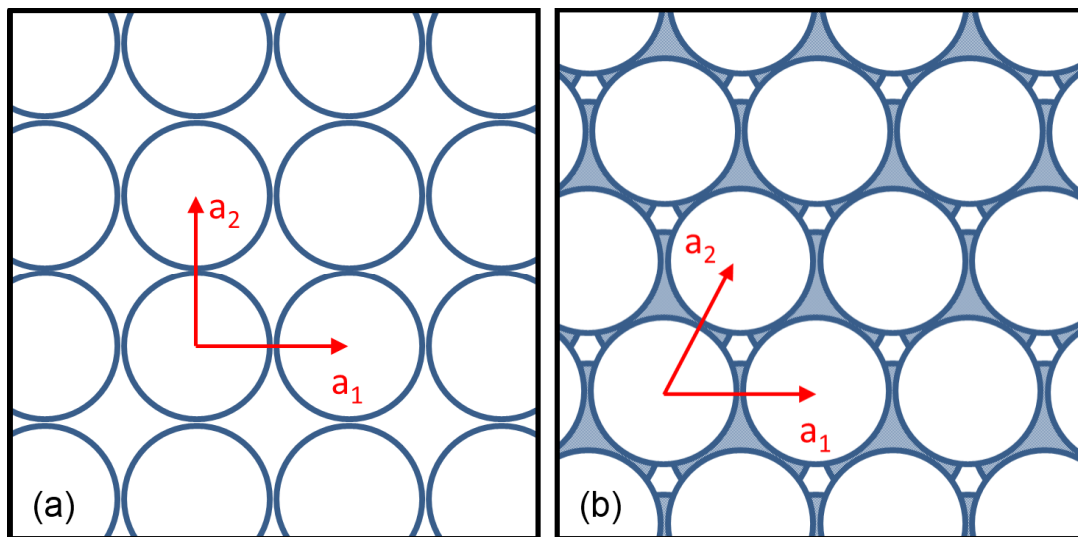


Figure 2.5. Schematics of the (a) fcc(100) crystallographic facet and the (b) fcc(111) facet. Atoms in the subsurface of fcc(111) are also shown to distinguish the *hcp* and *fcc* 3-fold hollow sites.

sites in Figure 2.5(b) indicate the presence of a subsurface atom at that location in the real (111) surface, and are conventionally referred to as *hcp* hollows. Hollow sites that lack a subsurface atom in the (111) surface are called *fcc* hollows. When *fcc* and *hcp* hollows are distinguished, the space group of the surface facet is $p3m1$, and a 3-fold rotation axis passed through each lattice site. If, on the other hand, the effects of the subsurface layer are neglected, the (111) surface facet has the full symmetry of the hexagonal lattice (including a 6-fold rotation axis), and belongs to space group $p6m$.

2.3.3.2 Representation of the (100) and (111) lattices

Since, in the cluster expansion, energy depends only on the occupation of lattice sites and the effects of local relaxations are lumped into the ECIs, it is unnecessary to keep track of the precise location of each atom in three dimensional space. We need only maintain the “spin” (+1 or -1) at each lattice position. The primitive unit cells of both the (100) and (111) surface contain only a single lattice point, so these can be efficiently

stored in two-dimensional arrays, the zero-based indices of which equal the integer components of position vectors.

First, the basis vectors of the (100) (square) surface may be written as column vectors in a matrix.

$$\mathbf{S} = [\mathbf{s}_1 \quad \mathbf{s}_2]; \mathbf{S} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \quad (2.15)$$

And for the (111) (hexagonal) surface as

$$\mathbf{H} = [\mathbf{h}_1 \quad \mathbf{h}_2]; \mathbf{H} = \begin{bmatrix} 1 & 1/2 \\ 0 & \sqrt{3}/2 \end{bmatrix} \quad (2.16)$$

The position vector $\mathbf{r}$ of any atom in the (100) surface may then be written

$$\mathbf{S} \cdot \mathbf{r} = r_1 \mathbf{s}_1 + r_2 \mathbf{s}_2 \quad (2.17)$$

where the components of $\mathbf{r}$ are integers; hence the occupation of all sites can be stored in an integer-indexed 2D array, e.g. `lattice[r1][r2]`. The same is of course true of the (111) surface.

2.3.3.3 *Symmetry-equivalent clusters in (100) and (111)*

The primary challenge of implementing a cluster expansion-based code is developing an efficient strategy to account for every instance of a cluster (e.g. the first nearest-neighbor pair cluster) permitted by the space group of the underlying lattice. For simple clusters, like pair interactions, it is relatively easy to think of “hard coded” schemes to accomplish this task, but as the clusters grow in size and complexity this approach becomes cumbersome, error-prone, and difficult to maintain. A flexible,

automated scheme that accepts a representative of any valid cluster as input and generates the full, symmetry-equivalent set would be much preferred.

A few definitions make discussion more convenient. The technical, group-theoretic term for the collection of all symmetry-equivalent instances of a cluster in the lattice is the *orbit*^{51,52}. The individual instances themselves (that is, a particular nearest neighbor pair) will be referred to as *figures*. Equation (2.14) can be more compactly stated with these definitions in mind.

$$E(\sigma) = \sum_{\alpha} J_{\alpha} \Phi_{\alpha}(\sigma) \quad (2.18)$$

where

$$\Phi_{\alpha}(\sigma) = \sum_{\gamma} \prod_i \sigma_{\gamma,i} \quad (2.19)$$

The sum in eq. (2.19) is over the figures in the orbit of cluster α , and product is over the sites in the γ th figure. Φ_{α} is referred to as a *cluster function*. Φ_{α} for the empty cluster (Φ_0) is by definition equal to the number of lattice sites.

Developing a simulation to apply eq. (2.18) to a lattice can be broken down into two intertwined problems. The first is identifying an algorithm and set of data structures to efficiently calculate cluster functions in the context of the type of simulations to be performed. The second is the expansion of a cluster into all the figures in its orbit; that is, populating the aforementioned data structures.

2.3.3.4 Algorithm and Data Structures

One approach to the first problem is to construct a set of figures for each cluster in such a way that after the set has been individually applied to every site in the lattice, every figure in that cluster's orbit is included only once.

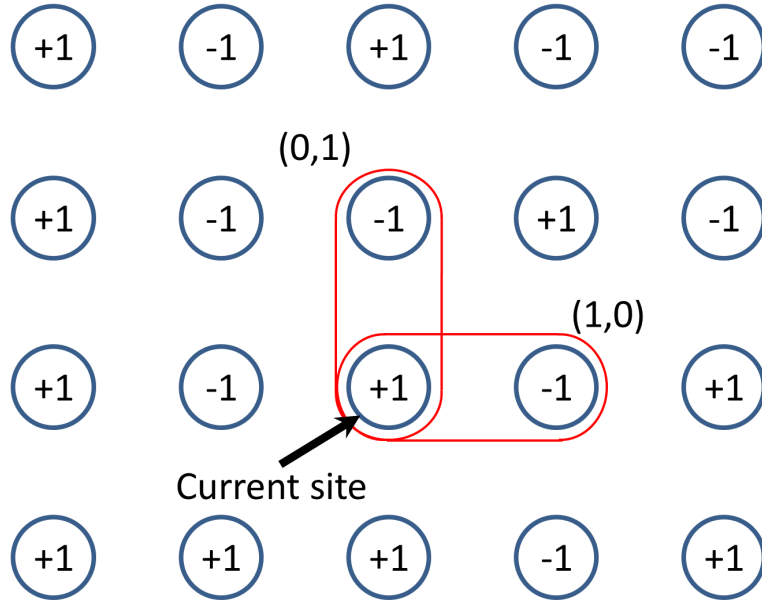


Figure 2.6. First nearest-neighbor pairs in fcc(100).

For example, for the nearest neighbor pair cluster in the (100) surface, the list of figures generated by this strategy might be $\{(1, 0); (0, 1)\}$, with each ordered pair in the set representing a vector in the $\mathbf{S}$ basis [eq (2.15)]. The vectors are the positions of one site in a nearest neighbor pair relative to the site that the list is currently being applied to. (See Figure 2.6.) The other two nearest neighbor pairs that the current site belongs to, those formed with sites at $(-1,0)$ and $(0,-1)$, would be included in the sum when those sites were visited.

Using this strategy, it is very easy to calculate the energy of the lattice by iterating over every site. On the other hand, it is quite inconvenient to calculate the *change* in energy due to swapping the spin (from +1 to -1 or vice versa) of a site. This is so because a swap implies that the products of all of the figures that a site is part of need to be recalculated, but the list of figures is incomplete by design. Since calculating the energy

change due to a swap is a very frequent operation in Monte Carlo simulations, this is perhaps a poor strategy.

This problem is alleviated if the list contains every figure (again, in relative coordinates) that an individual site participates in, rather than a truncated list designed to avoid duplicates. For the nearest neighbor pair, this would be $\{(1,0); (0,1); (-1,0); (0,-1)\}$. If site i is swapped, the change to the nearest neighbor pair cluster function is computed by iterating over the list of figures

$$\Delta\Phi_2 = (\sigma_{i,new} - \sigma_{i,old}) \cdot \sum_{\gamma} \prod_{j \neq i} \sigma_{\gamma,j} \quad (2.20)$$

In this case, the sum is over the γ figures in the list, rather than over the whole orbit, and the product is over the unchanged sites. The same is true for all clusters in the expansion, and the change in the energy is obtained from summing over the changes in the cluster functions multiplied by their ECIs. ($\Delta E = \sum_{\alpha} J_{\alpha} \cdot \Delta\Phi_{\alpha}$). Note that when two sites that are part of the same figure are changed simultaneously (as when they are swapped with one another in a Monte Carlo move), it is necessary to compute the effects of their changes sequentially.

Although constructing lists in this fashion greatly facilitates calculating *changes* in energy, it introduces the problem of multiple counting when the energy is initially calculated; since every figure that a site participates in is counted when that site is visited, the same figure is counted again when the other sites in the figure are visited. Correcting for this is as simple as dividing each cluster function by the number of sites in each of its figures, m_{α}

$$E(\sigma) = \sum_{\alpha} J_{\alpha} \frac{\Phi_{\alpha}(\sigma)}{m_{\alpha}} \quad (2.21)$$

However, the efficiency of the calculation of E is lowered relative to the first strategy, which may be important if the simulation requires a large number of fresh energy calculations. Since Monte Carlo simulations typically rely on ΔE calculations, the full-list strategy is still the preferred one.

2.3.3.5 *Generating Figures*

Regardless of the lattice, generating the complete list of figures that a site participates in follows roughly the same procedure. Briefly: The positions of $m_\alpha - 1$ sites of a single, representative figure are read in. The m_α th site is assumed to be the origin, (0,0), and the positions of the other sites are given relative to it. A series of symmetry operations of the lattice is applied to the figure to reorient it about the origin, and the resulting figures are added to the list. Additional figures are generated by shifting each of these figures to place each of their sites at the origin. The final step is removal of the large number of duplicates that these operations typically produce.

The detailed procedure for the fcc(111) surface, including *hcp* and *fcc* hollows, is described in Figure 2.7. Two symmetry operations are used to generate new orientations of clusters in this surface: Reflection of the input figure across [11] (the line passing through the origin, rotated $\pi/6$ relative to the horizontal) and rotation of the resulting pair of figures about the 3-fold axis at the origin. (When the subsurface is neglected, the axis is 6-fold).

For the (100) surface, the input figure is reflected across the x-axis, then both the resulting figures are reflected across the y-axis to produce a total of four. These four are rotated (and copied) about the 4-fold axis at the origin.

The transformation of the coordinates of each site under reflection can be obtained by inspecting the lattice: in the (111) case, the reflection across [11] results in

the transformation $(r_1, r_2) \rightarrow (r_2, r_1)$. In the (100) surface, reflection across the x- and y-axis is accomplished by sign changes. The rotations are performed using rotation matrices of the form⁵³

$$\mathbf{R}_\theta = \begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix} \quad (2.22)$$

The rotated vector $\mathbf{r}'$ is the result of the matrix multiplication $\mathbf{R}_\theta \mathbf{r}$. Vectors in the (111) surface must undergo a change of basis before they are rotated, and then be restored to the $\mathbf{H}$ [eq. (2.16)] basis⁵².

$$\mathbf{r}' = \mathbf{H}^{-1} \mathbf{R}_\theta \mathbf{H} \cdot \mathbf{r} \quad (2.23)$$

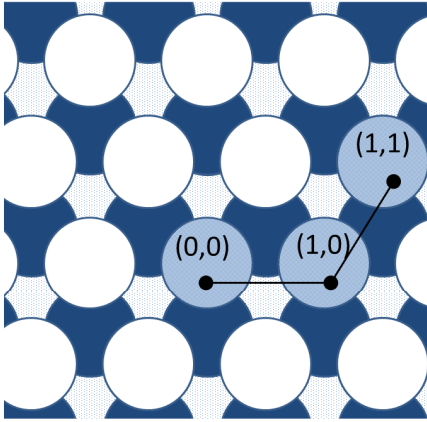
$$\mathbf{r}' = \mathbf{R}'_\theta \cdot \mathbf{r} \quad (2.24)$$

For the rotations about the 3-fold and 6-fold axes,

$$\mathbf{R}'_{2\pi/3} = \begin{bmatrix} -1 & -1 \\ 1 & 0 \end{bmatrix} \quad (2.25)$$

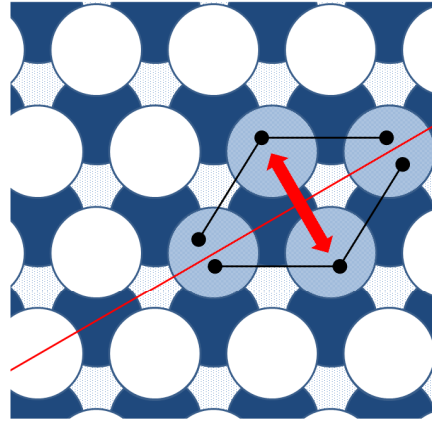
$$\mathbf{R}'_{\pi/3} = \begin{bmatrix} 0 & -1 \\ 1 & 1 \end{bmatrix} \quad (2.26)$$

Step 0. Read in the figure.



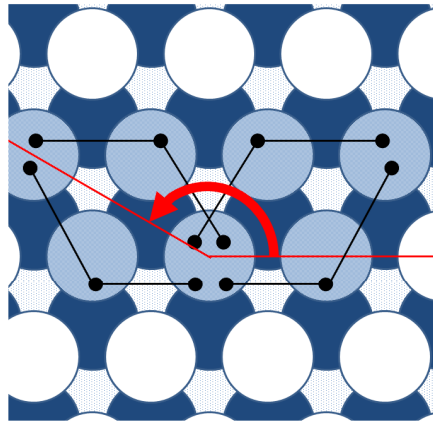
This 3-body figure can be described using the sites (1,0) and (1,1), their coordinates relative to the origin, which is assumed to be included.

Step 1. Reflect across [11]



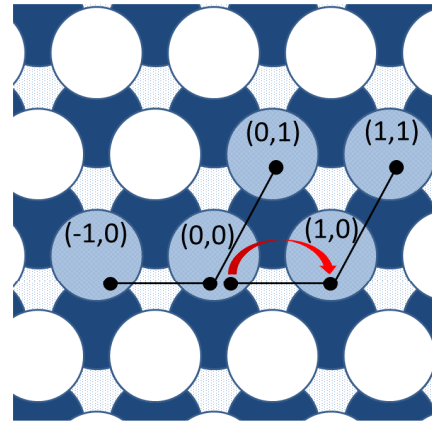
Reflection of the input figure across [11] results in a second 3-body figure that contains two of the same sites as the first.

Step 2. Rotate through $2\pi/3$



Both figures are copied and the copies are rotated about the 3-fold axis that passes through the origin. These two new figures are again copied and rotated (not shown).

Step 3. Shift figures to new origin



After the reflection and rotation operations have been completed, new figures are created from every figure in the list by shifting each of their sites to the origin.

Figure 2.7. Procedure to generate an orbit of figures from a representative input figure in the fcc(111) surface.

2.3.4 Cluster Selection

Most CE Hamiltonians reported in the literature are constructed using DFT-based training sets of (configuration, energy) pairs. This is also my approach, although examples of fitting to experimental data also exist⁵⁴.

Determining how best to truncate the expansion (i.e. deciding which clusters to include) is one of the chief difficulties of constructing a CE. If too few clusters are included, the expansion will be a poor fit to the training set. On the other hand, if too many clusters (or the wrong clusters) are included, an expansion with poor predictive ability may result due to overfitting.

Cross validation (CV) has been proposed to detect and prevent overfitting, while also providing a measure of the predictive ability of a CE model⁵⁵. The optimal set of clusters with respect to a given training set of DFT results is obtained by minimizing the CV score (ξ) which is given by:

$$\xi^2 = \frac{1}{N} \sum_{n=1}^N \left(E_{DFT}^{(n)} - E_{CE}^{(n)} \right)^2 \quad (2.27)$$

where $E_{DFT}^{(n)}$ is the DFT energy of the n th of N total configurations in the training set, and $E_{CE}^{(n)}$ is a prediction of the same energy by a CE with a particular set of clusters. The ECIs used in the calculation of $E_{CE}^{(n)}$ are obtained (by minimization of the squared error) for a subset of the full training set that excludes the n th configuration, so that $E_{DFT}^{(n)} - E_{CE}^{(n)}$ is a genuine prediction error. Consequently, the CV score of a truncated CE is a sum over N prediction errors obtained from N independent fittings of its associated ECIs.

2.3.4.1 CV Minimization

Identifying the set of clusters that minimizes the CV score is itself a challenging problem. In the *fcc* lattice, even if interactions are limited to the third nearest-neighbor

distance, there are a total of 60 different clusters which can be combined in different ways to give 2^{60} possible cluster expansions⁵⁶. Candidate solutions to the CV score minimization problem can be encoded as binary sequences, where a 1 indicates inclusion of a cluster and a 0 indicates exclusion. This is somewhat reminiscent of a set of genes, which is perhaps what has prompted some to employ genetic algorithms⁵⁶. Simulated annealing⁵⁷⁻⁵⁹, which we have used in our published work, seems to give satisfactory results, as well.

Simulated annealing is a global optimization technique which is conceptually based on the actual metallurgical process of annealing. By heating a metal sample to high temperature, then permitting it to cool slowly, its atoms have the opportunity to overcome kinetic barriers trapping them in local minima and assume their thermodynamically preferred configuration. Similarly, in simulated annealing, candidate solutions to an optimization problem are permitted to travel “uphill” and out of local minima in order to more fully explore the problem space. The candidate solution in the current iteration is randomly changed to produce a new one (in our case, a cluster’s “bit” is flipped on or off), the objective function is computed (the CV score, ξ), and then the ratio of the new solution’s Boltzmann factor to that of the old one is used to determine whether the move is accepted. A randomly generated number [0..1] on the uniform distribution is compared to

$$P = e^{-(\xi_{new} - \xi_{old}) \cdot \beta} \quad (2.28)$$

and the move is accepted if P is smaller. P is of course greater than unity when $\xi_{new} < \xi_{old}$, so movements further down into minima are always accepted. The parameter β is a fictitious inverse temperature, and is adjusted from some initial value on a schedule as the simulation proceeds. At the beginning of the simulation, β is small, implying a high temperature, which permits easy escape from local minima and

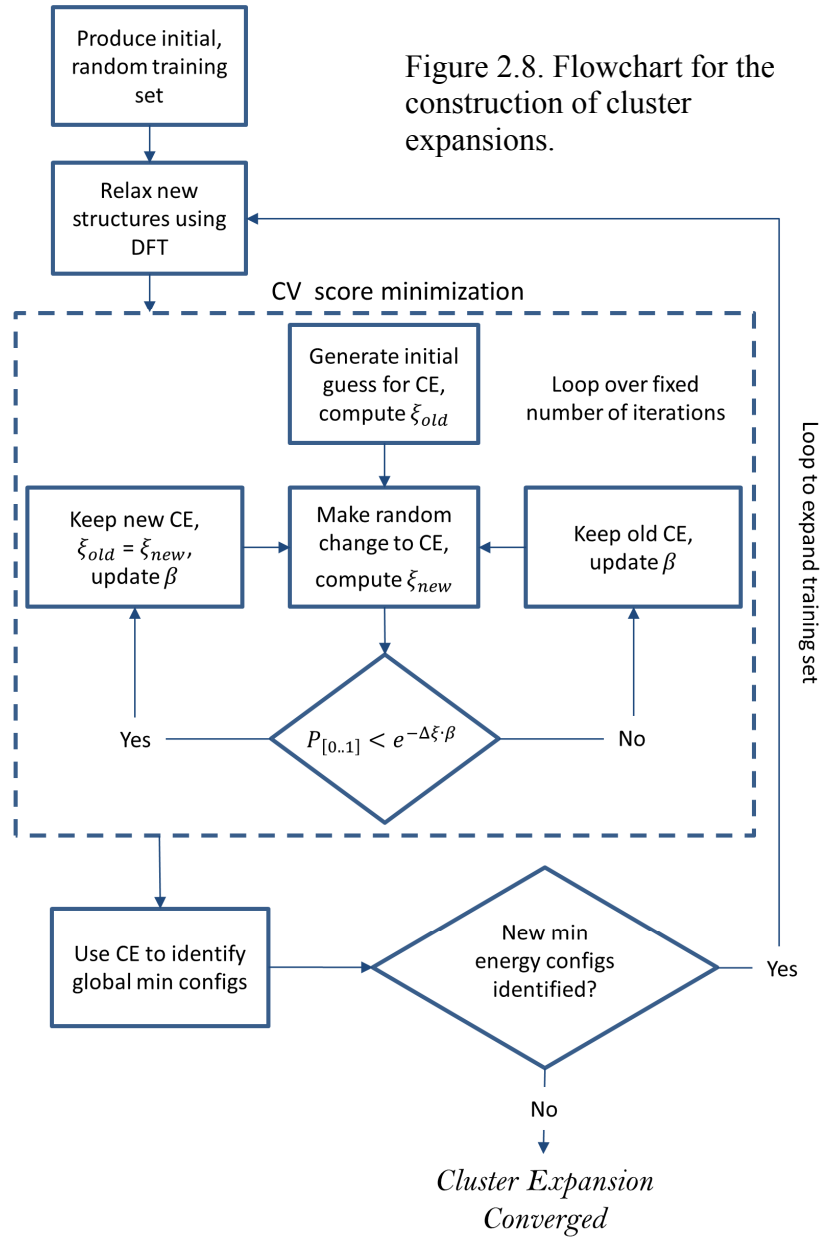
exploration of the space. As β is slowly increased, the simulation becomes trapped in what is hopefully the global minimum. The number of iterations, the initial and final values of β , and the cooling schedule (which need not be simply linear in the iteration number) can significantly affect the outcome of the optimization, and it is typically necessary to explore several combinations of these parameters to achieve confidence in the result.

A pair of hierarchical rules has also been proposed, that (1) if an n -body cluster is included, then include all n -body clusters of smaller spatial extent, and (2) If a cluster is included, include all its subclusters⁶⁰. In unpublished work, we have used these rules to construct tree-like graphs of cluster dependencies which greatly reduce the number of possible cluster expansions, in some cases to the point where it becomes practical to locate the guaranteed global minimum CV score by “brute force” enumeration of all permitted CEs.

The CV score provides a criterion to judge the predictive quality of a CE with respect to a given training set, but it provides no assurance that the training set itself contains adequate information to construct a genuinely predictive model. Because the training set is finite, important clusters may be left out of the CE, or spurious clusters may be left in. However, recognizing that the reason for constructing a CE is often to predict likely (i.e. low energy) configurations suggests a method of reducing this risk: After constructing a CE, use it to predict ground-state configurations, which can then supplement the training set. In this way, the training set is iteratively expanded and the CE is refined, especially in terms of its ability to distinguish between energetically low-lying configurations^{55,61}.

The overall scheme is presented in a flowchart in Figure 2.8. A training set is initialized with (configuration, energy) pairs from DFT calculations. These are used to

create a trial CE by minimizing the CV score. The trial CE is then used to predict minimum-energy configurations. If these configurations are not already present in the training set, their energies are calculated using DFT and they are included. If, on the other hand, all the minimum-energy configurations predicted by a trial CE are already present, it is considered to be fully converged and ready for use.



2.3.4.2 ECI Fitting

For each of the N terms in eq. (2.27), the ECIs of the cluster expansion being examined are fit to a portion of the training set which contains $N_s = N - 1$ structures, so that the energy of the N th can then be predicted. Each of these fits can be construed as a problem in quadratic programming⁶², that is, minimization of a function of the form

$$f(\mathbf{x}) = \mathbf{a}^T \mathbf{x} + \frac{1}{2} \mathbf{x}^T \mathbf{G} \mathbf{x} \quad (2.29)$$

Subject to zero or more inequality constraints

$$s(\mathbf{x}) \equiv \mathbf{C}^T \mathbf{x} - \mathbf{b} \geq 0 \quad (2.30)$$

and zero or more equality constraints

$$s(\mathbf{x}) \equiv \hat{\mathbf{C}}^T \mathbf{x} - \hat{\mathbf{b}} = 0 \quad (2.31)$$

To demonstrate that this is the case, we write the average of the squared errors between the DFT and CE-calculated energies of the N_s surfaces of the training set:

$$\varepsilon^2 = \frac{1}{N_s} \sum_{n=1}^{N_s} \left(E_{DFT}^{(n)} - E_{CE}^{(n)} \right)^2 \quad (2.32)$$

Substituting eq. (2.18) for $E_{CE}^{(n)}$, we have

$$\varepsilon^2 = \frac{1}{N_s} \sum_{n=1}^{N_s} \left(E_{DFT}^{(n)} - \sum_{\alpha=1}^{N_c} J_{\alpha} \Phi_{\alpha}^{(n)} \right)^2 \quad (2.33)$$

The quantity in parentheses is then expanded, and the terms not involving unknowns (the ECIs) are moved to the left hand side. Also, all terms are multiplied by a factor of $1/2$.

$$\begin{aligned}
\frac{1}{2}\varepsilon^2 N_s - \frac{1}{2} \sum_{n=1}^{N_s} \left(E_{DFT}^{(n)} \right)^2 \\
= \frac{1}{2} \left[\sum_{\alpha=1}^{N_c} J_{\alpha} \Phi_{\alpha}^{(n)} \right]^2 - \frac{1}{2} \sum_{n=1}^{N_s} E_{DFT}^{(n)} \sum_{\alpha=1}^{N_c} J_{\alpha} \Phi_{\alpha}^{(n)}
\end{aligned} \tag{2.34}$$

Because ε^2 is the only non-constant value on the left hand side, minimizing the right hand side also minimizes it. We rewrite eq. (2.34) in matrix form, which is seen to be the same as equation (2.29).

$$f(\mathbf{J}) = \frac{1}{2} \mathbf{J}^T \bar{\Phi} \mathbf{J} + \mathbf{E}^T \mathbf{J} \tag{2.35}$$

In this equation, $\mathbf{J}$ is the vector of ECIs, $\bar{\Phi}$ is a matrix whose elements i,j equal

$$\bar{\Phi}_{i,j} = \sum_{n=1}^{N_s} \Phi_i^{(n)} \Phi_j^{(n)} \tag{2.36}$$

And $\mathbf{E}$ is a vector whose elements i equal

$$E_i = -\frac{1}{2} \sum_{n=1}^{N_s} E_{DFT}^{(n)} \Phi_i^{(n)} \tag{2.37}$$

Since $\bar{\Phi}$ and $\mathbf{E}$ do not change, they can be pre-computed for each of the N partitions of the training set required by eq. (2.27). A number of free, open-source libraries exist for solving quadratic programming problems, such as the one by Di Gaspero and Moyer⁶³, which is based on the algorithm of Goldfarb and Idnani⁶⁴.

In Ref. 62, Lerch *et al.* recommend three constraints, which they attribute to Garbulsky and Ceder⁶⁵:

$$\begin{aligned}
|\Delta H_{DFT}(\sigma) - \Delta H_{CE}(\sigma)| &< \delta_1(\sigma) \\
|\Delta H_{DFT}^{GSL}(\sigma) - \Delta H_{CE}^{GSL}(\sigma)| &< \delta_2(\sigma) \\
|\Delta H_{DFT}^{lowest}(\sigma) - \Delta H_{CE}^{lowest}(\sigma)| &< \delta_3(\sigma)
\end{aligned} \tag{2.38}$$

Where ΔH refers to the mixing enthalpy of the examined system. The first constraint ensures that the prediction of ΔH for every individual structure in the training set is off by no more than δ_1 . The second and third constraints measure ΔH relative to, respectively, the ground state line (GSL) and the lowest energy structure of the same composition. The purpose of the latter two constraints is to help maintain the relative energetic ordering of configurations. In this scheme, each value of δ can be set independently:

$$\delta_{\{1,2,3\}}(\sigma) = \delta_{\{1,2,3\}}^{const} \exp\left(-\frac{\Delta H_{DFT}^{lowest}(\sigma)}{k_B T}\right) \quad (2.39)$$

This definition of δ tightens the constraint for lower-energy structures, with the intention of preserving the energy hierarchy near the ground state at the expense of greater error in the higher energy predictions. The constraints are controlled by a pair of user-provided parameters, δ^{const} and T . (Note that T is not the simulation temperature; it is input separately and controls only the extent to which the constraints are relaxed for higher energy structures.)

The constrained minimum may of course be greater than the unconstrained, and accordingly the cross validation score for the same set of clusters also may be higher when constraints are applied. Experience suggests that expansions with a larger number of clusters appear to be affected in this way to a smaller degree, perhaps because they are able to satisfy the constraints more easily. This disparity leads in practice to the selection of larger expansions by the scheme in Figure 2.8 when constraints are applied than when not. In all cases I examined, the size of the cluster expansion depends very sensitively on δ^{const} and T , with rapid increases occurring when either parameter approaches a certain

threshold from above. Since it is unclear whether a CE that satisfies the constraints in eqs. (2.38) actually possesses greater predictive ability, they should be used only with caution.

2.4 METROPOLIS MONTE CARLO

In the canonical (NVT) ensemble, the expectation value of a property $\langle A \rangle$ of a thermally equilibrated system can be calculated by⁶⁶

$$\langle A \rangle = \frac{\sum_i A_i \exp(-E_i/k_B T)}{Z} \quad (2.40)$$

In the sum, which is over every configuration in the ensemble, E_i and A_i are, respectively, the energy and measured value of A of configuration i . The exponential is called the Boltzmann factor, and is the relative probability of selecting configuration i at random from the ensemble; hence, it serves as a weighting factor in the average. Z is a normalization constant called the partition function, which is obtained by summing the weights over the entire ensemble, $Z = \sum_i \exp(-E_i/k_B T)$.

While for many systems there is no obvious, tractable way to directly calculate $\langle A \rangle$ using this expression, a Monte Carlo (MC) algorithm developed by Metropolis *et al.*^{67,68} can be used to obtain a reasonable estimate. The algorithm has four main steps.

1. The initial configuration (or the configuration from the previous iteration) is randomly changed to produce a new configuration.
2. The difference in the energies of the two configurations is calculated.
3. The probability of transitioning to the new configuration is determined using the ratio of their Boltzmann factors.

$$P_{old \rightarrow new} = \exp[-(E_{new} - E_{old})/k_B T] \quad (2.41)$$

This probability is compared to a random number between 0 and 1. If the random number is smaller, transition is successful. The microstate from the previous iteration is discarded, and the new microstate is kept. Otherwise, the previous microstate is retained.

4. Before the beginning of the next iteration, the properties of the configuration that was kept are calculated and accumulated.

After a preset number of iterations over these four steps, the data collected in the fourth step is averaged over the number of iterations to yield ensemble averages.

Metropolis *et al.* also provided a proof in Ref. 68 that the sequence of configurations produced by these four steps would tend to adopt the same distribution as the canonical ensemble; that is, the number of times any configuration i is visited in the simulation is proportional to the Boltzmann factor. For this reason, the unweighted average of a property over all the visited states should converge on the weighted average in eq. (2.40).

The proof proceeds as follows. Consider a large ensemble of systems. The number with configuration i is n_i . Every system undergoes a random change which (possibly) converts it to a different configuration. The probability that a random move will convert a particular configuration i into configuration j is P_{ij} . (We require that $P_{ji} = P_{ij}$.) Next, we assume that $E_i > E_j$, so that transitions from i to j are guaranteed. Therefore, the number of systems in the ensemble with configuration i that transition to configuration j will be

$$n_i P_{ij} \tag{2.42}$$

And the number that move in the opposite direction, from j to i , will be

$$n_j P_{ji} \exp[-(E_i - E_j)/k_B T] \quad (2.43)$$

The difference between eq (2.42) and (2.43) is the net number of systems that change from configuration j to i

$$P_{ij} \{n_j \exp[-(E_i - E_j)/k_B T] - n_i\} \quad (2.44)$$

After dividing by n_j , we see that if the following expression is true

$$\frac{n_i}{n_j} > \exp[-(E_i - E_j)/k_B T] \quad (2.45)$$

then the number of systems in configuration i that convert to j outnumber those that go in the opposite direction. In subsequent iterations, as n_j grows and n_i diminishes, the condition

$$\frac{n_i}{n_j} = \exp[-(E_i - E_j)/k_B T] \quad (2.46)$$

will eventually obtain for every pair of configurations i and j . When this has occurred, the ensemble of systems will have achieved a canonical distribution.

Note that while this proof demonstrates that the Metropolis algorithm eventually will produce an ensemble of configurations that satisfy the Boltzmann distribution, it offers no guarantee that it will do so quickly. Fortunately, it turns out that for many systems, the number of iterations required is modest. It is, however, typically necessary to ascertain through experimentation the convergence of ensemble-averaged properties

with number of iterations. For surface alloys, on the order of 10^3 - 10^4 iterations per atom has proven to be adequate.

Chapter 3: AuPd/Pd(111) and AuPt/Pt(111) Surface Alloys

3.1 INTRODUCTION

Alloys often exhibit catalytic properties superior to those of their pure constituent metals. A number of recent articles have reported enhanced activity and selectivity of certain gold-based bimetallic alloys. Au-Pd surface alloys, for instance, have been shown to promote CO oxidation⁶⁹⁻⁷², the direct synthesis of hydrogen peroxide^{6,73-77}, vinyl acetate synthesis⁷⁸⁻⁸¹, and the hydrogen evolution reaction⁸², among others. CO oxidation is also promoted by Au-Pt alloys⁸³, as well as *n*-hexane isomerization⁸⁴.

As explained in Chapter 1, attempts to explain enhancements in the catalytic properties of alloys are usually marshaled in terms of two related phenomena: the geometric (ensemble) effect and the electronic (ligand) effect⁸⁻¹¹. The ensemble effect is a change in the activity of a surface site due to particular arrangements of the two alloyed species in the site's vicinity. The ligand effect acts through modification of the local electronic structure that results from interactions between the different metallic species. Clearly, both effects depend on the arrangement of atoms in and near the surfaces of alloys. Unraveling and exploiting the synergistic catalytic properties of alloys will require characterizing and controlling them at the atomic scale.

A number of experimental and theoretical studies have been undertaken to image or otherwise infer details about the surfaces of alloys with atomic resolution and also to explain catalytic function in terms of these details. Maroun *et al.*⁶⁹ examined monolayer AuPd surface alloys on Au(111) substrates and concluded that ensembles containing at least one Pd atom are necessary for CO oxidation, while hydrogen adsorption occurs on Pd ensembles no smaller than dimers. Chen *et al.*^{78,79} offered evidence that second nearest neighbor pairs of Pd atoms are responsible for the enhanced activity of the AuPd(100) surface toward vinyl acetate synthesis. Calculations reported by Hwang and

coworkers⁷ suggest that Pd monomers surrounded by less active Au atoms are responsible for the heightened activity of AuPd surfaces toward direct H₂O₂ synthesis by suppressing O-O bond cleavage.

While studies such as these have been critical in advancing our understanding of catalysis on surface alloys, the difficulty of sample preparation and characterization has perhaps hindered efforts to systematically understand surface atomic arrangements using experiments. Theoretical efforts to supplement the available experimental data include the work of Boscoboinik *et al.*, who examined AuPd(111) surfaces using a nearest-neighbor pair model^{85,86}, and that of Bergbreiter *et al.* on AuPt(111) surfaces using longer range pairs⁸⁷. These studies demonstrate the usefulness of simulation tools in this area and also indicate the importance of the interactions between surface layer atoms in ensemble formation. However, the nature and consequences of interatomic interactions in surface alloys are still not fully understood.

In this chapter, we employ the simulation scheme presented in Chapter 2 to predict the equilibrium size and shape distributions of surface ensembles in AuPd/Pd(111) and AuPt/Pt(111) alloys at a range of temperatures and compositions. We begin by using density functional theory (DFT) to understand the nature of the interatomic interactions present in these two material systems. Next, using training sets composed of DFT results, we develop computationally inexpensive model Hamiltonians based on the cluster expansion method. Finally, we employ the Monte Carlo scheme to obtain thermally averaged ensemble size and shape distributions in the AuPd and AuPt surface alloys, which we present and explain in terms of interatomic interactions. By clarifying the connection between interatomic interactions and ensemble populations, we hope to offer guidance in the rational design of bimetallic catalyst materials.

3.2 METHODS

3.2.1 Density Functional Theory

Quantum mechanical calculations reported herein were performed on the basis of spin polarized density functional theory (DFT) within the generalized gradient approximation (GGA-PW91)⁸⁸, as implemented in the Vienna Ab-initio Simulation Package (VASP)⁸⁹. The projector augmented wave (PAW) method with a planewave basis set was employed to describe the interaction between ion cores and valence electrons. The PAW method is in principle an all-electron frozen-core approach that considers exact valence wave functions⁹⁰. Valence configurations employed are: $5d^{10} 6s^1$ for Au, $4d^9 5s^1$ for Pd, and $5d^9 6s^1$ for Pt. An energy cutoff of 350 eV was applied for the planewave expansion of the electronic eigenfunctions. To model the fcc (111) surface, we used supercell slabs that consist of either a rectangular $2\sqrt{3} \times 4$ surface unit cell (for the results in Section 3.3.1.), or a hexagonal 4×4 surface unit cell (for the training sets described in 3.2.2). Both shapes of cells include four atomic layers, each of which contains 16 atoms. The bottom three layers are pure Pd (111) or Pt (111) slabs, and the topmost is a monolayer alloy of the same species with Au. A slab is separated from its periodic images in the vertical direction by a vacuum space corresponding to seven atomic layers. The upper two layers of each slab were fully relaxed using the conjugate gradient method until residual forces on all the constituent atoms became smaller than 5×10^{-2} eV/Å, while the bottom two layers were fixed at corresponding bulk positions. The lattice constants for bulk Pd and Pt are predicted to be 3.95Å and 3.98Å, virtually identical to previous DFT-GGA calculations and also in good agreement with the experimental values of 3.89Å and 3.92Å⁹. For Brillouin zone integration, we used a $(2 \times 2 \times 1)$ Monkhorst-Pack mesh of k-points to determine the optimal geometries and total energies reported in 3.3.1. We increased the k-point mesh size up to $(7 \times 7 \times 1)$ to refine

corresponding electronic structures reported in 3.3.1 and to $(4\times4\times1)$ to refine the total energies for use in the training sets in 3.2.2. Previous calculations suggest that the chosen parameters are sufficient for describing the surface properties of the model systems considered^{7,91}.

3.2.2 Models for Alloy Surface Configurations

In this work, the fcc (111) surface was represented by a two-dimensional, hexagonal lattice with two types of 3-fold hollow sites. A hollow site is designated hexagonal close-packed (hcp) if an atom is present in the first subsurface layer directly beneath it and face-centered cubic (fcc) if not. We considered all possible clusters in this representation of the surface which have a maximum width less than or equal to the third nearest neighbor distance. A total of 36 meet this criterion, including the empty and point clusters.

The initial training sets for the AuPt and AuPd alloys each contained 30 model surfaces, with every possible surface composition ($\text{Au}_{16-x}\text{Pt}_x/\text{Pd}_x$, where $x = 0, 1, \dots, 16$) represented at least once. From these, a trial CE for each alloy was constructed by using simulated annealing to minimize the CV score as described in Chapter 2. The trial CEs were used to predict minimum-energy surfaces for all compositions, which then were relaxed using DFT and added to their respective training set if not already present. The trial CE was considered to be fully converged if it predicted no new minimum-energy surfaces. Otherwise, the enlarged training set was used to generate a new trial CE, and the procedure was repeated. For the AuPd surface alloy, convergence was achieved after four iterations, during which 26 model surfaces were added to the training set. The AuPt surface alloy required five iterations and 21 additional model surfaces. The selected clusters and ECIs appear in Table 3.1.

Table 3.1. Clusters and ECIs for the AuPd and AuPt cluster expansions. Pd/Pt are spin down (-1), and Au is spin up (+1).

AuPd		AuPt	
Cluster	ECI, eV	Cluster	ECI, eV
Empty	-4.24230529e-02	Empty	1.20756337e-02
Point	-1.27466453e-02	Point	2.44016540e-03
(1,0)	1.07907186e-02	(1,0)	-7.42265700e-03
(1,1)	-3.37387684e-05	(1,1)	2.36833928e-03
(2,0)	1.34503904e-03	(1,0); (0,1)	-1.01725048e-03
(1,0); (1,-1)	1.40957177e-03	(1,0); (1,-1)	1.28675590e-03
(1,0); (1,1)	4.26267110e-04	(1,0); (1,1)	-5.41111799e-04
(1,0);(2,0)	1.34073010e-03	(2,0); (2,-2)	2.99397774e-04
(2,0); (0,1)	4.88749936e-04	(2,0); (0,1)	2.22055731e-04
(0,2); (-1, 1)	2.23736043e-04	(1,0); (0,1); (1,1)	-3.45924976e-04
(1,-1); (2,-1); (2,0)	6.24028246e-04	(0,1); (1,1); (2,0)	4.43726281e-04
(0,1); (1, -1); (2,0)	2.64233213e-04	(1,-1); (2,-1); (2,0)	3.44624115e-04
(1,0); (2,0); (0,1)	3.40111699e-04	(1,0); (2,0); (0,1)	-3.30269726e-04
		(1,0); (2,0); (1,-1); (1,1)	-4.55763194e-04
		(0,1); (1,-1); (1,1); (2,0)	1.43284025e-04
		(1,0); (2,0); (0,1); (0,2)	-2.06468622e-04
		(1,0); (2,0); (0,1); (1,1); (0,2)	8.01443361e-04

For comparison, CEs that included only up to first nearest neighbor (1NN) pair interactions also were created for each alloy, taking:

$$E^{1NN}(\hat{s}) = J_0 + J_1 \sum_i s_i + J_{1NN} \sum_{i < j \in 1NN} s_i s_j \quad (3.1)$$

where J_0 , J_1 , and J_{PI} were fit to the training sets just described. Training set formation energies calculated using the 1NN CEs are compared to DFT in Figure 3.1 together with the longer-range, multisite ('3NN') CEs. Accounting for multibody and longer range interactions reduces the mean error of the AuPt CE by a factor of 9.8, and the AuPd CE by a factor of 4.2.

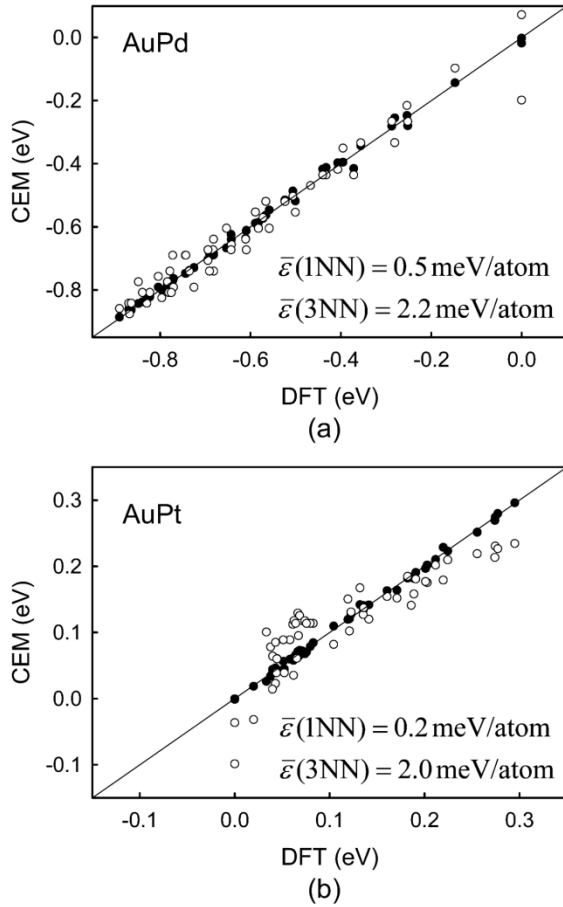


Figure 3.1. Parity plots showing discrepancies between CE and DFT predictions. Open circles are for 1NN models, and filled circles are for 3NN models. The mean errors, $\bar{\epsilon}(1NN)$ and $\bar{\epsilon}(3NN)$, are averages of the discrepancies over all N surfaces in the training sets, each of which has 16 surface atoms.

3.2.3 Monte Carlo (MC) simulations

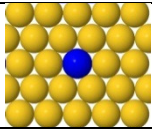
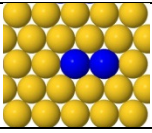
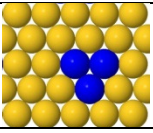
Using MC in the canonical (NVT) ensemble and CE Hamiltonians, we simulated AuPt and AuPd surface alloys with a Pt/Pd coverage between 5% and 50% at temperatures between 100K and 800K. All simulated surfaces contained 900 total spins.

To reduce the influence of the initial surface configurations on the final results, the simulations were all started at a high temperature of 1000K, then cooled to the target simulation temperature over a period of 1.8×10^7 steps (2×10^4 steps per spin). Then, the surfaces were permitted to equilibrate at the target temperature for 4.5×10^7 steps (5×10^4 steps per spin). In each step, the new microstate was generated by swapping a randomly selected Au atom with a randomly selected Pd/Pt atom. After the equilibration period, data collection began. The number, size, and shape of Pd/Pt ensembles in each sampled microstate were collected and averaged over 9×10^6 steps (10^4 steps per spin).

3.3 RESULTS AND DISCUSSION

3.3.1 Stability of small Pd/Pt ensembles: DFT calculations

Table 3.2. Calculated formation energies (in eV) of Pd/Pt ensembles. The yellow balls represent Au atoms, and the blue, Pd.

	M	D	T
			
AuPd	0.07	0.11	0.15
AuPt	0.25	0.24	0.23

We first calculated and compared the formation energies of small, isolated Pd/Pt ensembles [i.e., monomer (M), dimer (D), and *hcp* trimer (T)] in the AuPd/Pd(111) and AuPt/Pt(111) surface alloys (see the illustrations above Table 1) to examine their relative stability. Here, the ensemble formation energy per X atom (E_f , X = Pd, Pt) is given by: $E_f = \{E_{AuX} - E_{Au} + N_X(E_{Au-bulk} - E_{X-bulk})\}/N_X$, where E_{AuX} , E_{Au} , $E_{Au-bulk}$, and E_{X-bulk} represent the total energies of AuX/X(111), Au/X(111), bulk Au (per atom), and bulk X (per atom), respectively, and N_X indicates the number of X atoms in the AuX surface alloy. As

summarized in Table 3.2, predicted Pd monomer, dimer, trimer formation energies (per atom) are $E_f(M)=0.07$ eV, $E_f(D)=0.11$ eV, and $E_f(T)=0.15$ eV, respectively; taking these values, $M + M \rightarrow D$ and $M + D \rightarrow T$ agglomeration reactions tend to be endothermic by 0.08 eV [$\Delta E_D = 2 \times E_f(D) - 2 \times E_f(M)$] and 0.16 eV [$\Delta E_T = 3 \times E_f(T) - 2 \times E_f(D) - E_f(M)$], respectively. This suggests that Pd would have a tendency to remain isolated, rather than forming aggregates in the AuPd surface alloy. In contrast, the corresponding agglomeration reactions for Pt turn out to be slightly exothermic, i.e., $\Delta E_D = -0.02$ eV and $\Delta E_T = -0.05$ eV; implying that Pt may favor clustering.

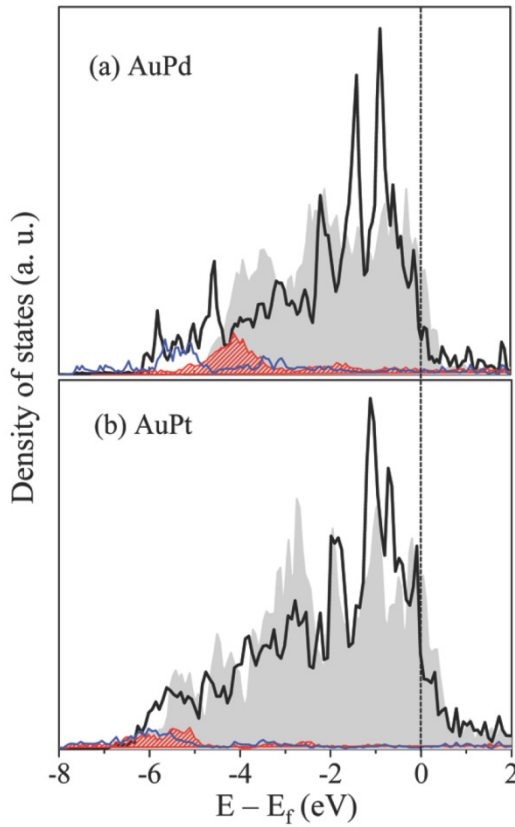


Figure 3.2. Density of states projected on the outmost s and d states of Pd/Pt monomer and pure Pd/Pt(111) surfaces. The s and d states are represented respectively by the shaded gray and patterned red areas in the monomer cases and by the thick black and thin blue solid lines in the pure surface cases. The vertical dotted line indicates the Fermi level position.

Figure 3.2 shows the local density of states (LDOS) projected onto the *d*-bands of a Pd/Pt monomer in the AuPd/AuPt surface alloy; LDOS plots for pure Pd(111)/Pt(111) surfaces are also presented for comparison. The LDOS of the Pd monomer noticeably

broadens as compared to the Pd(111) case; in particular, the onset of the high binding energy tail shifts down below -6eV (from around -5eV in Pd(111)) while the peaks near the Fermi level ($-1\text{eV} < E - E_f$) appear to be reduced. On the other hand, the Pt monomer exhibits more pronounced LDOS peaks in the low binding energy region ($-2\text{eV} < E - E_f$) at the cost of reduction in the higher binding energy peaks ($E - E_f < -2\text{eV}$). As a result of these differences in the LDOS, the d -band centers for Pd and Pt monomers are shifted relative to the respective pure Pd and Pt surfaces. In the Pt case, the d -band center of the monomer is 0.09 eV higher than that of Pt(111). The shift is in the opposite direction for Pd; the monomer is 0.07 eV lower than Pd(111). These results unequivocally demonstrate that, in AuPt surface alloys, the homonuclear Pt-Pt interaction is energetically more

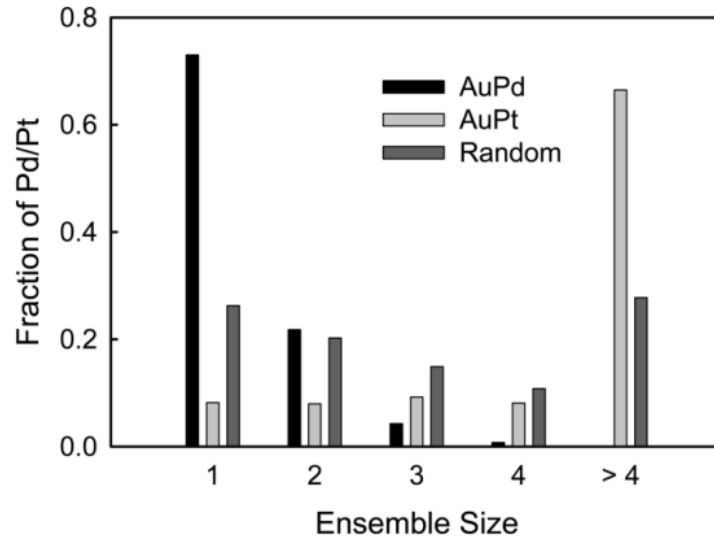


Figure 3.3. Ensemble Size Distribution at $T=300\text{K}$ and $\Theta=20\%$. In the AuPd surface alloy (black bars, leftmost in each group), smaller ensembles are preferred. Larger ensembles are preferred in the AuPt surface alloy (light gray, center in each group). Results for the random alloy (dark gray, rightmost in each group) are included for comparison.

favorable than the heteronuclear Pt-Au interaction, while in AuPd surface alloys, the heteronuclear Au-Pd interaction is stronger. This opposite tendency in the interatomic interactions may result in markedly different atomic arrangements in AuPd and AuPt surface alloys, as discussed in the following sections.

3.3.2 Surface atomic arrangements: MC simulations

3.3.2.1 Ensemble size distributions

Using MC simulations, we first calculated the size distributions of ensembles on AuPd and AuPt alloy surfaces at $T=300\text{K}$ and a Pd/Pt coverage of $\theta=20\text{ at.}\%$. Figure 3.3 shows how Pd and Pt are distributed into small ensembles of size $N = 1-4$, and also the fractions of each which exist in larger islands containing more than four contiguous atoms. For comparison, predictions made using a random alloy of non-interacting spins are also included. In AuPd, most of the Pd atoms, around 73%, exist as monomers. This is about 2.8 times larger than predicted by the random model. As N increases, the Pd fraction decreases sharply, becoming comparable to the random alloy for $N = 2$, but almost vanishing for $N > 4$. Relative to the random model, the formation of small ensembles is clearly preferred on the AuPd surface. This is consistent with the energetic favorability of Au-Pd interactions relative to Pd-Pd; as ensembles become larger, the number of Au neighbors per Pd atom tends to decrease. In AuPt, where the reverse relationship holds, our calculations show a preference for larger ensembles. The majority of Pt atoms, about 67%, are part of ensembles with $N > 4$. This is about 2.4 times larger than the fraction predicted by the random model. For smaller ensembles with $N = 1$ to $N = 4$, the Pt fraction is less than the random prediction.

Figures Figure 3.4 and Figure 3.5 show the effects of temperature and coverage on monomer and dimer populations in AuPd and AuPt surface alloys. Behavior in the

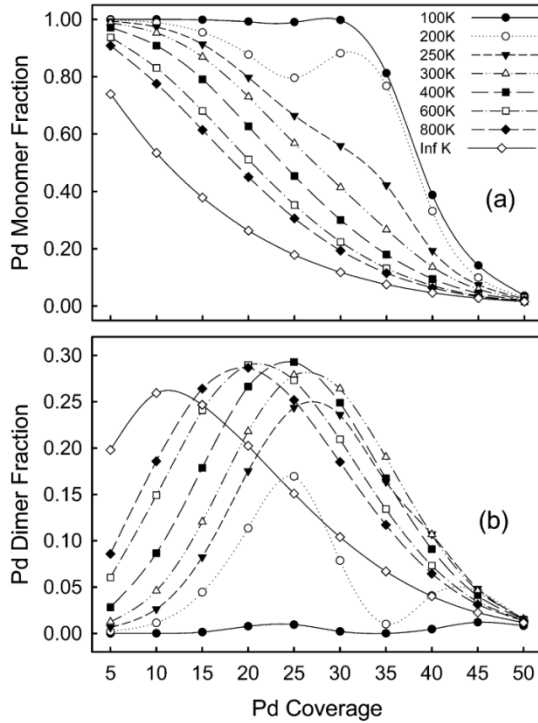


Figure 3.4. Average fraction of surface Pd atoms in monomers a) and dimers b) in AuPd surface alloys at several levels of coverage and temperature. As temperature increases, the monomer population declines, and the peak in the dimer population shifts toward higher coverage.

high (“infinite”) temperature limit, where atomic interactions are negligible, can be represented by the random alloy. Results for the random alloy are also a helpful reference for explaining and comparing the finite temperature behavior of the two alloys.

At infinite temperature, the fraction of surface Pd/Pt atoms that exist as monomers [Fig. Figure 3.4(a)] monotonically decreases with increasing coverage. This is a consequence of the fact that when the surface contains few Pd/Pt atoms, the probability of finding two or more together is low, but as the surface becomes more crowded, it increases. Unlike the monomer plot, the infinite temperature dimer plot [Fig. Figure 3.4(b)] passes through a maximum at approximately $\theta=12\%$. As more Pd/Pt atoms crowd the surface, the probability of randomly placing two together increases. This explains the initial rise. However, the same is true of trimers, tetramers, and other, larger

ensembles. The fraction of Pd/Pt atoms in dimers must at some point give way to the growing fraction in larger ensembles and begin to diminish.

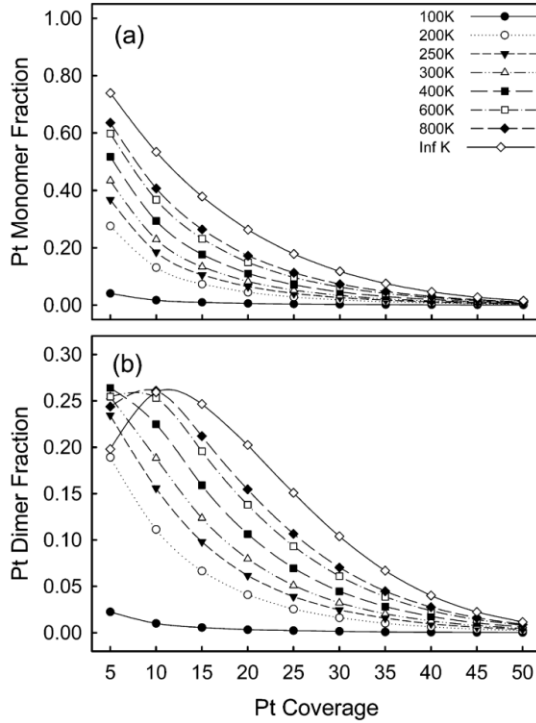


Figure 3.5. Average fraction of surface Pt atoms in monomers a) and dimers b) in AuPt surface alloys at several levels of coverage and temperature. As temperature increases, the monomer population also increases, and the peak in the dimer population shifts toward lower coverage.

The overall shape of most of the finite temperature Pd monomer plots [Fig. 3Figure 3.4 (a)] resembles the infinite temperature limit. The $T = 100\text{K}$ and 200K plots are exceptions. The maxima they exhibit at $\theta=30\text{--}35\%$ can be attributed to the stability of the $(\sqrt{3}\times\sqrt{3})R30^\circ$ ordered phase¹⁹, as will be explained in greater detail below. Regardless of temperature, at $\theta = 5\%$, between 74% and 100% of Pd atoms are monomers, but at $\theta=50\%$, fewer than 4% are. As expected, reducing the temperature (thereby increasing the contribution of interatomic interactions) results in a significant enhancement of the monomer population at all levels of coverage. At $\theta = 30\%$ and $T=100\text{K}$, close to 100% of Pd atoms exist as monomers, while at $T = \infty$, only around 12% do. Even at 800K , the monomer fraction differs from the random model by as much as 24 percentage points (at $\theta = 10\%$).

Plots of the Pd dimer fractions [Fig. 3.4(b)] at the finite temperatures considered exhibit maxima, just as at infinite temperature. However, relative to the random alloy, the maxima are shifted increasingly toward higher coverage as temperature decreases. The shift is equal to about 15 percentage points in the $T = 250\text{K}$ case. This is apparently due to the preference for small ensembles in the AuPd surface alloy. The preference for monomers over dimers delays the rise of the dimer fraction, and decline of the dimer fraction likewise is delayed by the preference for dimers over larger ensembles.

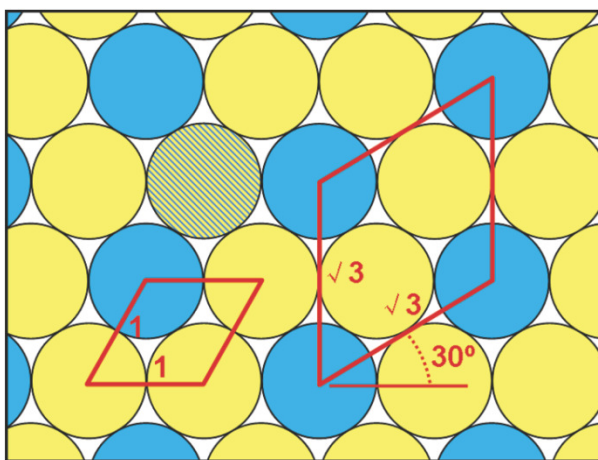


Figure 3.6. The $(\sqrt{3} \times \sqrt{3})R30^\circ$ ordered surface. Yellow atoms are Au and blue atoms are Pd. The polygon on the left shows the unit cell for the hexagonal lattice with unit length basis vectors. The polygon on the right shows the unit cell for the ordered surface. The striped atom is Au in the perfectly ordered surface. If it is swapped with one of the three adjacent Pd atoms, a Pd trimer is formed. A Pd tetramer is formed if it is swapped with any non-adjacent Pd atom.

The $T = 100\text{K}$ and 200K dimer plots have minima at $\theta=30\text{--}35\%$ that coincide with the previously mentioned maxima in the monomer plots. These features in the low temperature dimer and monomer plots can be explained by the stability of the ordered $(\sqrt{3} \times \sqrt{3})R30^\circ$ surface, which can form at a Pd coverage of exactly $1/3$. As illustrated in Figure 3.6, every Pd atom is surrounded by six Au nearest neighbors and six Pd second nearest neighbors. The surface is unique in that: i) it is the only one with a coverage of $1/3$ in which all Pd atoms can exist as monomers; and ii) no such surfaces exist at Pd coverage $> 1/3$. The CE predicts the $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase to be the ground state for the

Au₂Pd surface. Moreover, swapping any pair of dissimilar atoms creates either a Pd trimer, which incurs an energy penalty of 0.12 eV, or a tetramer, with a penalty of 0.18 eV. These energy penalties are not trivial, particularly at low temperatures. In the MC scheme, the probability of transitioning from the ground state to a microstate containing a single trimer at T=200K is $\exp(-0.12\text{eV}/k_B T) = 9.5 \times 10^{-4}$. This explains the strong preference for monomers and near absence of dimers on low-temperature AuPd surfaces with $\theta \approx 1/3$.

In the AuPt surface alloy, the effects of temperature on the populations of monomers and dimers are all the opposite of those for AuPd, due to the energetic favorability of Pt-Pt interactions over Au-Pt. Monomer populations [Fig. Figure 3.5 (a)] decrease with temperature for all levels of coverage. At T=100K and $\theta=5\%$, about 4% of surface Pt exists as monomers, compared to 74% in the random alloy. Even at 300K, the fraction rises to only about 43%. Maxima in the AuPt dimer plots [Fig. Figure 3.5 (b)] are clearly visible only in the 600K and 800K trends. They have been shifted as in the AuPd surface, but toward lower, rather than higher, coverage.

3.3.2.2 Shape distributions of trimers and tetramers

Finally, we examined the shapes of ensembles in AuPt, AuPd, and random surface alloys. Here, only trimers and tetramers are considered. Four shapes of trimers and ten shapes of tetramers are possible in the fcc (111) surface. They are shown schematically in Figure 3.7. The order of their labeling (A-D for trimers and A-J for tetramers) corresponds to their spatial extent in the surface.

Figure 3.8 shows the predicted shape distributions of trimers and tetramers in a surface with $\theta = 30\%$ at $T=300\text{K}$. In the random alloy, around 12% of trimers are compact-fcc (Shape A), 12% are compact-hcp (B), 51% are bent-linear (C), and 25% are linear (D). These fractions differ from one another despite there being no difference in the formation energies of the four shapes. This can be understood by recognizing that if

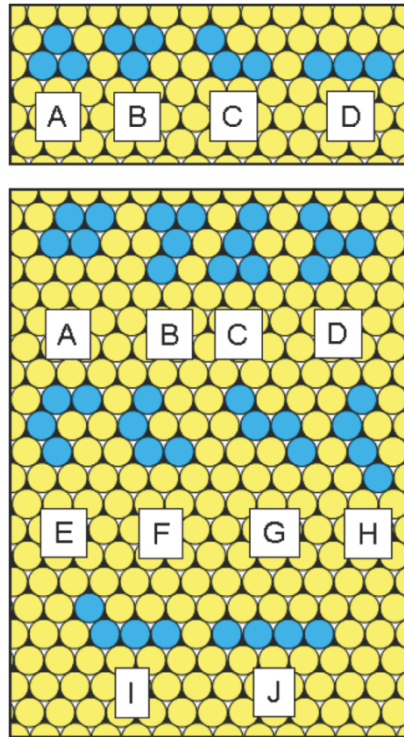


Figure 3.7. The four types of contiguous trimers (upper panel) and ten types of contiguous tetramers (lower panel) in the fcc (111) surface, accounting for the two types of 3-fold hollow sites. Black interstitial fill marks the presence of an atom in the first subsurface layer.

the total number of orientations of each shape is counted separately, there are actually 11 possible trimers in the surface, rather than 4. The two compact shapes account for one each, the bent-linear shape accounts for six, and the linear shape accounts for three, as shown in Figure 3.9. Each of the 11 total orientations is equally probable, so the compact-hcp and compact-fcc shapes each account for $1/11$ ($= 9.1\%$) of the total number of

trimers, bent-linear for 6/11 (=54.5%), and linear for 3/11 (=27.3%). These fractions differ somewhat from the ones obtained via MC simulation and reported in Figure 3.8. The discrepancies appear to be an effect of coverage. In the low coverage limit, our simulations show that the MC results approach the fractions just calculated, but as

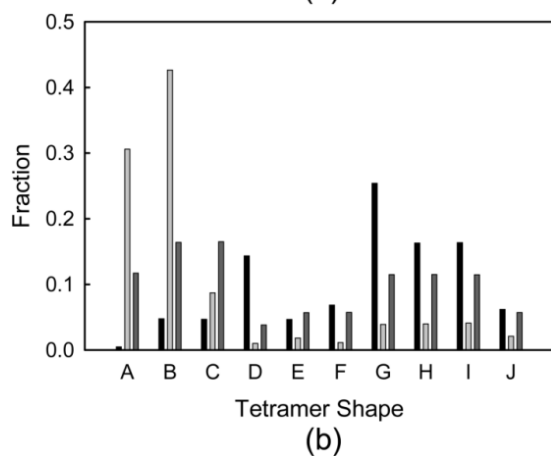
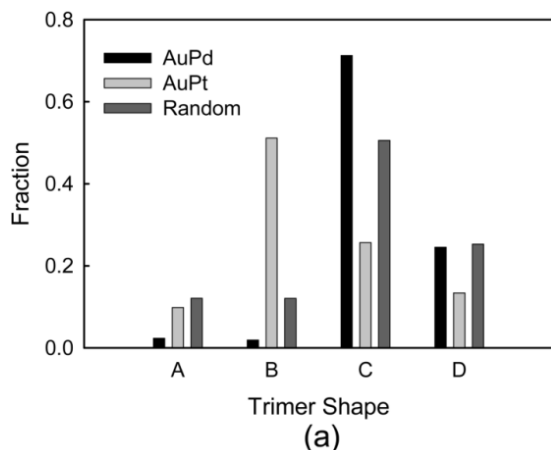


Figure 3.8. Trimer and tetramer shape distributions at $T=300\text{K}$ and $\Theta=30\%$. More compact trimers (those with more homonuclear interactions) are favored in the AuPt (light gray, center bars) surface, and more extended trimers (with more heteronuclear interactions) are favored in AuPd (black, leftmost bars).

coverage increases the compact trimer fraction rises at the expense of the bent-linear and linear fractions. All of the foregoing applies in a similar way to tetramers. Further details will be presented elsewhere.

The AuPt and AuPd shape distributions differ a great deal from one another and from the random alloy results. The fractions of Pd trimers [Figure 3.8(a)] that adopt the compact-fcc and compact-hcp shapes are smaller than the random model predictions by

factors of 5.2 and 6.4, respectively. The compact-fcc and -hcp trimer fractions are much larger in the AuPt case than in AuPd, around 0.8 and 4.2 times the size of the random prediction. Here, we note that the large difference between the populations of *fcc* and *hcp* compact trimers (shapes A and B) in AuPt is due to the difference in their formation energies. To capture this effect, a model Hamiltonian must consider multisite interactions; pair interactions alone may be insufficient. For the bent-linear trimer shape, the Pd fraction is about 1.4 times larger than the random prediction, while the Pt fraction is smaller by about half. The Pd fractions for the compact tetramer shapes A, B, and C are all much smaller than the prediction for either AuPt or the random alloy, but as can be seen in Figure 3.8(b), the fractions for the more extended tetramers D-I are comparatively larger. Conversely, in the AuPt alloy, relatively few tetramers have the extended shapes (D-I), but a large fraction are compact (A-C).

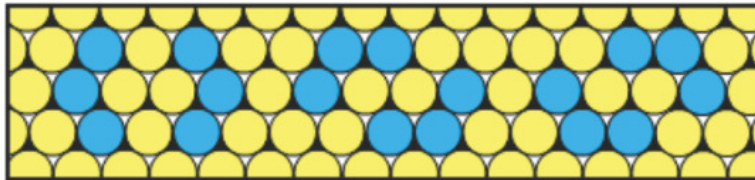


Figure 3.9. Every trimer and tetramer shape possesses one or more orientations. The six possible orientations of the bent trimer (trimer shape C) are shown here for illustration.

The differences in the AuPd and AuPt shape distributions can once again be explained by interatomic interactions. Compact ensembles contain a larger number of homonuclear, nearest-neighbor interactions than extended ones. The compact trimers contain three such interactions, while the bent-linear and linear each contain two. The most compact tetramer shape (A) contains five, tetramers B and C contain four, and the remainder each contain three. Accordingly, in the AuPd alloy, where heteronuclear

interactions are favored over homonuclear, the fraction of trimers and tetramers that have compact shapes is smaller than in the AuPt alloy. The opposite is true of the more extended shapes, which are more likely to be found in AuPt.

3.4 SUMMARY

Using the cluster expansion (CE) method, model Hamiltonians were constructed for AuPt/Pt(111) and AuPd/Pd(111) surface alloys. These cluster expansions match DFT-calculated energies to within a fraction of an meV per surface atom. They are also sufficiently computationally inexpensive to enable their use in Monte Carlo (MC) simulations. We used the MC scheme to predict the size and shape distributions of Pd and Pt surface ensembles for a range of compositions and temperatures. The results of the MC simulations show that the surface ensemble populations are strongly influenced by the interatomic interactions present in AuPt/Pt(111) and AuPd/Pd(111) surface alloys. The origin of these interactions is revealed by DFT predictions of the formation energies and electronic structures of small Pt and Pd ensembles in the model alloys, which show that homonuclear (Pt-Pt) interactions are favored in AuPt surface alloys, while heteronuclear (Au-Pd) are favored in AuPd. As a consequence, AuPd exhibits a strong preference for small ensembles compared to the AuPt alloy and a random alloy (with no interactions), according to our MC simulations. For example, at 300K and 20% coverage, 73% of surface Pd atoms are monomers. The corresponding quantities in the AuPt and random alloys are predicted to be 26% and 8%, respectively. Similarly, at this level of coverage and temperature, a negligible fraction of surface Pd belongs to ensembles that contain five or more contiguous atoms, but around 67% of surface Pt is part of ensembles of this size. The differences in interatomic interactions also explain the influence of coverage and temperature on monomer and dimer populations in the two alloys.

Monomer populations in AuPd are seen to increase as temperature is reduced, while the reverse happens in AuPt. Maxima in the dimer populations are also shifted in opposite directions as temperature increases, toward higher coverage in AuPt and toward lower in AuPd. Our MC simulations also demonstrate that compact ensembles which contain a greater number of homonuclear interactions are favored in AuPt, while more extended shapes are preferred in AuPd. The computational scheme described here can be extended to evaluate a host of other potential influences on ensemble formation in bimetallic surfaces, such as their crystallographic orientation, degree of strain, the presence of adsorbates, interactions with the catalyst support, and their bulk composition.

Chapter 4: AuPd/Pd(100) and AuPt/Pt(100) Surface Alloys

4.1 INTRODUCTION

In the last chapter, the effects of differing interatomic interactions on atomic arrangement in AuPd/Pd(111) and AuPt/Pt(111) surface alloys were evaluated. We now report on a similar treatment of the same alloys; this time in the (100) surface facet. The AuPd(100) surface is known to be significantly more active toward vinyl acetate synthesis than not only pure Pd(100) and Au(100), but also the (111) surface facet of the AuPd alloy⁷⁹⁻⁸¹. Unpublished calculations performed in the Hwang Group also suggest that the AuPd(100) surface may exhibit unexpected activity toward the oxygen reduction reaction.

As before, density function theory calculations were used to construct cluster expansion Hamiltonians for use in Monte Carlo simulations. After sharing details pertaining to the construction of the CEs, we report and discuss the results of the MC simulations, specifically the populations of small ensembles of contiguous Pd or Pt atoms (monomers and dimers). We explain these in terms of the interatomic interactions present in AuPd and AuPt surface alloys. We also compare some of our predictions to available experimental data.

4.2 COMPUTATIONAL METHODS

4.2.1 Density functional theory

Quantum mechanical calculations reported herein were performed on the basis of spin polarized density functional theory (DFT) within the generalized gradient approximation (GGA-PW91)⁸⁸, as implemented in the Vienna Ab-initio Simulation Package (VASP)⁸⁹. The projector augmented wave (PAW) method with a planewave basis set was employed to describe the interaction between ion cores and valence

electrons. The PAW method is in principle an all-electron frozen-core approach that considers exact valence wave functions⁹⁰. Valence configurations employed are: $5d^{10} 6s^1$ for Au, $4d^9 5s^1$ for Pd, and $5d^9 6s^1$ for Pt. An energy cutoff of 350 eV was applied for the planewave expansion of the electronic eigenfunctions. To model the fcc(100) surface, we used supercell slabs that consist of a square 4×4 surface unit cell. The cell includes four atomic layers, each of which contains 16 atoms. The bottom three layers are pure Pd(100) or Pt(100) slabs, and the topmost is a monolayer alloy of the same species with Au. A slab is separated from its periodic images in the vertical direction by a vacuum space corresponding to seven atomic layers. The upper two layers of each slab were fully relaxed using the conjugate gradient method until residual forces on all the constituent atoms became smaller than 5×10^{-2} eV/Å, while the bottom two layers were fixed at corresponding Pd or Pt bulk positions. The lattice constants for bulk Pd, Pt, and Au are predicted to be 3.95Å, 3.98Å, and 4.18 Å, respectively, virtually identical to previous DFT-GGA calculations and also in good agreement with the experimental values of 3.89Å, 3.92Å, and 4.08 Å⁹². For Brillouin zone integration, we used a $(2\times 2\times 1)$ Monkhorst-Pack mesh of k points to determine the optimal geometries. We increased the k-point mesh size up $(4\times 4\times 1)$ to refine the total energies for use in the training sets described in 4.2.2. Previous calculations suggest that the chosen parameters are sufficient for describing the surface properties of the model systems considered^{7,91}.

4.2.2 Cluster expansion Monte Carlo

The surfaces we simulated contained 900 surface atoms. In order to adequately sample the configuration space of a binary alloy, it is not unusual to attempt on the order of 10^4 swaps per lattice site. Hence, we required a fast and accurate means of calculating how energy varies with atomic configuration. For this purpose, we constructed CE

Hamiltonians by fitting to DFT-based training sets of small model surfaces meeting the description in section 4.2.1. The procedure we followed closely matches the one described in Chapter 2.

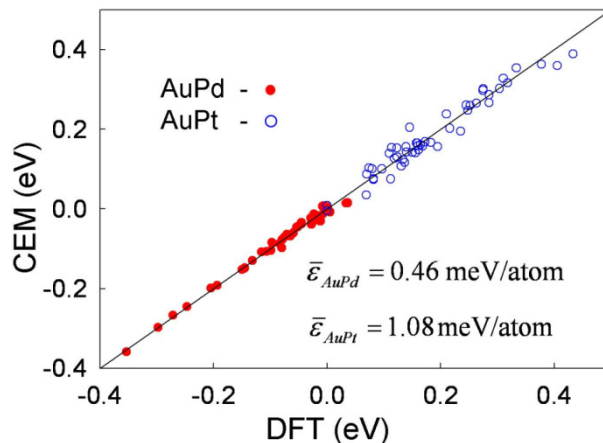


Figure 4.1. Parity plots showing discrepancies between CE and DFT predictions. Filled, red circles are for the AuPd cluster expansion, and open, blue circles are for AuPt. The mean errors ($\bar{\epsilon}$) are averages of the discrepancies over all surfaces in the training sets, each of which has 16 surface atoms.

The training sets initially contained 30 model surfaces, but to help guard against the possibility of bias, they were iteratively expanded during the fitting procedure. In each iteration, a trial cluster expansion was created by identifying the subset of terms in a pool which included pairs and multi-body interactions up to the third nearest-neighbor (3NN) distance that minimized the cross validation score³¹ with respect to the training set. The trial CE was used to predict new minimum-energy surfaces, which were then added to the training set. The trial CE was considered to be converged when it predicted no new minimum-energy surfaces. The AuPt training set was expanded by this procedure to contain a total of 49 model surfaces, and the AuPd training set contained 42. Figure 4.1

shows the discrepancies between the final CE- and DFT-predicted energies for the alloy surfaces in the training sets. Table 4.1 shows the clusters and their associated ECIs.

Table 4.1. The clusters and ECIs for AuPd/Pd(100) and AuPt/Pt(100). Pd/Pt are spin down (-1), and Au is spin up (+1).

AuPd		AuPt	
Cluster	ECI, eV	Cluster	ECI, eV
Empty	-3.3111e-3	Empty	1.7889e-2
Point	3.9978e-3	Point	5.4025e-3
(1,0)	5.6123e-e	(1,0)	-9.9535e-3
(1,1)	-3.9613e-3	(1,1)	-2.7995e-3
(1,0); (1,-1)	-9.1449e-4	(2,0)	2.3880e-3
		(1,0); (1,-1)	-2.4864e-3
		(1,0);(1,1);(1,-1)	-7.4130e-4

4.3 RESULTS AND DISCUSSION

4.3.1 Atomic arrangements in the random, AuPd and AuPt alloys

For the purpose of comparison, we first considered a random alloy, in which there are no interatomic interactions. Because there are no interactions, all microstates of a random alloy have the same energy, and therefore, regardless of the simulation temperature, the Boltzmann factor calculated for any given pair of microstates is equal to unity. The Boltzmann factor also approaches unity as $T \rightarrow \infty$ in non-random alloys, so the random alloy can be seen as representing the high temperature behavior of the AuPd and AuPt surface alloys.

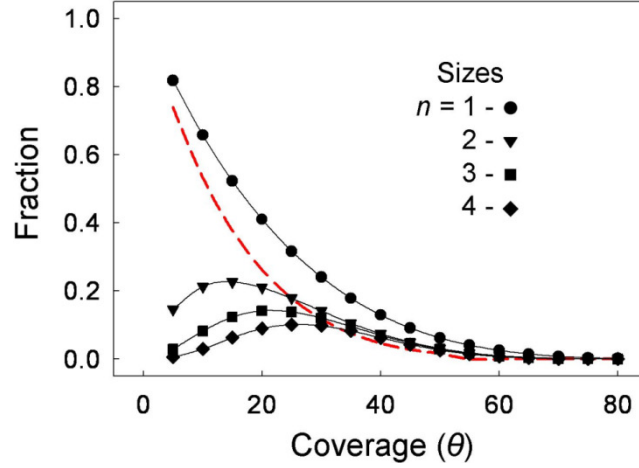


Figure 4.3. Ensemble sizes in a random fcc(100) surface alloy of two fictitious, noninteracting species. The unbroken plots show the fractions of atoms of one species which belong to ensembles of size n , as a function of that species' surface coverage in units of atomic percent. The dashed plot is for the monomer ($n = 1$) in the fcc(111) surface alloy, which has six first nearest-neighbors instead of four.

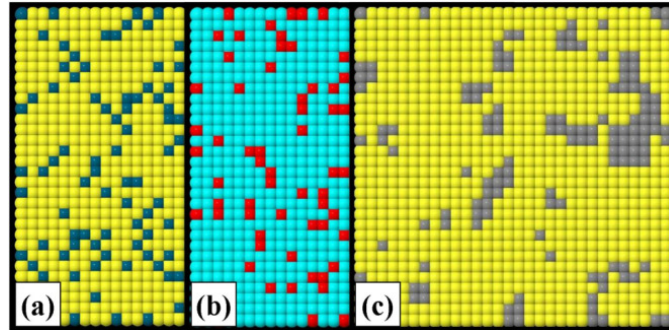


Figure 4.2. Snapshots from simulations of (a) AuPd, (b) the random alloy, and (c) AuPt at $\theta = 0.15$ and $T = 300\text{K}$. Note the tendency of Pt to agglomerate while the 1NN shells of most Pd atoms are filled entirely by Au.

Figure 4.3 shows the size distribution of ensembles of same-species atoms which

are contiguous through first nearest-neighbor (1NN) relationships as a function of coverage in units of atomic fraction (θ). Monomers ($n=1$; that is, a single atom of one species that has four first nearest-neighbors of the opposite species) are seen to monotonically decrease with increasing θ , while trends for larger-sized ensembles all pass through maxima. This can be understood by considering that the likelihood of creating a dimer or larger ensemble by placing an atom next to a monomer of the same species increases with θ . For the same reason, the trends for the dimers and other, larger

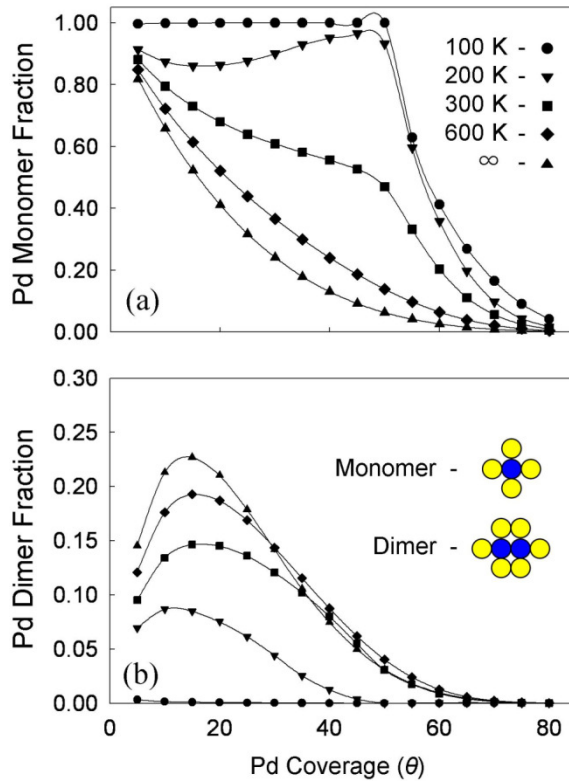


Figure 4.4. Average fraction of surface Pd atoms in (a) monomers and (b) dimers in AuPd surface alloys at several levels of coverage and temperature. As temperature increases, the monomer population declines, and the dimer population increases.

ensembles initially rise as θ increases, then begin to fall as they themselves are converted to still larger ensembles. The monomer trend for the (111) surface (dashed line), which is also included for comparison, lies significantly below the monomer trend for the (100) surface. This is due to the fact that every atom has six first nearest-neighbors with which

to form larger ensembles in the (111) surface, but only four first nearest-neighbors in the (100) surface.

The random alloy is a helpful guide to understanding qualitatively the arrangement of atoms in the AuPd and AuPt(100) surface alloys, to which we now turn. Snapshots (single microstates) from simulations of the random, AuPd, and AuPt alloys with $\Theta = 0.15$ at $T = 300\text{K}$ are shown in Figure 4.2. Figure 4.4(a) and (b) show the monomer and dimer trends in AuPd as a function of temperature and Θ , and Figure 4.5(a) and (b) show the same for AuPt. The corresponding random alloy ('infinite' temperature) results are also included on each plot.

In the AuPd alloy, all of the finite temperature monomer trends lie above the infinite temperature trend. In general, as temperature is lowered, an increasing number of Pd atoms are surrounded entirely by Au. The higher temperature trends decrease

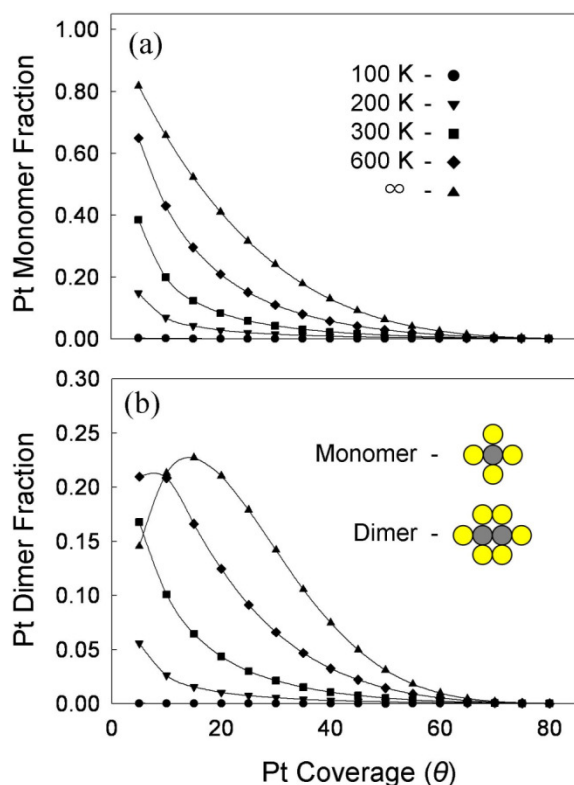


Figure 4.5. Average fraction of surface Pt atoms in (a) monomers and (b) dimers in AuPt surface alloys at several levels of coverage and temperature. As temperature increases, the monomer population also increases, and the peak in the dimer population shifts toward lower coverage.

monotonically, just as the infinite temperature trend does, but at lower temperature, this ceases to be the case. A shoulder is apparent in the 300K trend, the 200K trend has a maximum, and the 100K trend is nearly constant until it drops off suddenly, all at $\Theta \approx 0.5$. The dimer plots for the AuPd alloy exhibit the opposite behavior in that they all lie beneath the infinite temperature plots, and the population of dimers is reduced as temperature is lowered.

The temperature-dependent trends for the monomer and dimer populations in the AuPt alloy are quite different from those in the AuPd alloy. The populations of monomers at all finite temperatures are lower than in the random alloy and appear to increase with increasing temperature, the opposite of what was found for AuPd. Although the populations of the dimers are also typically lower than in the infinite temperature case (except at low Pt coverage, where the trends cross), reducing the temperature appears mainly to have shifted the trends to lower Θ rather simply reducing them as in the AuPd alloy.

Many of these observations can be explained in terms of the contrasting interatomic interactions in the AuPd and AuPt surface alloys¹⁷. In the AuPt alloy, homonuclear (Pt-Pt) interactions are energetically more favorable than heteronuclear (Pt-Au). This explains the relative scarcity of Pt monomers, which are completely surrounded by Au nearest neighbors. The AuPt dimer trends appear shifted to lower Θ because of the tendency of Pt atoms to cluster into larger ensembles which contain more Pt-Pt interactions. As the temperature is reduced, dimers may be more readily formed from monomers available in the surface (resulting in a shift in the initial rise in the dimer population trends), but also more readily converted into trimers and other larger ensembles (resulting in a shift in the decline).

In contrast to AuPt, heteronuclear interactions dominate in the AuPd surface alloy, which leads to the energetic favorability of Pd monomers and, to a lesser extent, dimers at the expense of larger ensembles. The preference for Au-Pd interactions also leads to long range ordering at low temperatures, which explains the unusual features centered around $\Theta = 0.5$ in the AuPd monomer plot. In the $c(2 \times 2)$ ordered surface (Figure 6), which is the ground state for this level of Pd coverage, every atom is surrounded by

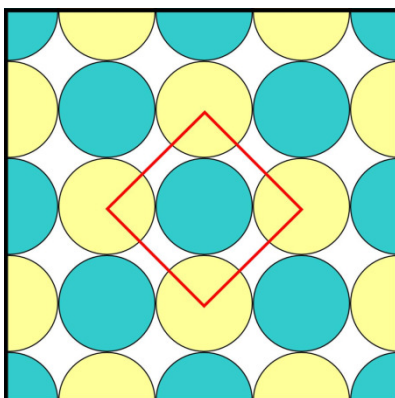


Figure 4.6. The $c(2 \times 2)$ ordered surface. Every Pd (blue) atom has four Au (yellow) nearest neighbors, and vice versa.

atoms of the opposite type, and the number of heteronuclear interactions is maximized. A related set of features occurs in the AuPd(111) ensemble distributions due to the $(\sqrt{3} \times \sqrt{3})R30^\circ$ ordered surface (Chapter 3).

4.3.2 Comparison of AuPd(100) simulation results to experiment

Goodman and coworker⁹³ have experimentally ascertained atomic arrangements in the (100) surface of one AuPd alloy sample. They prepared the (1:1 atomic ratio) sample by repeated cycles of Ar^+ sputtering and annealing, followed by annealing without sputtering at 550°C for 30 minutes. The sample was then permitted to cool to room temperature prior to STM imaging. Sample preparation and imaging were conducted in UHV conditions. The surface Pd coverage was determined by LEISS to be $\Theta = 0.1$. Statistics were collected from images of three separate locations on the surface. Rather than counting contiguous groups of atoms as we have in Figure 4.3, Figure 4.4,

and Figure 4.5, unique arrangements of the 8 nearest neighbors (4 first nearest-neighbors plus 4 second nearest-neighbors; see the labels on the horizontal axis of Figure 4.7) surrounding every surface Pd atom were tallied. The totals from the images were compared to their corresponding expectation values in the random alloy, which were analytically calculated.

In Figure 4.7, we have reproduced some of the results they reported along with

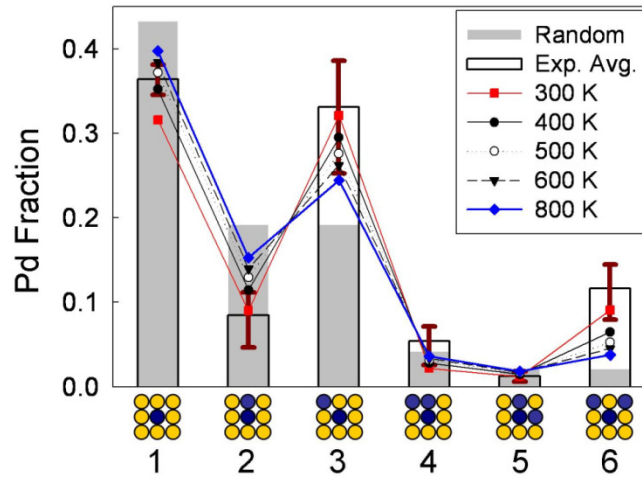


Figure 4.7. Frequency of occurrence of different Pd site-types as predicted by simulation and reported by Goodman and coworkers based on their experimental observations. The site-types depicted on the horizontal axis are among the most probable in a random fcc(100) surface alloy with $\Theta = 0.1$. One site-type with a probability equal to that of the 4th has not been included because no experimental results were reported for it. The empty bars are an average of the site counts taken from three STM images and the error bars show the maximum and minimum. The filled gray bars are for the random alloy and the points are the simulation predictions for temperatures between 300K and 800K.

our MC predictions for several temperatures between 300K and 800K. Simulation results

for a range of temperatures have been included since it is difficult to know unambiguously the equilibration temperature that the experimental results represent. The two sets of results are in basic agreement with regard to the direction of the deviation from the random alloy. That is, in both the experimental results and the MC predictions, site-type 1 was encountered somewhat less frequently than would be expected in a random alloy, site-type 2 also less, site-type 3 more, and so on. Site-types 4 and 5 are exceptions; however, together they account for only a small fraction of Pd sites, and in both cases, the simulation results and the random probabilities are within the window of experimental observations. The correspondence between experiment and simulation helps to validate our approach, the uncertainty in the equilibration temperature and the relatively small number of STM images included in the analysis notwithstanding. We further believe that our findings lend support to the proposal that, “the thermodynamic properties of AuPd alloys can be used to tailor surface ordering”⁹³, at least in some cases.

4.3.3 Additional short-range order in AuPd(100): 2NN pairs of Pd monomers

Examination of both the 1NN and 2NN shell around every surface Pd atom highlights a manifestation of AuPd interatomic interactions which is not readily apparent from the plots of monomers and dimers in Figure 4.4 and Figure 4.5 and which extends beyond the distinction between homo- and heteronuclear interactions which we have so far employed. The central atoms in site-types 1, 3, and 6 in Figure 4.7 are all Pd monomers which have four Au first-nearest neighbors. It is in their 2NN shells that the three site-types differ from one another. It is apparent that Pd monomers with no Pd second nearest-neighbors (site-type 1) are somewhat less likely than in the random alloy, while those with one or two (site-types 3 and 6) are a great deal more likely.

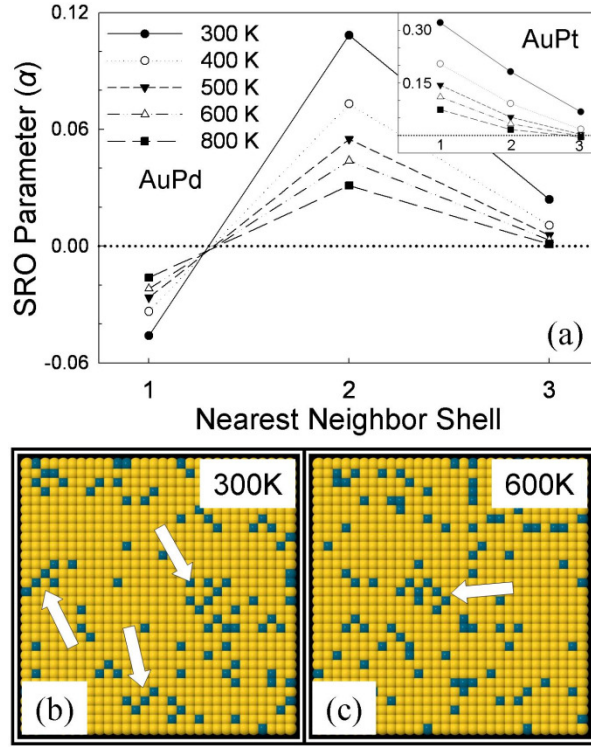


Figure 4.8. (a) The short-range order parameter (α) at the 1st, 2nd, and 3rd nearest neighbors distances for a AuPd surface with $\Theta = 0.1$. The horizontal, dotted reference line is for the random alloy, which has no SRO ($\alpha = 0$). $\alpha < 0$ indicates heteronuclear correlation and $\alpha > 0$ indicates homonuclear. The inset shows α for the AuPt surface alloy at the same Θ . In (b) (lower left) and (c) (lower right), arrows indicate some small regions of 2NN Pd-Pd correlation in a snapshot from a simulation of the AuPd surface at $T = 300\text{K}$ and 600K .

The short range order (SRO) parameter⁹⁴ $\alpha(r) = 1 - p_{AB}(r)/x_B$, where x_B is the overall fraction of the surface atoms which are species B, and $p_{AB}(r)$ is the probability of finding a B atom a distance of r from an A atom, shows this as well [Figure 4.8(a)]. In a completely random alloy, $\alpha(r)$ is always 0. In the simulated AuPd alloys, at the 1NN

distance, α is negative, indicating a surplus of Pd-Au 1NN pairs. At the 2NN distance, α is positive, showing Pd-Pd correlation. Some SRO persists at the 3NN neighbor distance, but it is much lower. The simulation snapshots in Figure 4.8(b) and (c) help to illustrate these more quantitative measures of atomic arrangement. White arrows indicate a few of the small patches of Pd monomers standing at the second and third nearest neighbor distance from one another. A plot of $\alpha(r)$ for a AuPt surface alloy at the same temperature and level of coverage is included in the inset of Figure 4.8 (a) for comparison.

It is instructive to compare the DFT-predicted formation energies of an isolated Pd monomer and the c(2×2) ordered surface, in which all 1NN interactions are heteronuclear and all 2NN interactions are homonuclear. The formation energies were calculated using $E_f = \{E_{AuPd} - E_{Au} + N_{Pd}(E_{Au-bulk} - E_{Pd-bulk})\}/N_{Pd}$, where E_{AuPd} , E_{Au} , $E_{Au-bulk}$, and $E_{Pd-bulk}$ represent the total energies of AuPd/Pd(100), Au/Pd(100), bulk Au (per atom), and bulk Pd (per atom), respectively, and N_{Pd} indicates the number of Pd atoms in the AuPd surface alloy. We found that the formation energy per Pd atom of a monomer is about 0.02 eV higher than that of the c(2×2) ordered surface.

The lower E_f of the c(2×2) ordered surface helps explain the abundance of sites that include 2NN Pd-Pd pairs in Figure 4.7, the degree of 2NN SRO seen in Figure 4.8 (a), and the visible patches of ordered monomers in Figure 4.8(b) and (c). It also highlights the danger of neglecting longer range (>1NN) interactions when modeling surface alloys. A Hamiltonian that includes only 1NN pair interactions would yield the same E_f for the Pd monomer and the c(2×2) ordered surface and thus would be expected to incorrectly predict their relative contributions to ensemble averaged properties of AuPd surface alloys. It is true that heteronuclear, 1NN pair interactions can produce some degree of SRO at longer range because they in effect “push” like atoms out of the 1NN shell into longer range shells which they consequently enrich. However, when we

adjusted a 1NN pair model to yield the same SRO at the 1NN distance as our cluster expansion at $T = 500\text{K}$ and $\Theta = 0.1$, it predicted negligible 2NN SRO, in sharp contrast to both the experimental and cluster expansion-based simulation results. Since correctly predicting 2NN SRO may be important in explaining the catalytic properties of surface alloys⁶, this discrepancy argues against the use of 1NN pair models for this purpose.

4.4 SUMMARY

Using density-functional theory calculations, we created two cluster expansion Hamiltonians, one for AuPd/Pd(100) surface alloys, and the other for AuPt/Pt(100). Pair and multi-body interactions up to the 3NN distance were considered for inclusion in the models. The cluster expansions were used in canonical ensemble Monte Carlo simulations of AuPd and AuPt surface alloys over a range of temperature and Pd or Pt coverage. The simulations show that the differing interatomic interactions present in the two alloys result in dramatically different arrangements of atoms. In the AuPt alloy, in which homonuclear (Pt-Pt) interactions prevail, the population of isolated Pt monomers is depressed compared to the random alloy, but increases with temperature. The population of Pt dimers exhibits a maximum which is shifted toward lower coverage as the temperature decreases. Heteronuclear (Au-Pd) interactions are stronger in the AuPd alloy, which favors the formation of monomers and, to a lesser extent, dimers. The population of Pd monomers decreases with temperature, while the dimer population increases. At low temperature and a Pd coverage of $\Theta = 0.5$, heteronuclear interactions also lead to the formation of a $c(2 \times 2)$ ordered surface, in which the four first nearest-neighbors of every atom is of the opposite species. We also compared some of the results from our simulations of the AuPd surface alloy to the reported experimental findings of Goodman and coworkers. The two were found to be in substantial agreement, lending support to our

approach and also to their proposal that the thermodynamics of AuPd alloys might be used to tailor their surface atomic arrangements. One observation common to both our simulations and their experiments is the existence of a greater-than-expected number of 2NN pairs of Pd monomers; the catalytic importance of this ensemble has already been demonstrated experimentally. It is noteworthy that Hamiltonians based only on 1NN pair interactions would appear to be inadequate to account for the frequency with which 2NN Pd pairs are encountered in the AuPd (100) surface. These results increase our confidence that our approach, Monte Carlo simulation based on cluster expansions, is capable of providing insight into the atomic arrangements of surface alloys for the purpose of elucidating their catalytic properties.

Chapter 5: The Strained AuPd/Pd(100) Surface Alloy

5.1 INTRODUCTION

The application of strain has been investigated extensively as a method of modifying the catalytic properties of metal surfaces. Theoretical and experimental studies of late transition metal surfaces, for example, have revealed that biaxial strain induced by, for example, a lattice mismatch between a pure, epitaxially deposited metal overlayer and a dissimilar metal substrate can lead to modified surface reactivity^{11,95-104}. However, the potential effects of biaxial strain on the arrangement of atoms in a surface alloy have, so far as we know, not been investigated nearly so extensively. Owing to the demonstrated importance of ensemble effects in many catalytic systems, this is a shortcoming that we wished to address.

In this chapter, we report the results of a theoretical investigation of the influence of strain on the atomic arrangement of AuPd/Pd(100) surface alloys. We considered three different strain conditions: Strain-free, 2% compressive strain, and 4% tensile strain. We chose this alloy and facet largely because it is known to host a greater-than-expected concentration of catalytically interesting second nearest-neighbor (2NN) pairs of Pd monomers. We first generated cluster expansion (CE) Hamiltonians from the results of density functional theory (DFT) calculations on a training set of model surfaces, which we then used in canonical ensemble Monte Carlo simulations of surface alloys to obtain finite-temperature predictions of their properties. The key result of this study is that under 2% compressive strain, the tendency of the surface to order and to form 2NN monomer pairs is increased compared to the strain-free case, while under 4% tensile strain, it is reduced.

5.2 METHODOLOGY

5.2.1 The Cluster Expansion Method

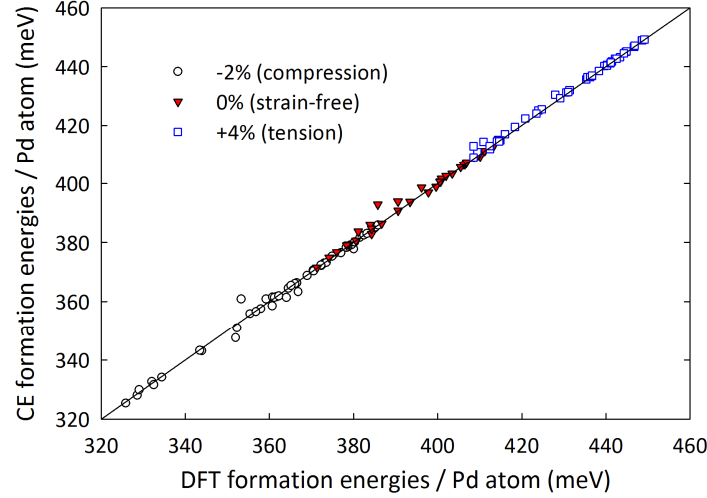


Figure 5.1. Formation energies per surface Pd atom (E_f/N_{Pd}) of the model surfaces in each training set, where $E_f = E_{AuPd} - (E_{Au} + N_{Pd} \cdot \Delta E_{Pd-Au})$. In this expression, E_{AuPd} and E_{Au} are, respectively, the total energies of the model surface in question and a model surface with a pure Au surface layer, and ΔE_{Pd-Au} is the difference in the cohesive energies of bulk Pd and Au.

In this work, we chose to model the energetics of the strained AuPd/Pd(100) surface by preparing separate cluster expansions for each of the strain conditions that we considered, each having its own training set of model surfaces (described in the following section). Cross validation score minimization was used to select from among candidate 2-body clusters with up to 5th nearest-neighbor interactions and 3- and 4-body clusters with up to 4th nearest-neighbor interactions. To improve sampling of the low energy region of the potential energy surface, the training sets were also iteratively expanded to include global minima as they were discovered by candidate CEs. The procedure we followed is described in greater detail in Chapter 2.

The final CE for the compressive strain case contained a total of 14 clusters, and the associated training set contained 51 model surfaces. For the strain-free and tensile cases, these quantities were (14 clusters, 45 surfaces) and (15 clusters, 49 surfaces), respectively. The clusters and ECIs for each strain condition are shown in Table 5.1.

Table 5.1. Clusters and ECIs for each strain condition considered. Pd is spin down (-1) and Au is spin up (+1).

2% Compression		Strain-Free		4% Tension	
Cluster	ECL, meV	Cluster	ECL, meV	Cluster	ECL, meV
Empty	1.85450636e+02	Empty	2.04188719e+02	Empty	2.19039037e+02
Point	-1.92351093e+02	Point	-2.08394424e+02	Point	-2.27812364e+02
(1,0)	7.30184811e+00	(1,0)	5.44405978e+00	(1,0)	4.80639218e+00
(1,1)	-4.24548795e+00	(1,1)	-3.86100527e+00	(1,1)	-2.12944464e+00
(2,0)	7.30438761e-01	(1,0);(0,1)	-3.41407295e-01	(2,0)	-3.50272344e-01
(2,1)	3.35283741e-01	(1,0);(2,0)	8.54348214e-01	(1,0);(0,1)	-4.95481534e-01
(1,0);(0,1)	-4.19913803e-01	(1,1);(2,0)	-1.56993104e-01	(1,0);(2,0)	1.34674051e+00
(1,0);(2,0)	9.15397099e-01	(0,2);(2,1)	-1.24900792e-01	(1,1);(2,1)	2.02970429e-01
(1,1);(2,0)	-3.81950900e-01	(1,1);(2,1); (1,2)	1.97837618e-01	(0,2);(2,1)	-1.51739369e-01
(0,1);(2,1)	1.32076102e-01	(1,1);(2,1); (2,0)	2.02586151e-01	(0,1);(1,1); (1,2)	1.68068397e-01
(2,1);(1,2)	-1.24055321e-01	(0,2);(1,1); (2,1)	-3.06952291e-01	(1,1);(2,1); (2,0)	1.87181144e-01
(1,1);(2,1); (1,2)	2.93404379e-01			(0,2);(1,1); (2,1)	-2.66476399e-01
(0,2);(1,1); (2,1)	-1.57010033e-01			(0,2);(1,2); (2,1)	1.69105310e-01
(0,1);(1,1); (2,1)	-1.11313251e-01				
(1,1);(1,-1); (2,0)	-4.98309871e-01				

5.2.2 Density functional theory

The DFT calculations were spin polarized and used the GGA-PW91 functional⁸⁸ as implemented in the Vienna Ab-initio Simulation Package (VASP)⁸⁹. The projector augmented wave (PAW) method with a planewave basis set was employed to describe the interaction between core and valence electrons⁹⁰. The valence configurations employed to construct the ionic pseudopotentials are $5d^{10} 6s^1$ for Au and $4d^9 5s^1$ for Pd. An energy cutoff of 350 eV was applied for the planewave expansion of the electronic eigenfunctions. For Brillouin zone integration in the model surfaces, a $(6 \times 6 \times 1)$

Monkhorst-Pack mesh of k-points was used. This is a higher k-point density than we used previously to study the energetics of surface alloys, but it was deemed to be necessary in order to adequately resolve the effects of strain.

As in our previous work, the models used to represent AuPd/Pd(100) surfaces in our DFT calculations were four layer slabs, each consisting of a 4×4 AuPd(100) surface layer atop three additional (100) layers of pure Pd. The top and bottom of the slabs were separated through a periodic boundary by the equivalent of 7 atomic layers. The bottom two layers were fixed at bulk positions, and the top two were relaxed until all the atomic force components were smaller than 0.03 eV/Å. Biaxial strain was simulated by uniformly changing the surface-parallel dimensions of the supercell by -2%, 0%, or +4% of the bulk Pd value, which was determined by DFT to be 3.961 Å. The surface-perpendicular separation of the fixed Pd layers was also adjusted to account for strain-induced relaxation in that direction. The extent of the relaxation was determined by applying biaxial strain to a bulk Pd sample, then minimizing the energy with respect to the supercell size along the perpendicular direction. The ratio of applied strain to response determined from these calculations is -0.689 and -0.586 for 2% compression and 4% tension, respectively, which closely match a Hooke's law-based prediction made using experimentally measured 0K elastic stiffness constants for Pd (-0.665)³⁰.

Predictions made using the cluster expansions are compared to DFT results in Figure 1. Each point represents the formation energy (on a per Pd atom basis, defined in the caption) of a model surface from the CE training sets. The energies span a range of approximately 140 meV, and the CE predictions exhibit only very small departures from the DFT reference energies.

5.2.3 Monte Carlo Simulations

Once completed, the three cluster expansions were incorporated into canonical ensemble Monte Carlo simulations of the AuPd/Pd(100) surface. All of the surfaces we simulated contained 30×30 (100) surface unit cells for a total of 900 atoms. The surfaces were first annealed at high temperature and then cooled and equilibrated at the simulation temperature over a period of 7×10^5 steps per site. Properties of the atomic configuration were then calculated and averaged over 1×10^5 steps per site. The candidate configurations evaluated at the beginning of each step were generated by swapping randomly selected Au and Pd atoms. Past experience has shown this procedure to be adequate to erase any bias from the initial configuration and to achieve consistency between repeated runs at the same simulation temperature and composition.

5.3 RESULTS AND DISCUSSION

5.3.1 Monte Carlo Simulations

Figure 5.2 shows snapshots from simulations of select AuPd/Pd(100) surfaces with different composition ratios and degrees of strain. While some qualitative trends may be evident from the images, they are chiefly intended to complement and aid in the interpretation of the results which will be presented in Figure 5.3 and Figure 5.4, in which each “point” is an average over all the configurations visited in the course of a separate MC simulation, as just discussed.

Figure 5.3 shows the effect of strain on the population of Pd monomers in AuPd/Pd(100) at $T = 300\text{K}$. The monomer population is found to be increased by

Degree of strain

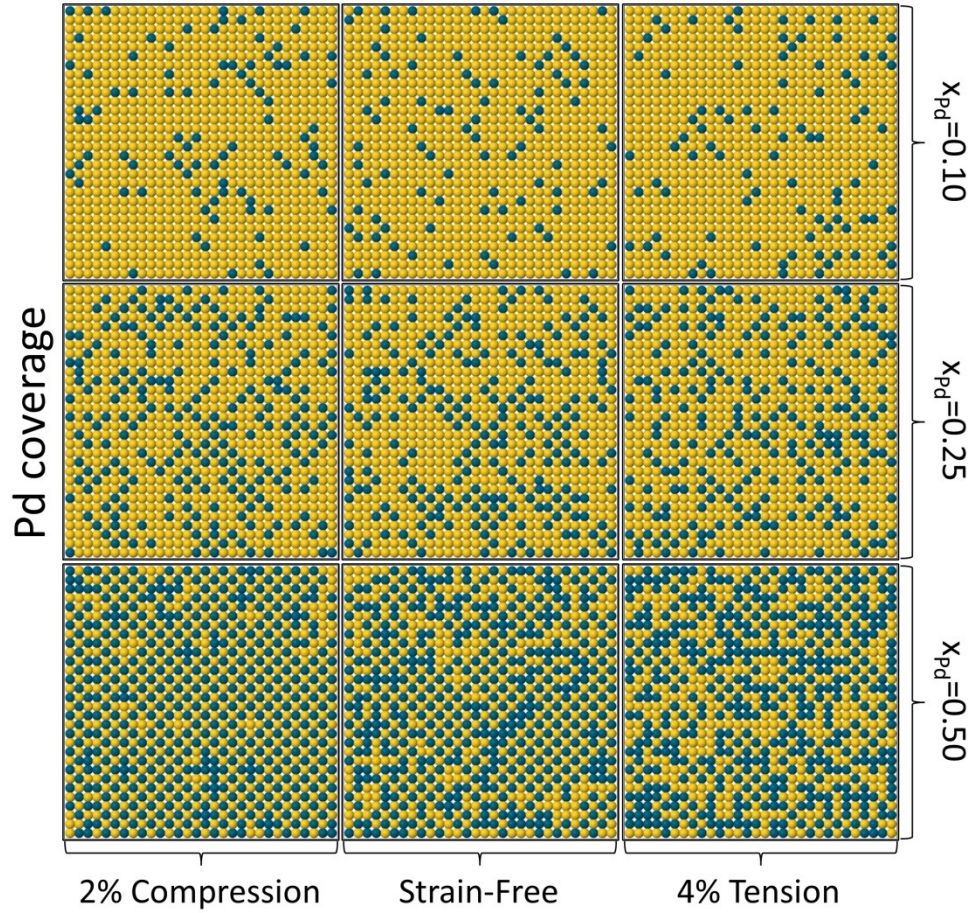


Figure 5.2. Snapshots from MC simulations of AuPd/Pd(100) under different strain conditions and with different levels of Pd coverage, x_{Pd} .

compression and reduced by tension, relative to the strain-free case, over the entire composition range considered. The strain effect becomes greatest at a Pd atomic fraction of $x_{\text{Pd}} = 0.45\text{-}0.50$, where the population of monomers in the compressively strained surface is about 1.8 and 3.3 times larger than in the strain-free and tensile cases, respectively.

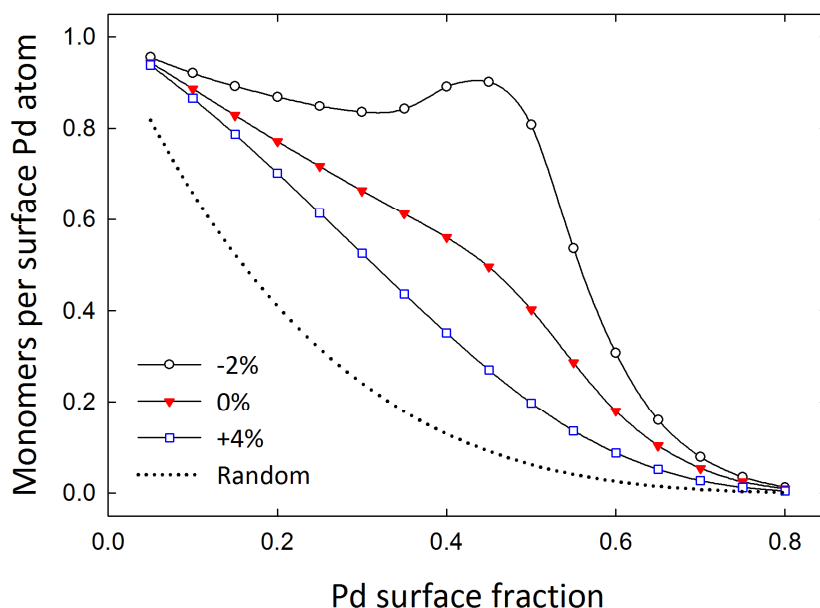


Figure 5.3. Number of Pd monomers per surface Pd atom at $T = 300$ K, obtained from MC simulation, under compressive (-2%), strain-free (0%), and tensile (+4%) conditions.

It can also be seen that under all three strain conditions (-2%, 0%, 4%), the population of monomers is larger in the AuPd/Pd(100) surface than in a random alloy (which has no interatomic interactions). In our previous work on AuPd surfaces, we showed that Pd monomers form in greater-than-expected numbers because of a preference for heteronuclear (Au-Pd) over homonuclear (Au-Au, Pd-Pd) interactions. The differences between the population of monomers in the strained surfaces suggest that compressive strain strengthens heteronuclear interactions relative to homonuclear ones, and that tensile strain weakens them.

Due to their importance in a number of surface reactions, we next considered how strain affects the population of 2NN pairs of Pd monomers. In Figure Figure 5.4, we plot the number of 2NN pairs per surface Pd atom as a function of x_{Pd} and degree of strain, as obtained from MC simulations at $T = 300$ K. The number of 2NN pairs is increased by

compressive strain and reduced by tensile strain. The strain effect becomes especially pronounced in the region of $x_{\text{Pd}} = 0.5$, where the number of pairs in the compressed surface is almost 8 times greater than in the tensile case.

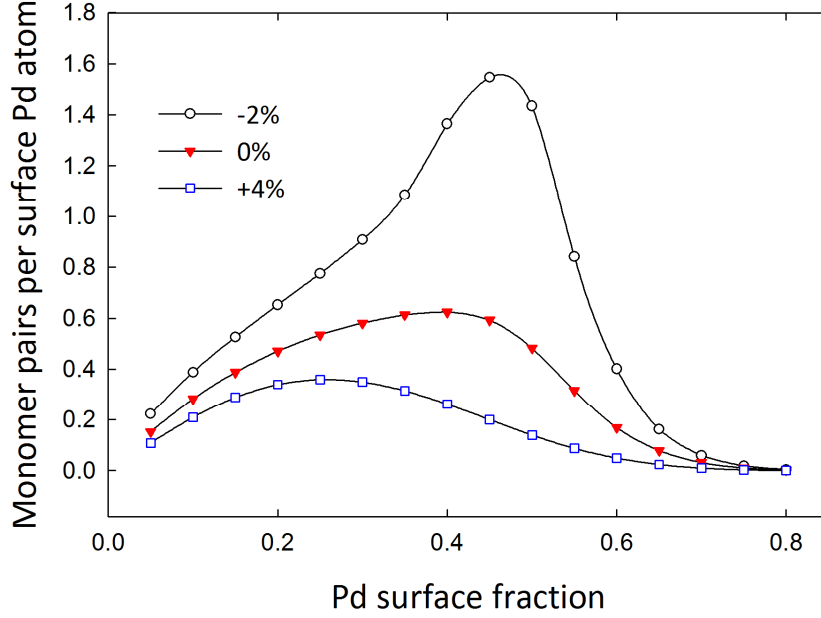


Figure 5.4. Number of 2NN pairs of Pd monomers per surface Pd atom at $T = 300$ K, obtained from MC simulation, under compressive (-2%), strain-free (0%), and tensile (+4%) conditions.

The origin of this sizeable difference between the compressive and tensile surfaces at $x_{\text{Pd}} = 0.5$ can be clarified by examining the last row of snapshots in Figure 5.2. In particular, the compressed [5.2(c)] surface appears to be well ordered, with several extended $c(2 \times 2)$ -like patches. Note that in the (100) surface facet, $c(2 \times 2)$ order maximizes the number of monomers and 2NN monomer pairs. Patches of $c(2 \times 2)$ order also exist in the strain-free surface [5.2(f)], but are visibly smaller, and in the 4% tensile case [5.2(h)], they have nearly vanished.

This effect of strain on ordering can be measured using the Warren-Cowley short range order (SRO) parameter⁹⁴, which we restrict here to the first nearest neighbor shell:

$$\alpha = 1 - \frac{p_{AB}}{x_B} \quad (5.1)$$

In eq. (5.1), p_{AB} is the probability (in an alloy of A and B atoms) that a first nearest neighbor of a randomly selected A atom will be a B atom, and x_B is the fraction of B atoms in the surface. In a completely random alloy, there is no tendency for A atoms to preferentially attract either A or B atoms into their 1NN shells, so $p_{AB} = x_B$, and therefore $\alpha = 0$. On the other hand, in a AuPd(100) surface alloy with $x_B = 0.5$ and perfect $c(2 \times 2)$ order, the 1NN shell of every atom is populated entirely by dissimilar atoms, so $p_{AB} = 1$, and $\alpha = -1$.

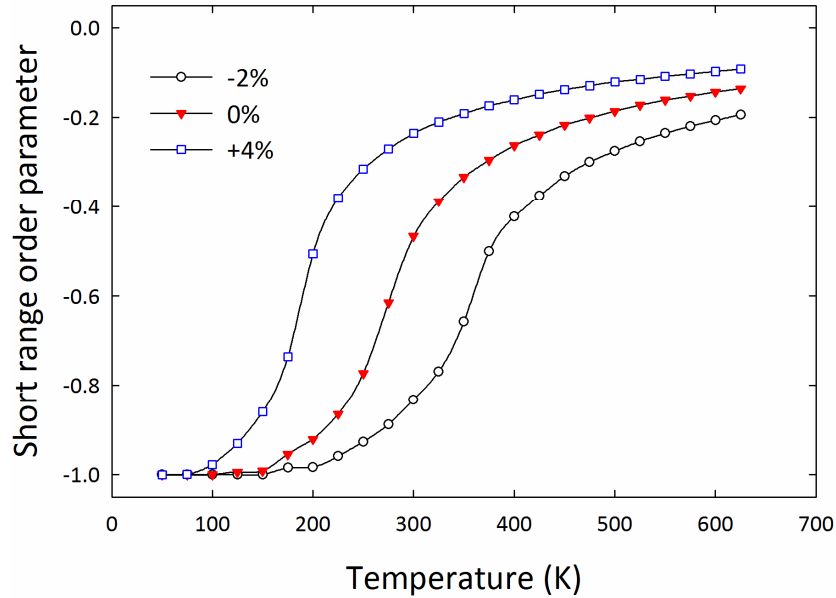


Figure 5.5. Short-range order as a function of temperature when $x_{Pd} = 0.5$.

Figure 5.5 shows the MC-predicted dependence of α on temperature and strain for $x_{Pd} = 0.5$. The plots indicate that at low temperatures, the AuPd/Pd(100) surface exhibits perfect $c(2 \times 2)$ order under all three strain conditions considered. As the

temperature rises, the arrangement of Au and Pd atoms in the surface becomes increasingly random; however, compressive strain is seen to significantly delay the deterioration of order.

These results clearly demonstrate that compressive strain promotes the formation of monomers and stabilizes $c(2\times 2)$ -like order in the AuPd/Pd(100) surface. To gain more insight into this finding, we turned next to examining how the surface electronic structure is modified by alloying and strain.

5.3.2 Electronic Structure

Figure 5.6 shows the electron density of states (DOS) projected onto the d orbitals of Pd and Au atoms in the strain-free $c(2\times 2)$ surface; results for the unalloyed Pd/Pd(100) and Au/Pd(100) surfaces are also shown for comparison. Formation of the $c(2\times 2)$ surface alloy is found to significantly enhance the Pd DOS in the high binding tail about 4-6 eV below the Fermi level [Figure 5.6(a), top panel].

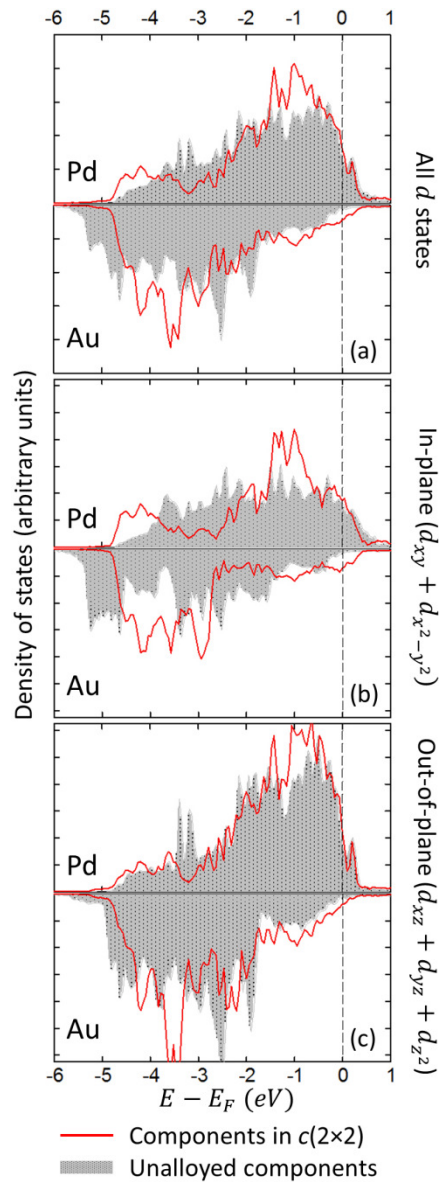


Figure 5.6. Surface Pd d DOS (red line, upper panels) and Au d DOS (red line, lower panels) for the strain-free $c(2\times 2)$ surface, compared to their respective pure surfaces, Pd/Pd(100) and Au/Pd(100) (grey backgrounds). All plots have been normalized independently and shifted to place the Fermi energy at 0 eV. For clarity, the scales of the graphs showing the In-plane (b) and Out-of-plane (c) components have also been magnified $2\times$ relative to the Total (a).

As can be seen by comparing the top panels of Figure 5.6(b) and (c), this enhancement is due almost entirely to a downshift of in-plane ($d_{xy} + d_{x^2-y^2}$) states; the out-of-plane ($d_{xz} + d_{yz} + d_{z^2}$) states in the tail region are affected comparatively little. A concurrent upshift of Au in-plane states also occurs [Figure 5.6(b), lower panel], indicating significant hybridization between the in-plane Au 5d and Pd 3d states, which may contribute to the stability of the $c(2 \times 2)$ surface.

To better understand the relative stability of different arrangements of surface atoms under different strain conditions, we compared the $c(2 \times 2)$ surface and a $p(4 \times 2)$ -ordered surface which is shown schematically in Figure 5.7; the $p(4 \times 2)$ surface has the same composition ($x_{\text{Pd}} = 0.5$) but a smaller number of Au-Pd nearest neighbors. As expected, the $c(2 \times 2)$ surface is energetically more stable than the $p(4 \times 2)$, and the

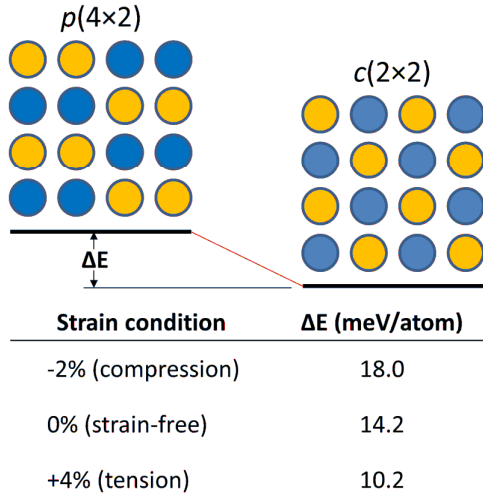


Figure 5.7. Strain-dependent differences in the total energies of the $p(4 \times 2)$ and $c(2 \times 2)$ surfaces that we examined.

difference is greatest under compression and least under tension. The strain effect on relative stability can be explained by examining the electronic structures of the two surfaces.

As shown in Figure 5.8, under all three strain conditions considered, the Pd d DOS of both surfaces show enhancement in the tail region (below around -4 eV from the

Fermi level); this is due apparently to in-plane Au 5*d*-Pd 4*d* hybridization. The two surfaces nonetheless differ in that the enhancement is consistently more pronounced in

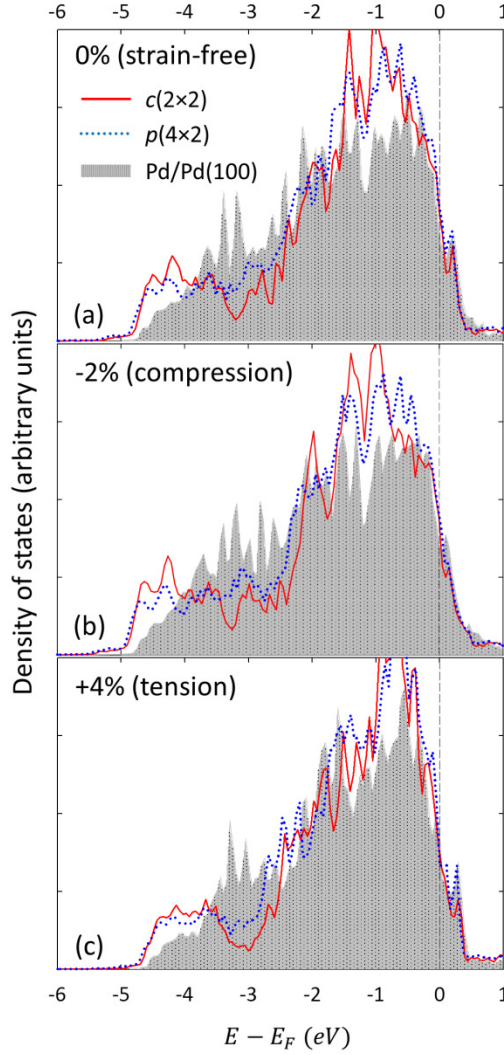


Figure 5.8. Surface Pd *d* DOS for the $c(2 \times 2)$ (red, solid line) and $p(4 \times 2)$ (blue, dotted line) surfaces compared to Pd/Pd(100) (grey background) under different strain conditions. All plots have been normalized independently and shifted to place the Fermi energy at 0 eV.

$c(2 \times 2)$, due to its larger number of Au-Pd neighbors. This difference is visibly largest when the surfaces undergo compression [Figure 5.8(b)] and smallest when they undergo tension [Figure 5.8(c)], paralleling the trend in their relative stability as described earlier. This suggests that compressive strain stabilizes $c(2 \times 2)$ -like order (and also promotes monomer formation) by, at least in part, magnifying the effects of in-plane *d*-*d* hybridization between neighboring Au and Pd atoms.

5.4 SUMMARY

Using density-functional theory calculations, we created three cluster expansion Hamiltonians for the AuPd/Pd(100) surface alloy undergoing biaxial strain: one for 2% compression, one for the strain-free case, and the last for 4% tension. Pair interactions up to the 5NN distance and 3- and 4-body interactions up to the 4NN distance were considered for inclusion in the models. The cluster expansions were used in canonical ensemble Monte Carlo simulations of the strained surface alloys over a range of temperature and Pd.

The simulations show that differing strain conditions result in dramatically different arrangements of atoms. In particular, compressive strain was seen to increase the number of Pd monomers relative to the strain-free case, and tensile strain was seen to reduce it. The number of second nearest-neighbor pairs of Pd monomers was similarly enhanced by compressive strain. Short range order in the $x_{\text{Pd}} = 0.5$ surface is also maintained until significantly higher temperatures in the compressed surface.

We also examined the effects of strain and atomic configuration on the d-band electron density of states of two AuPd(100)/Pd surfaces: one with c(2×2) order and the other with p(4×2) order. After comparing the Au and Pd d-band DOS of these two surfaces to one another under different strain conditions, we concluded that hybridization between in-plane Au and Pd *d* states, evidenced by an enhancement in the Pd d-band DOS at high binding energy, may be responsible for the improved stability of the c(2×2) surface under compressive strain.

These results increase our confidence that our approach, Monte Carlo simulation based on cluster expansions, is capable of providing insight into and perhaps even optimizing the atomic arrangements of surface alloys for the purpose of elucidating and improving their catalytic properties.

Chapter 6: Near-surface layers of the bulk AuPd(100) alloy

6.1 INTRODUCTION

In previous chapters, the surfaces of alloy catalysts were modeled using relatively thin slabs, in which alloying was confined to the topmost layer. Using this model, we investigated how finite-temperature atomic configuration was modified by variables such as strain, crystallographic surface facet, and chemical composition. The same basic model has been used to great benefit in a large number of other theoretical and experimental investigations of alloy catalysts.

However, surface-confined alloys can be relatively difficult to construct experimentally and likely are unstable at elevated temperatures, which limits their technological relevance. As a result, experimental workers have shown considerable interest in characterizing more convenient and applicable model systems. The Goodman group, for example, has studied surface segregation and surface atomic arrangement in thin, 10-layer AuPd alloys deposited on Mo(110) substrates^{105,106}. In these experiments, overall Au-Pd ratio, annealing temperature, and annealing time were systematically varied. They similarly examined the (100) surface facet of a bulk AuPd alloy that had a 1:1 atomic ratio⁹³. In another study, Tysoe and coworkers evaporated multiple layers of Au onto the (111) surface facet of a single crystal Pd substrate and investigated the effects of annealing temperature on surface segregation and other structural properties^{107,108}.

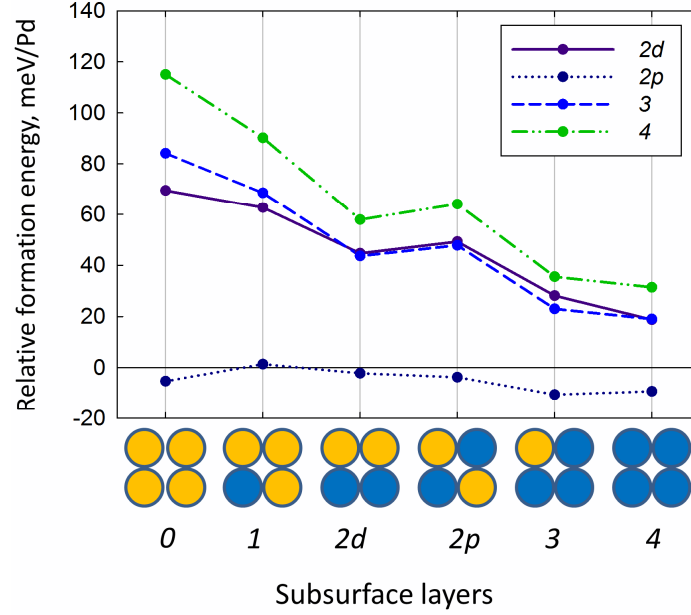


Figure 6.1. Formation energy of four, 2×2 surface configurations as a function of subsurface atomic arrangement. $E_f(\mathbf{i}, j) = E_{i/j} - (E_{0/j} + N_{Pd} \cdot \Delta E_{Pd-Au})$, where $E_{i/j}$, $E_{0/j}$, and ΔE_{Pd-Au} are the total energies of the surface i on subsurface j , pure Au surface (i.e. 0) on subsurface j , and the difference in the cohesive energies of bulk Pd and Au. N_{Pd} is the number of Pd atoms in the surface. The formation energies in the plot are additionally divided by N_{Pd} and presented relative to $E_f(\mathbf{1}, j)$.

The likely presence of near-surface configurational disorder raises concerns about the applicability of the surface-confined alloy model to these more complex systems. For example, the effects on surface atomic arrangement of subsurface disorder are largely unknown and may be quite significant. The results shown in Figure 6.1 would seem to confirm this suspicion. There we have plotted the relative stability of four distinct arrangements of Au and Pd atoms in a (100), 2×2 surface (vertical axis) as a function of the atomic arrangement of the 1st subsurface layer (horizontal axis). It can be seen that as

the concentration of Pd in the subsurface is lowered and its atomic configuration changes, the relative stability of the surface layers is substantially altered.

A theoretical strategy that addresses the interrelationships between all of these variables (bulk composition, surface composition, temperature, and surface and subsurface atomic arrangement) would clearly be of benefit in understanding the properties of alloy catalysts. Indeed, this need has been recognized by others, and several attempts to provide such a framework have been reported. However, they all suffer from various shortcomings. A number of studies have relied upon empirical potentials (such as the Embedded Atom Method), which may lack sufficient accuracy to correctly predict finer details of the surface atomic arrangement¹⁰⁹⁻¹¹³. The cluster expansion based studies conducted by Yuge *et al.* surmount this particular difficulty, but are somewhat complex (in simulations of Pt-Rh and Cu-Pt surfaces, their approach led to CEs with 39 and 51 ECIs, respectively), and, as will be discussed later, they also may encounter certain methodological problems^{114,115}.

In this chapter, a new method of predicting the surface concentration and surface atomic arrangement of binary alloys as a function of temperature and bulk composition will be described. A bulk AuPd alloy terminated by a (100) surface facet will be used as an example. As in previous chapters, the approach is based on a Monte Carlo simulation scheme, but in the grand canonical, rather than the canonical, ensemble. The surface terminated bulk was modeled as multilayer slab, which represented the near-surface region, in thermal and chemical equilibrium with a bulk reservoir of Au and Pd atoms. The energetics of the two systems were described using a cluster expansion Hamiltonian constructed on the basis of density functional theory calculations.

After a brief description of the technical details pertaining to the DFT calculations, the results of a DFT-based study of AuPd(100) slabs will be reported. The

purpose of this study was to identify the minimum size of slab needed to achieve energetic convergence and also to establish a set of simplifying assumptions that could be made in the formulation of a cluster expansion for the system.

Next, construction of the cluster expansion will be described. The procedure in this chapter differs in important ways from the approach used in previous ones.

Finally, the grand canonical ensemble Monte Carlo (GCMC) simulation scheme will be discussed. An initial attempt was made to use a framework known as Direct Exchange Monte Carlo (DEMC)¹¹⁰ to implement GCMC, but was found to fail in certain cases. The reasons for this failure will be clarified.

After the method has been fully explained, simulation results will be discussed in light of the experimental findings of other researchers as well as the results presented in earlier chapters.

6.2 DENSITY FUNCTIONAL THEORY

The DFT calculations were spin polarized and used the GGA-PW91 functional⁸⁸ as implemented in the Vienna Ab-initio Simulation Package (VASP)⁸⁹. The projector augmented wave (PAW) method with a planewave basis set was employed to describe the interaction between core and valence electrons⁹⁰. The valence configurations employed to construct the ionic pseudopotentials are $5d^{10} 6s^1$ for Au and $4d^9 5s^1$ for Pd. An energy cutoff of 350 eV was applied for the planewave expansion of the electronic eigenfunctions. For Brillouin zone integration in the model surfaces studied in section 6.2, a $(4 \times 4 \times 1)$ Monkhorst-Pack mesh of k-points was used, regardless of slab thickness. For those used in the training sets described in section 6.5, which were all the same thickness, but varied in lateral dimension, we employed a $(N \times N \times 1)$ mesh, where N was adjusted to maintain a consistent density. For the $2 \times 2 \times 15$ atom slabs, $N = 6$.

In all cases the equivalent of at least 7 layers of vacuum space separated the top and bottom surfaces of the slabs through the periodic boundary. All atoms in the slabs were permitted to relax until all of their force components were smaller than 0.02 eV/Å.

6.3 SLAB ENERGETICS

In the method used by Yuge *et al.* in Refs. 114 and 115, a set of clusters which was previously found to reasonably capture the energetics of the bulk is re-used in the slab. However, because the symmetry of the clusters is broken by the surface, they become layer dependent. This is illustrated by a pair of diagrams in Ref. 115 which is reproduced in Figure 6.2. The left panel shows the set of clusters in the bulk, and the right panel shows their expansion into a much larger set in a nine layer slab. Each of the 51 slab clusters has its own ECI. This procedure received somewhat limited justification by an appeal to the convergence of the layer-dependent ECIs to their bulk values (see Figure 4 in Ref. 115).

While it is more than plausible that interatomic interactions in an alloy would be affected by the presence of a surface, it would be beneficial to determine the ways and

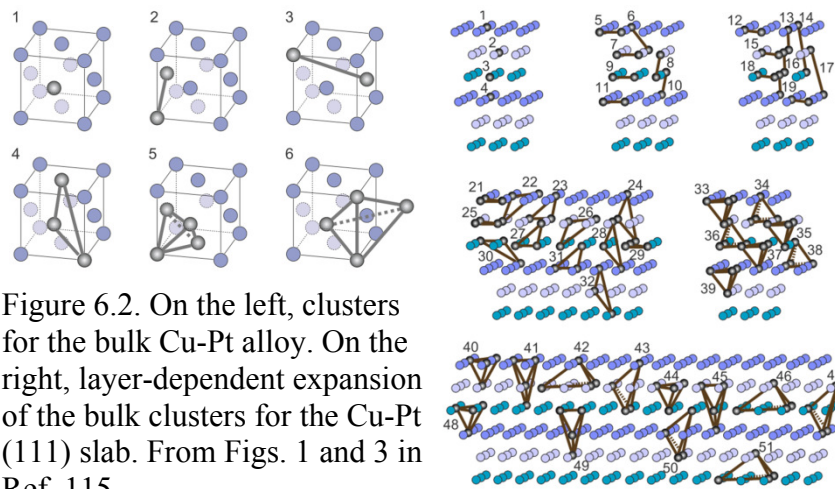


Figure 6.2. On the left, clusters for the bulk Cu-Pt alloy. On the right, layer-dependent expansion of the bulk clusters for the Cu-Pt (111) slab. From Figs. 1 and 3 in Ref. 115.

extent to which this actually occurs before formulating a perhaps overly complex

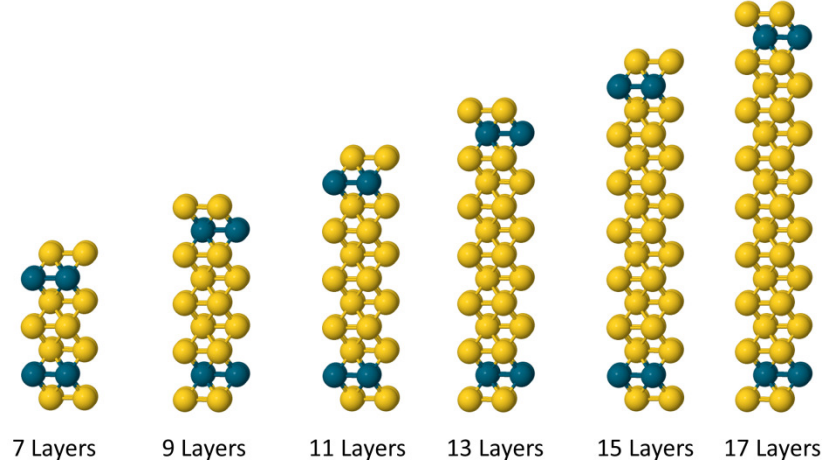


Figure 6.3. Structures with between 7 and 17 (100) layers were used to determine the convergence of relative formation energies within a AuPd slab.

Hamiltonian. Other concerns—such as the slab thickness required for convergence of the layer-dependent energetics—must also be addressed.

Figure 6.3 shows a side view of the structures we used to answer some of these questions. Each is an Au slab terminated by (100) surface facets on top and bottom. Two layers in each slab were replaced by Pd impurity layers, and the slabs were fully relaxed using DFT. The pairs of Pd layers, which were always mirror images of one another, had one of the 2×2 atomic arrangements schematically shown along the horizontal axis of Figure 6.1. In the text, these will be referred to as “impurity layers”, and also by label in italicized text, e.g. *1*, *2d*, etc.

The formation energies of the Pd impurity layers were calculated using

$$E_f = (E_{AuPd} - E_{Au} - N_{Pd} \cdot \Delta E_{Pd-Au}) / N_{Pd} \quad (6.1)$$

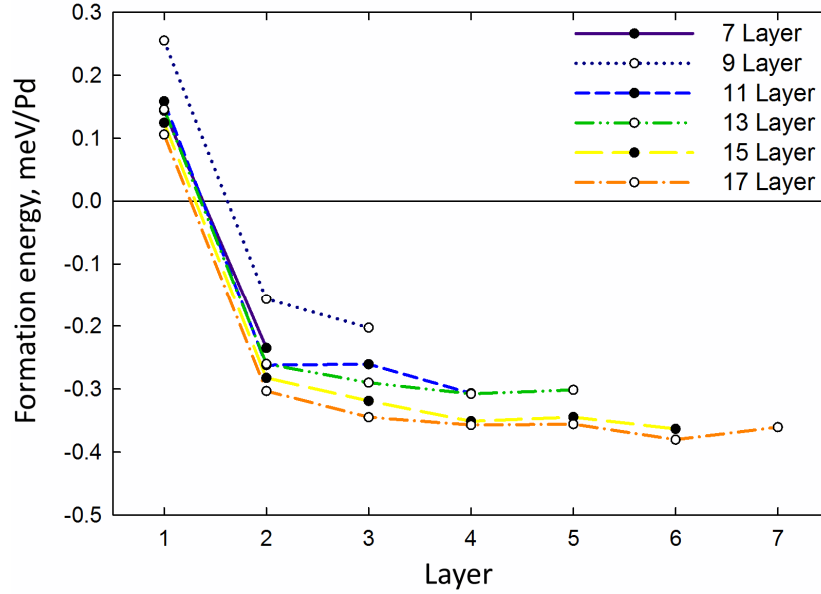


Figure 6.4. Formation energy of I as a function of slab thickness and depth.

in which E_{AuPd} and E_{Au} are the total energies of the alloy slab and the pure Au slab, ΔE_{Pd-Au} is the difference in the cohesive energies of bulk Pd and Au, and N_{Pd} is the total number of Pd atoms in the slab.

To limit interaction of the impurity layers with one another, we only examined slabs in which they were vertically separated by at least three Au layers.

Figure 6.4 shows the formation energies of I as a function of slab thickness and depth. As the impurity layer is pushed from the surface to the 1st subsurface layer, a large, approximately 0.4 eV/atom reduction in formation energy occurs. This is expected; as previously mentioned, Au preferentially segregates to the surface of bulk AuPd alloys, and the surface energy of Au is significantly lower than Pd (1.626 J m^{-2} vs 2.034 J m^{-2})¹¹⁶. We also note that in the 17 layer slab, the formation energy of I is seen to have attained almost 97% of its value in the 7th layer. This suggests that the effects of the surface are fairly shallow. On the other hand, the formation energies themselves depend

considerably on the overall thickness of the slab. It is not until the slabs achieve a thickness of at least 15 layers that they appear to converge.

Figure 6.5 shows the per Pd atom formation energies of $2d$, $2p$, 3 , and 4 relative to 1 , all within the same layers. Examining the relative formation energies in this way removes the sizable layer-dependence of the absolute formation energies, which facilitates closer examination of their differences.

In the 7 layer slab, the relative formation energies are all positive, while in the 9 layer slab, they are mostly negative. When the slab thickness grows to 11 and then 13 layers, the ranking of their stability follows the trend $2p < 2d < 3 < 4$, regardless of depth, but the energy of $2p$ relative to 1 changes significantly between the 11 and 13 layer slabs. The relative formation energies in the 15 and 17 layer slabs exhibit the same overall ordering regardless of depth ($1 < 2p < 2d < 3 < 4$) and seem generally more similar to one another than any other adjacent pair.

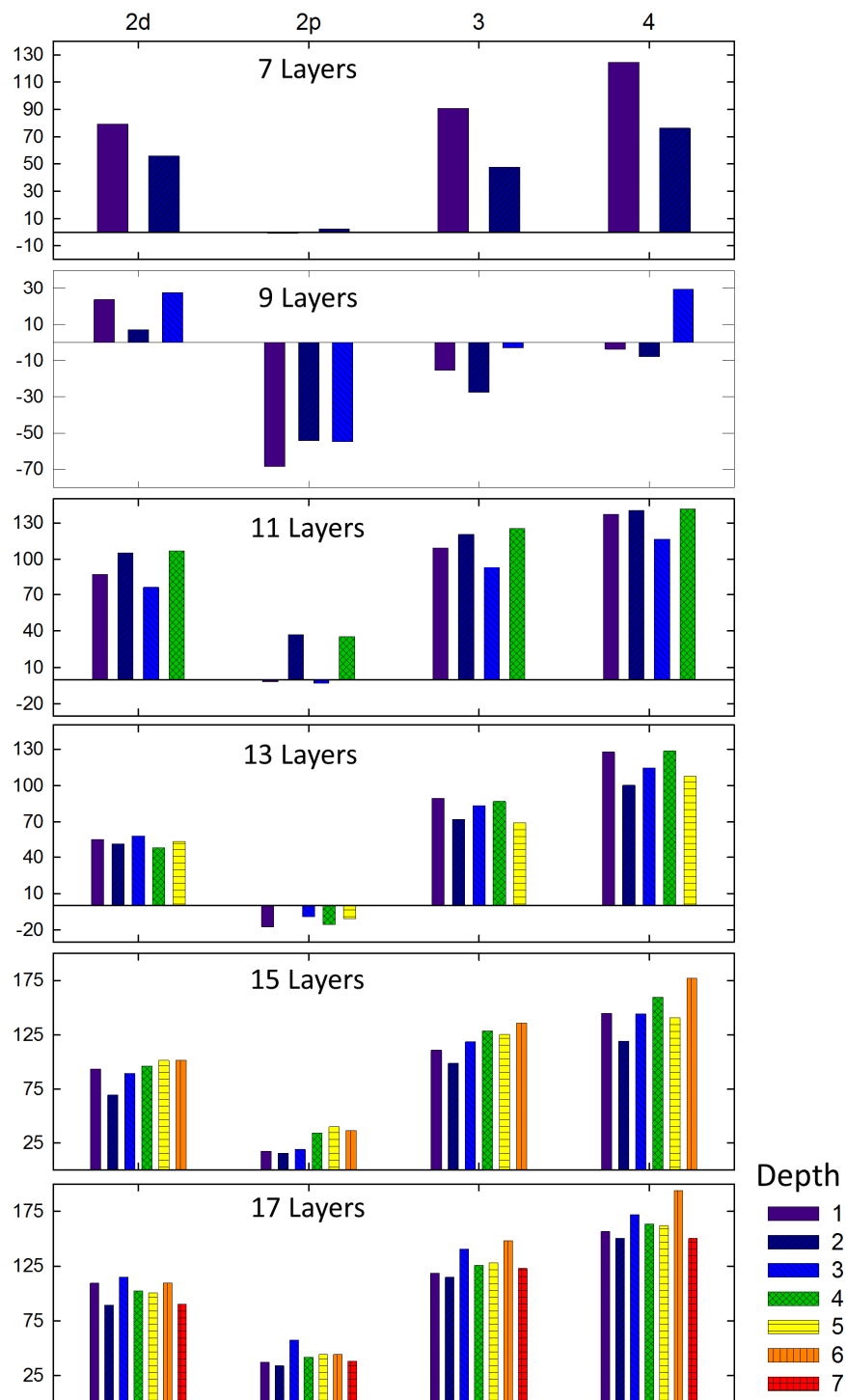


Figure 6.5. Formation energies, per Pd atom and relative to I , of each surface layer type, as a function of depth and slab thickness. Layer 1 is the surface layer.

In, the relative formation energies in the 15 and 17 layer slabs are compared directly. The formation energies of the impurity layers are generally higher in the 17 layer slabs by an average of about 10-20 meV. Trends in the 15 layer and 17 layer slabs share few features in common, apart from minima that occur in all of the relative formation energies at a depth of 2.

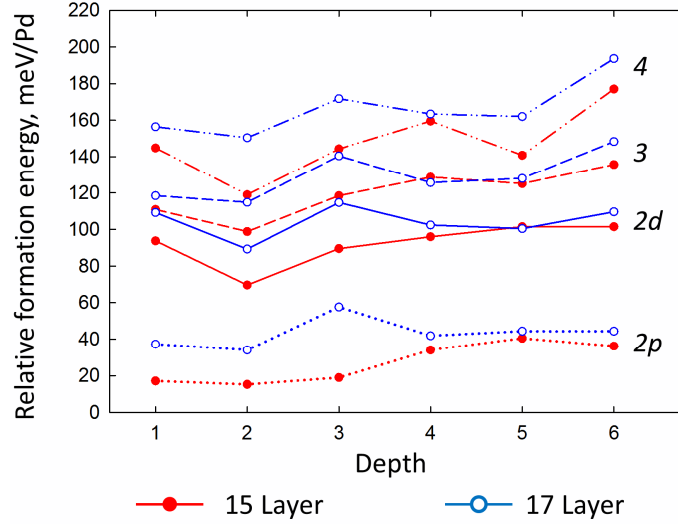


Figure 6.6. A comparison of the depth-dependent formation energies of the impurity layers labeled 2p, 2d, 3, and 4 relative to 1 in the 15 and 17 layer slabs. A depth of 1 corresponds to the surface layer.

These dissimilarities between the 15 and 17 layer slabs indicate that convergence with respect to slab thickness was not perfectly achieved, even at 15 layers. At the same time, the limits of our computational resources demand that we must accept some amount of error. Considering also that the surface segregation energy of Pd in the Au slab is on the order of 400 meV, we found the errors associated with the 15 layer slab model acceptable, and this is the model we chose to use for the development of our cluster expansion.

We also note that the strong variation of the relative formation energies with slab thickness creates some suspicion about the 7 and 9 layer slabs used by Yuge *et al.* in their simulations of the Pt-Rh and Cu-Pt surfaces. Although the layer-dependent cluster expansion Hamiltonians they developed may have been quite accurate in these slabs, it is questionable whether many of the simulation results they obtained would continue to hold for thicker ones, let alone bulk Pt-Rh or Cu-Pt crystals.

This leads to the final observation we will make about the results in Figure 6.4, Figure 6.5, and Figure 6.6. Although we chose to accept a 15 layer slab as a model of the AuPd(100) subsurface, we remain conscious of the fact that the relative formation energies in slabs of this thickness exhibit depth dependence somewhat different from in 17 layer slabs. A model Hamiltonian that perfectly reproduced the energetics of 15 layer slabs would therefore provide slightly incorrect results for 17 layer and (presumably) thicker slabs. For this reason, we concluded that a cluster expansion that attempts to replicate all of the fine, layer-dependent energetic details of the 15 layer slab would be pointlessly complex.

6.4 CLUSTER EXPANSION METHOD

In light of this conclusion, we formulated a cluster expansion scheme in which depth-dependence appears explicitly only in the point clusters, i.e. the on-site energies. The remainder of the slab formation energy

$$E_f = E_{AuPd} - (N_{Au} \cdot E_{Au} - N_{Pd} \cdot E_{Pd}) \quad (6.2)$$

is expanded using a set of three-dimensional clusters that (potentially) could have included pairs out to the fifth nearest-neighbor distance (in the 3D fcc lattice) and 3- and 4-body interactions out to the fourth nearest-neighbor distance—a total of 29 unique clusters. If a cluster contains a site that falls outside of the slab, its product is equal to 0.

The point cluster ECIs were constrained to converge to a bulk value a fixed number of layers beneath the surface. The set of clusters used in the final expansion, as well as the number of layer-dependent point cluster ECIs, were chosen based on their cross validation score. Further discussion of the optimization procedure and construction of the training set, which presented some unique difficulties not encountered in previous chapters, is reserved for the following section.

One advantage to this formulation of the cluster expansion is that it obviates the need for creation of a separate CE for the bulk reservoir, which can be modeled using the slab CE minus the layer dependent point clusters. It also permits arbitrary increases in the thickness of the GCMC simulated slab because of the assumption that interatomic interactions do not depend on depth.

6.5 TRAINING SETS

Recall that the process to construct cluster expansions for the surface alloys was iterative in nature. From an initial training set of randomly generated surface alloys, a trial cluster expansion was created by minimizing the cross validation score. Then this cluster expansion was used to locate ground state configurations for every possible surface composition with (up to) a 4×4 unit cell. These were relaxed using DFT and added to the training set if not already present. At the beginning of the next iteration, a new trial CE was created. This process was repeated until the trial CE discovered no new ground state configurations.

The rationale for this approach was that since we are practically limited in the number of model surfaces that can be included in our training set, the CE should be trained to accurately predict the differences in the energies of low-energy configurations

in particular, since it is these configurations that mostly determine the finite temperature properties of the surface.

In the present case, however, this approach would almost certainly lead to a highly inaccurate cluster expansion at the temperatures that we wished to consider. Experimentally, the (100) surface of the 1:1 AuPd alloy contains about 10% Pd after an 800 K anneal⁹³. On the other hand, we have estimated that the segregation of a Pd atom from the 1st subsurface layer of an Au slab to its surface incurs a penalty of about 400 meV. We would therefore not expect the ground state configuration of a slab to contain any surface Pd atoms until the subsurface had been completely filled. The atomic configurations that would result from the iterative procedure are thus likely to be highly non-representative of what we would reasonably expect to find in reality.

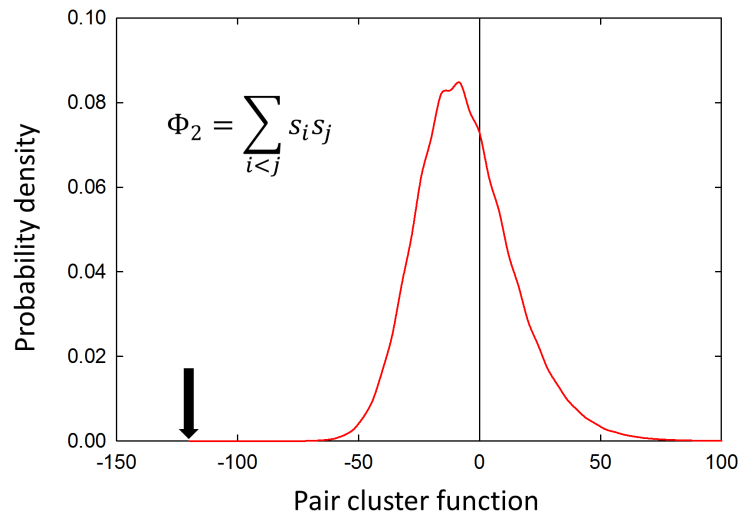


Figure 6.7. Probability density of the pair cluster function in a $2 \times 2 \times 15$ slab. The arrow indicates the minimum value.

What if we created a training set composed entirely of randomly generated slabs? To help answer this question, we constructed a normalized distribution of the 1NN pair

cluster function ($\Phi_2 = \sum_{i<j} s_i s_j$) in a 15 layer, 2×2 slab with a AuPd ratio of 1:1. It was created by calculating Φ_2 for 100 million randomly generated samples. Φ_2 was selected as a measure of atomic configuration because it is both simple to calculate and readily indicates whether one slab compared to another is more ordered (a larger number of 1NN pairs of unlike atoms; in smaller Φ_2) or segregated (a larger number of 1NN pairs of like atoms; larger Φ_2). It is also typically an important term in a cluster expansion, and so the distribution of Φ_2 values in a training set is of immediate interest to the question at hand. This distribution is shown in Figure 6.6.

The arrow on the horizontal axis of Figure 6.6 indicates the position of the minimum value of Φ that can be attained in a 15 layer, 1:1 slab, that is, Φ_2 of the slab that contains the maximum possible number of 1NN interactions between unlike atoms. Its location far to the left of the peak indicates how narrowly distributed randomly generated slabs are likely to be compared to the full spectrum of possible slabs, which raises doubts about the efficacy of a purely random training set.

In light of the concerns that have been raised, we developed an alternative procedure to build a training set for the slab CE Hamiltonian. The motivating concept was to modify the random Φ_2 distribution by introducing a 1NN interaction. Intuitively, in a canonical ensemble MC simulation of even a non-random (i.e. containing interactions) alloy, the Φ_2 distribution of all the visited microstates will coincide with the random distribution in Figure 6.6, provided that the simulation is performed at a sufficiently high temperature. As temperature is lowered and the influence of the 1NN interaction on the arrangement of atoms in the slab begins to be manifested, the distribution will shift and change shape. Hence, by selecting microstates from MC simulations conducted over a range of temperatures, we should be able to construct a training set with a broader range of Φ_2 values than would be achievable by purely

random sampling. Furthermore, if the 1NN interaction chosen is a reasonable estimate of the AuPd 1NN interaction, these slabs should contain a more representative selection of the kinds of atomic configurations found in actual AuPd slabs.

The 1NN interaction we used was obtained by fitting (using least squares) a limited CE with only a 1NN pair interaction

$$E = J_0 + J_1 \sum_i s_i + \sum_{i<j} s_i s_j \quad (6.3)$$

to the small training set of AuPd alloys shown in Figure 6.8, the mixing energies of which are compared to the experimental mixing energy¹¹⁷.

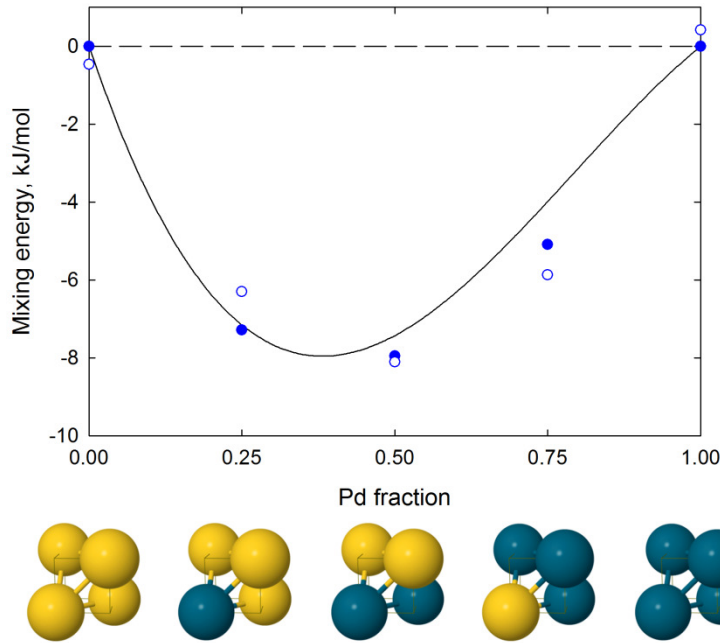


Figure 6.8. The training set for the 1NN CE is shown along the horizontal axis, along with the Pd fraction of each configuration. The DFT-predicted (solid circles) and CE-predicted (open circles) mixing energies are shown in the plot along with the experimentally derived curve (solid line) from Ref. 117.

Using this CE, we conducted canonical ensemble MC simulations of the 15 layer, 2×2 slab over a range of compositions and temperatures. After an initial phase of equilibration, $\langle \Phi_2 \rangle$ (the angle brackets denote an ensemble average) was calculated. Finally, a single representative microstate was chosen at random from each simulation with the constraint that its Φ_2 had to fall within 0.25 standard deviations of the average for its composition and temperature.

Values of Φ_2 for a 50% Pd slab at six temperatures are indicated using arrows in Figure 6.9, which, for comparison, also again shows the random Φ_2 distribution. The Φ_2 values themselves are located to the left of the peak of the random distribution. This

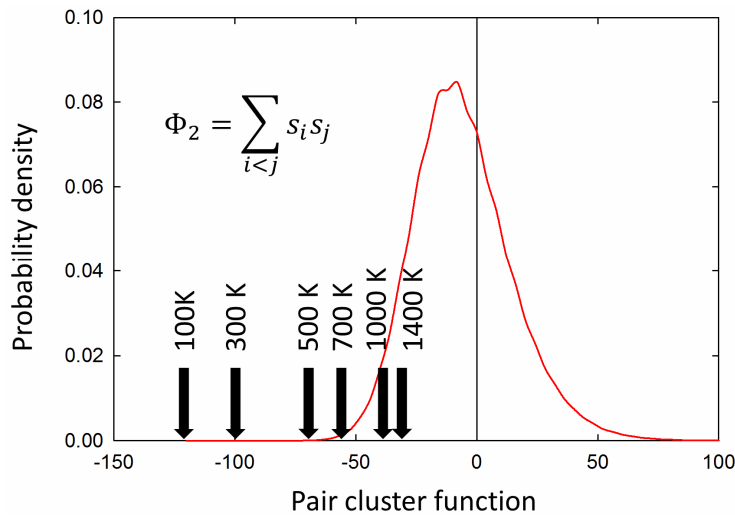


Figure 6.9. Probability density of the pair cluster function in a $2 \times 2 \times 15$ slab. The arrow indicates the minimum value. The arrows indicate values of the pair cluster function for slabs taken from simulations conducted at the indicated temperatures.

is consistent with the preference for heteronuclear interactions in AuPd alloys, which tends to decrease Φ_2 . They are also all in a tail region of the random distribution, from which they are unlikely to be selected by chance. These results show that the introduction

of a 1NN pair interaction is a simple and intuitive way to, in effect, bias the random selection of slabs to increase their configurational diversity and applicability to the system in question—in this case, a AuPd slab.

The training set we built using this procedure contained a total of 66 slabs. The largest number of these (42) contained 2×2 layers, but eighteen $3\times 2\times 15$ and six $4\times 2\times 15$ slabs were also included. The overall Pd fraction of these slabs varied between 15% and

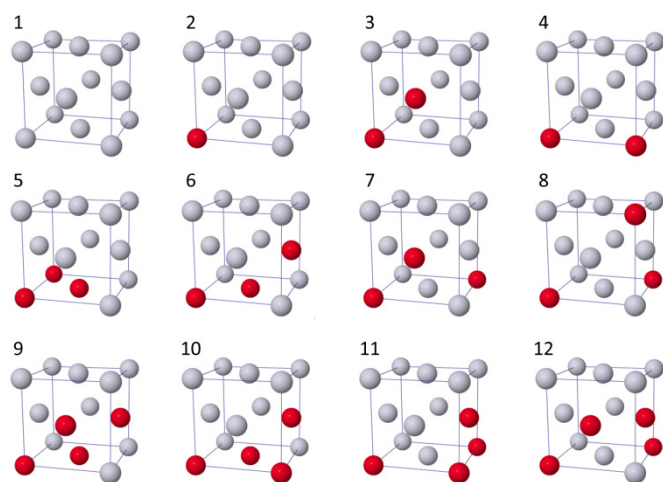


Figure 6.10. Clusters in the AuPd(100) expansion, indicated by the red atoms in each unit cell. The numbers correspond to the entries in Table 6.1.

85%. The MC simulation temperatures were 100 K, 300 K, 500 K, 700K, 1000 K, and 1400 K. The surface-parallel lattice constant chosen for the slabs was the average of the DFT-derived Au and Pd lattice constants. Vegard's Law¹¹⁸, which accurately describes AuPd alloys, states that the lattice constants of alloys obey the lever rule, so a simple average corresponds to a Au: Pd ratio of 1:1.

6.6 CROSS VALIDATION

Using the training set just described, a cluster expansion was constructed by identifying the set of clusters that minimized the cross validation score. This optimization was performed using simulated annealing, and resulted in a final CV score was 1.178 meV/atom. The final expansion included a null cluster, three point clusters (corresponding to sites in the surface layers, the first subsurface layers, and the bulk), two pairs, four trimers, and four tetramers, for a total of 14 total parameters. The clusters themselves appear in Figure 6.10 and ECIs in Table 6.1.

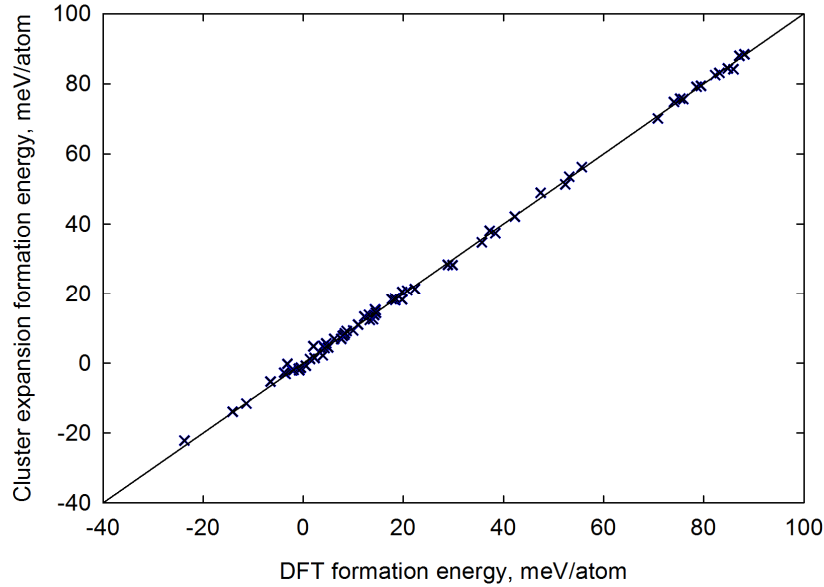


Figure 6.11. Formation energies of the training set slabs predicted by the cluster expansion versus the DFT predictions.

In Figure 6.11, the DFT formation energies of the training set slabs are compared to the corresponding CE predictions. As can be seen, the two are in good agreement with one another.

As an additional check on the validity of CE, we performed canonical ensemble MC simulations of the slab in which alloying was permitted only in the topmost surface

layers, and the subsurface layers contained only Pd. We compared the results of these simulations to results from Chapter 5 for the AuPd(100) surface alloys under strain.

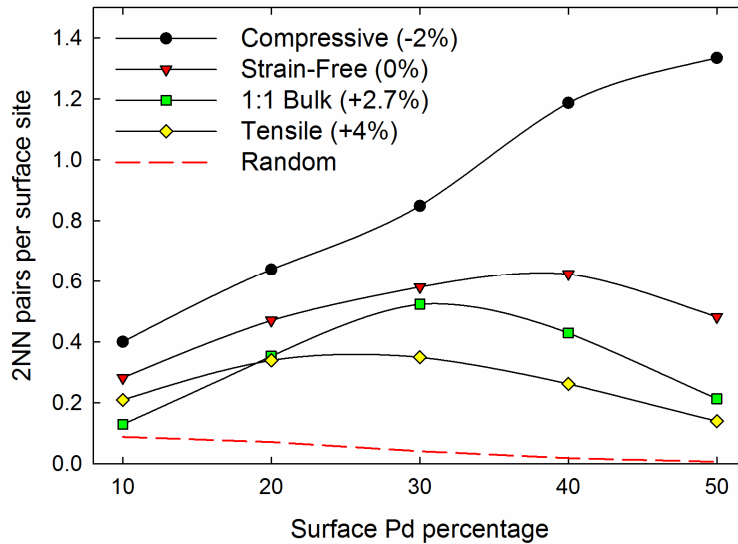


Figure 6.12. Population of 2NN pairs of Pd monomers in the AuPd/Pd(100) surface. The results for compressive, strain-free, and tensile strain are based on the CEs developed in Chapter 5.

Figure 6.12 shows the population of 2NN Pd monomer pairs at 300K as a function of Pd surface coverage for the slab (Bulk 1:1 in legend), the random surface alloy, and the AuPd surface alloys under strain-free, compressive, and tensile strain conditions. Figure 6.13 shows the temperature dependence of the Warren-Cowley short range order parameter for the same systems, but with 50% Pd coverage. In both figures, the results for the slab fall for the most part between the results for the strain-free and tensile cases. This is as expected, since the lattice constant of the slabs in the training set corresponds to 2.7% tensile strain.

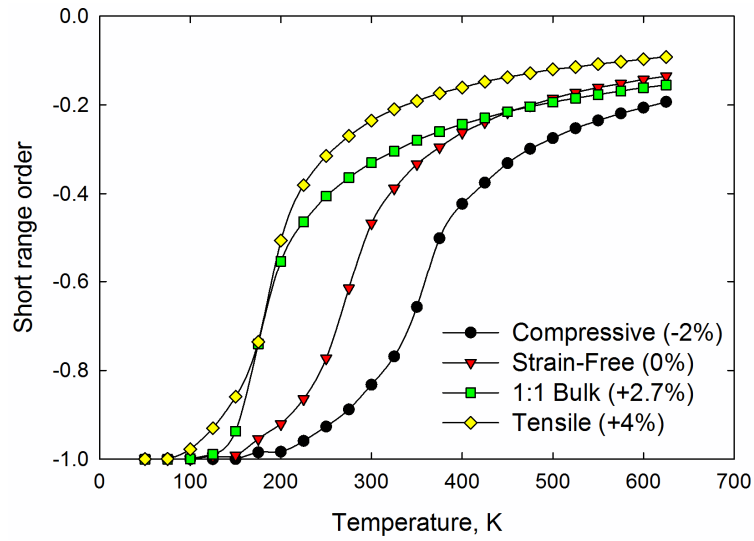


Figure 6.13. Short range order parameter in the AuPd/Pd(100) surface with a Pd coverage of 50%. The results for compressive, strain-free, and tensile strain are based on the CEs developed in Chapter 5.

Table 6.1. ECIs for the bulk and near-surface region of AuPd(100). Pd is spin down (-1) and Au is spin up (+1).

Cluster Number	ECI, eV	Note
1	1.979630E-02	
2	-2.029820E-01	Surface
	-4.653230E-02	Subsurface
	-3.084700E-02	Bulk
3	1.286190E-02	
4	1.543120E-03	
5	2.455640E-03	
6	9.411140E-04	
7	2.780580E-04	
8	-1.414850E-03	
9	-1.247460E-04	
10	-2.661940E-04	
11	-1.287840E-04	
12	3.777410E-04	

6.7 GRAND CANONICAL ENSEMBLE MONTE CARLO

In canonical ensemble MC, the volume, composition, total number of atoms, and temperature of the simulated system are fixed. This was an appropriate choice of ensemble for the surface alloys considered in previous chapters, because atomic exchange between their simulated two-dimensional surfaces and their subsurface layers was, by assumption, disallowed, and, as a result, their compositions were well-defined.

The same is not true of a bulk AuPd alloy with a free surface. In the previously mentioned experiments reported by the Goodman group, they found that after cleaning their 1:1 atomic ratio AuPd sample by argon sputtering, then annealing at 800 K, its surface contained 90% Au. Significantly, the segregation of Au from the bulk to the surface would have changed the bulk composition by only a negligible amount from the initial 1:1 AuPd ratio, since the number of surface sites is minuscule compared to the number of bulk sites. The near-surface layers in the real sample are in effect in equilibrium with a bulk reservoir of Au and Pd atoms, the composition of which equals the overall composition of the sample. To achieve the same effect in a canonical ensemble MC simulation of the system, a potentially very large number of subsurface layers would have to be considered explicitly. If too few layers were included, the composition of the *bulk* would differ substantially from the *overall* (bulk + near-surface layers) composition, which is the real independent variable for the simulation.

An alternative and more attractive approach that avoids this difficulty is to perform MC simulations in the grand canonical ensemble (GCMC), in which the volume and temperature of the simulated system remain fixed, but the composition is allowed to change through the exchange of atoms with a constant chemical potential (μ) reservoir. As just suggested, in a simulation of the AuPd(100) surface, the near-surface layers are considered the system, and the bulk is considered the reservoir. The Boltzmann factor for the grand canonical ensemble in a two component system is⁶⁶

$$\exp[(-E + N_1 \cdot \mu_1 + N_2 \cdot \mu_2)/kT] \quad (6.4)$$

where N_i is the number of atoms of each species, and μ_i is their corresponding chemical potentials, on an atomic basis. The ratio of the Boltzmann factor written for two systems is then

$$P = \exp[(-\Delta E + \Delta N_1 \cdot \mu_1 + \Delta N_2 \cdot \mu_2)/kT] \quad (6.5)$$

In our simulations, we add the constraint that the total number of atoms in the slab remains constant (i.e. there are no vacancies, interstitial defects, or surface adatoms), and therefore,

$$P = \exp[(-\Delta E + \Delta N_2 \cdot \Delta\mu)/kT] \quad (6.6)$$

from which it is clear that only the *difference* between the chemical potentials of Au and Pd must be known. A definition of $\Delta\mu$ can be obtained by rearranging the fundamental property relation for the Helmholtz free energy.

$$\begin{aligned} dA &= -SdT - pdV + \mu_1 dN_1 + \mu_2 dN_2 \\ dA &= -SdT - pdV - \mu_1 dN_2 + \mu_2 dN_2 \\ \left(\frac{\partial A}{\partial N_2}\right)_{T,V} &= \Delta\mu \end{aligned} \quad (6.7)$$

Using this definition, $\Delta\mu$ could be approximated by conducting canonical MC simulations on bulk (periodic in all directions) AuPd over a range of temperature and composition, then numerically differentiating the ensemble-averaged energies $\langle E \rangle$ (approximately equal to the free energy A) along the isotherms with respect to changes in Pd composition. However, a seemingly more simple and elegant simulation strategy called Direct Exchange Monte Carlo (DEMC) has also been proposed¹¹⁰.

In a DEMC simulation of the AuPd(100) system, bulk AuPd would first be thermally equilibrated using canonical ensemble MC. Representative snapshots would then be taken from these simulations to serve as reservoirs in GCMC simulations of slabs. When an atom exchange move is attempted in GCMC, the energy change due to swapping a randomly chosen atom (Au→Pd or Pd→Au, as appropriate) in the reservoir is first computed. This is taken to equal $\Delta\mu$. The swap is then attempted in the slab, and the Boltzmann criterion is calculated. If the swap is successful, the new slab

configuration is kept. However, in order to preserve their composition, the swaps are never actually carried out in the reservoir.

The purported advantage of DEMC is that it is relatively simple to implement, but reduces the required number of reservoir MC simulations by at least a factor of 2, because $O(h^2)$ central differences require two data points. One of the downsides of DEMC, as we will see, is that it does not always work as expected.

6.8 LIMITATIONS OF DEMC

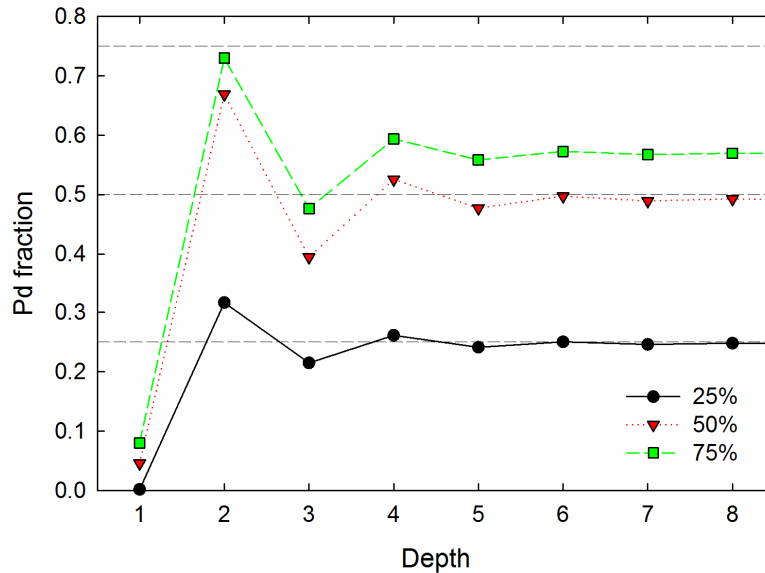


Figure 6.14. Depth-dependent Pd fraction at 800 K of systems with 25%, 50% and 75% bulk composition. Obtained using the DEMC method.

Bulk AuPd samples containing 25%, 50%, and 75% Pd in a $12 \times 12 \times 12$ configuration (1728 total atoms) were simulated at 800K using canonical ensemble MC to obtain reservoir structures for DEMC. The simulations consisted of a linear ramp from 1500K down to 800K over 17,280,000 steps (10,000 per site), followed by equilibration

at 800 K for another 17,280,000 steps. The configurations at the end of the equilibration phases of each simulation were taken as the reservoirs.

The slabs used in the DEMC simulations contained 4464 atoms in a $12 \times 12 \times 31$ configuration. The equilibration phase in these simulations also took 20,000 steps per site, including the temperature ramp. Data was collected over 10,000 steps per site. In each MC step, the new candidate microstate was constructed by either swapping a dissimilar pair of atoms within the slab, or by attempting to swap an atom with the reservoir. The choice of the type of swap was made randomly; swaps with the reservoir occurred with a 1 in 20 probability.

Figure 6.14 shows the variation of composition with depth for the three bulk compositions examined. The concentration of Pd is lowest in the topmost layer of all three slabs. It shoots up in the 1st subsurface layer, and then undergoes oscillations of decreasing amplitude with increasing depth, converging toward a constant value in the deepest layers. This oscillatory behavior is in qualitative agreement with atomistic simulations of surface segregation in other alloys.

In the 25% and 50% cases, the value to which the Pd concentration converges is just the corresponding bulk composition. However, in the 75% case, the DEMC-predicted Pd concentration in the deepest layers is approximately 57%.

The explanation for this surprising and apparently non-physical result can be understood by comparing $\Delta\mu(T, x)$ in the slab and reservoir systems as a function of overall Pd composition. In GCMC, the average composition of the simulated system will be the value at which its chemical potential equals the chemical potential of the reservoir. In Figure 6.15, we have plotted $\Delta\mu$ of the slab and bulk at 800K. These values were computed by differentiating $\langle E \rangle$ as described in section 6.7. As can be seen in Figure 6.15, at 25% and 50% bulk compositions, this condition is satisfied in each case by only

one slab composition, as indicated by the dashed lines. However, at approximately 65%, $\Delta\mu$ in the slab becomes smaller than $\Delta\mu$ in the bulk reservoir, and bulk compositions greater than this no longer uniquely correspond to a single slab composition. In the 75% case, slab compositions of approximately 72% and 57% both have matching $\Delta\mu$. The DEMC simulation will favor the more stable composition (see the experimental mixing energy in Figure 6.8), even though it is untenable that the subsurface layers of the AuPd(100) system, which are of course in physical contact with the “bulk”, would exhibit this behavior.

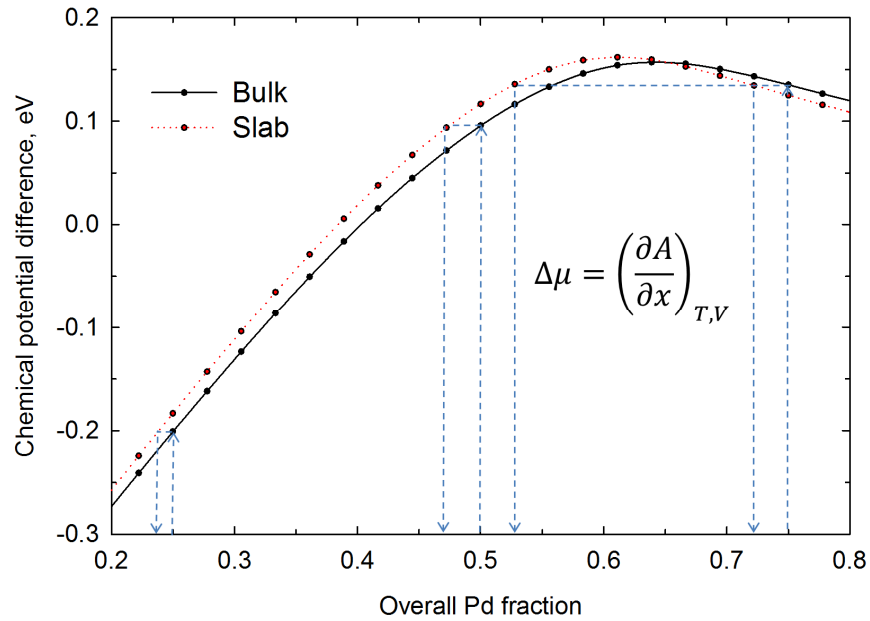


Figure 6.15. $\Delta\mu$ in a slab and a bulk reservoir, obtained by numerical differentiation of $\langle E \rangle$. The dashed lines leave the horizontal axis at the bulk composition, meet the bulk $\Delta\mu$ curve, cross over at constant $\Delta\mu$ to the slab curve, then go vertically downward to rejoin the axis at the composition of the slab that is in equilibrium with the bulk. At bulk compositions above $\sim 65\%$, the horizontal tie lines cross the slab curve twice, and a DEMC simulation will result in a slab with the lower composition.

For this reason, the remainder of the MC results reported in this chapter are based on cubic spline interpolations of plots like the ones shown in Figure 6.15 instead of the DEMC method. The SciPy package for the Python programming language was used to perform all necessary differentiation and interpolation¹¹⁹.

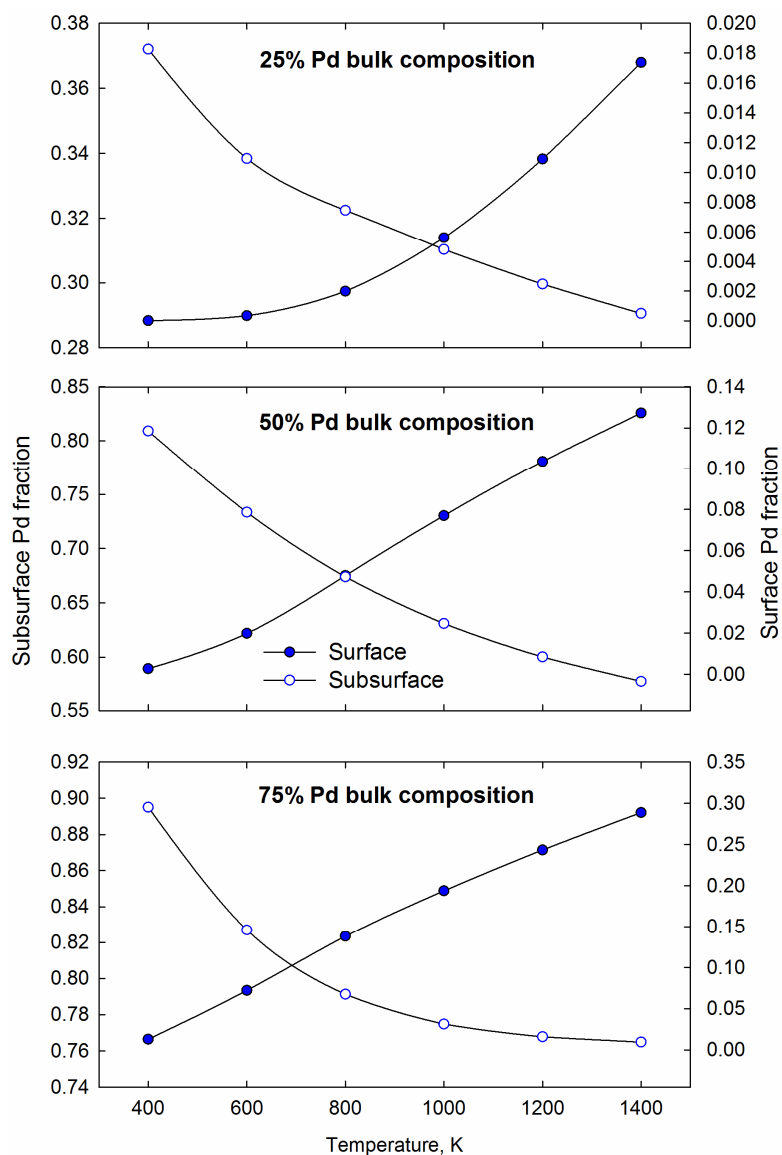


Figure 6.16. Pd fraction in the surface and 1st subsurface layers as a function of temperature and bulk composition, as predicted by GCMC simulation.

6.9 SURFACE AND SUBSURFACE COMPOSITIONS

Description of the overall method is now complete. In this section, we will discuss a few results of the simulations.

Figure 6.16 shows how the compositions of the surface and 1st subsurface layers of 25%, 50%, and 75% AuPd(100) slabs vary with temperature. Pd content in the surface layer is seen to always increase with temperature, while subsurface composition decreases. These two trends are easily understood in terms of what we already know about AuPd energetics, in particular, the significantly higher surface energy of Pd and the preference for heteronuclear interactions. As temperature is increased, higher energy microstates with greater surface Pd fractions are visited with greater frequency in the MC simulations. Although Pd in the 1st subsurface layer is still somewhat less stable than in the bulk (the bulk and 1st subsurface site ECIs differ by only about 15 meV), Pd concentrates there because it is attracted to the Au in the surface. As the surface Au fraction is diminished by increasing temperature, so also is the Pd fraction in the 1st subsurface layer.

At 25% bulk composition, the surface concentration of Pd remains very low over the entire examined temperature range. Even at 1400 K, it is predicted to be smaller than 2%. The surface of the 50% alloy is considerably more enriched in Pd, achieving a value of nearly 13% at 1400 K. The predicted surface Pd fraction is about 5% at 800 K, while the experimentally determined value is about 10%. This may suggest that Pd surface segregation is under-predicted by the simulation methodology that we developed, but it is also possible that the annealing time used in the experiment was inadequate to fully equilibrate the surface concentration profile. In the 75% alloy, the surface layer is predicted to contain as much as 30% Pd. The 75% alloy also contains considerably more

Pd in its 1st subsurface layer than either the 25% or the 50% alloys. Even at high temperature, it decreases to only about 76%.

In our MC simulations of AuPd(100) surface alloys (Chapters 4 and 5), we considered surfaces in which the Pd fraction was as high as 80%. The results in Figure 6.16 indicate that a Pd bulk composition in excess of 75%, as well as a high annealing temperature, would be necessary to achieve such high levels of Pd surface coverage in a bulk sample. On the other hand, the high Pd content of the 1st subsurface layer in a 75% bulk sample tends to confirm the applicability of the surface alloy model, which has a pure Pd subsurface, to the bulk alloy.

6.10 SUMMARY

In this chapter, the development of a scheme for modeling surface segregation and atomic configuration in surface terminated bulk alloys was presented. The scheme was based on density functional theory, the cluster expansion method, and grand canonical Metropolis Monte Carlo. The AuPd(100) surface was used as an example.

The first step in the development of the scheme required determining the minimum thickness of slab required to model the energetics the near-surface layers. For this purpose, the relative formation energies of five Pd-containing 2×2 surface layers in otherwise pure Au slabs were calculated at various depths in increasingly “thick” slabs. The formation energies were found to largely converge when the slabs reached a thickness of 15 layers, as judged by the differences between the 15 and 17 layer slabs. Accordingly, the 15 layer slab was selected as a model system.

The relative formation energies of the Pd surface layers appeared to depend only slightly on depth, and in fact the variation was judged to be comparable to the error introduced by using a 15 rather than a 17 layer slab model. For this reason, the decision

was made to include layer dependence only in the point clusters of the cluster expansion, which is necessary to account for the relatively large surface segregation energy of Pd (~ 400 meV for a Pd atom segregating from a bulk Au host to the surface).

Having established these criteria for the truncation of the cluster expansion, we turned next to the development of a DFT training set of model surfaces. We first reasoned that the approach used in earlier chapters of seeking ground state structures would likely fail due to the high surface energy of Pd. We also argued that using only randomly generated configurations would similarly produce non-representative configurations. Hence, we developed a scheme to generate more realistic configurations using a first nearest-neighbor pair interaction in canonical Monte Carlo simulations.

Using this training set, we constructed a cluster expansion for the AuPd(100) surface which included a total of 14 ECIs, including three separate point ECIs, one each for the surface, subsurface, and bulk. Excellent agreement was achieved between CE and DFT predictions of the formation energies of the training set surfaces, and comparisons between MC predictions made using this CE and the CEs developed in Chapter 5 were also reasonably consistent.

The slab cluster expansion was employed in grand canonical simulations of the near-surface layers of the AuPd(100) system using the Direct Exchange Monte Carlo scheme. The DEMC scheme was found to produce physically implausible results for a slab in equilibrium with a bulk reservoir with a Pd composition greater than $\sim 65\%$. For example, the deepest layers of a simulated slab in contact with a reservoir composed of 75% Pd were found to have a Pd composition of approximately 57%. This apparent error was found to occur because $\Delta\mu$ (the difference in the chemical potential of Au and Pd) in the slab crosses over and becoming smaller than $\Delta\mu$ in the reservoir at approximately 65%. In order to overcome this shortcoming in the DEMC method, the equilibrium slab

compositions for each temperature and reservoir composition that we examined were determined using an interpolation scheme.

Our simulations of the AuPd(100) surface were found to be in reasonable agreement with available experimental data; a 50% AuPd alloy is known to have a surface composition of $\sim 10\%$ Pd after annealing at 800 K, while our simulations predicted 5% Pd composition. The Pd composition in the subsurface layers was found to oscillate with depth due to the attraction between Pd and Au atoms. In order to achieve Pd surface compositions as high as those we considered in Chapters 4 and 5, we found that it may be necessary to employ high bulk Pd fractions.

Chapter 7: (111) Surface Alloys and the Scaled Pair Interaction

7.1 INTRODUCTION

As available computing resources have grown, so also has interest in theoretical catalysis studies that employ a combinatorial or high-throughput approach, in which the properties of multiple alloys are screened for their activity or selectivity toward a targeted reaction. In one such study, Dellamorte *et al.* used density functional theory calculations to predict the effectiveness of six Ag-based surface alloys for ethylene epoxidation and NO_x reduction, identifying several that outperformed pure Ag catalysts in subsequent experiments¹²⁰. Nørskov and coworkers investigated the methanation reaction ($\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$) on 117 different bimetallic alloy catalysts using DFT¹²¹. Based on their results, they synthesized and evaluated a Ni-Fe catalyst, which proved to be superior to the conventionally used Ni catalyst. In two large studies, Greeley *et al.* developed a library of almost 750 binary surface alloys, which were used to screen for catalysts for the oxygen reduction reaction and the hydrogen evolution reaction, also identifying a number of promising candidates^{122,123}.

These studies and others like them demonstrate that the combinatorial approach may be an effective strategy for uncovering new catalysts. However, one shortcoming they typically exhibit is a lack of attention to the way in which atoms are likely to be arranged in the alloys they consider. Dellamorte *et al.* assumed a $p(3\times 3)$ surface cell in their study, for instance; Greeley *et al.* used only pure overlayers and alloys with $(\sqrt{3} \times \sqrt{3})R30^\circ$ order. Although Greeley *et al.* also tested the stability of these systems in Ref. 123, they appear to have made no further attempts to determine the catalytic properties of those that did not pass, even though they comprised the great majority.

It seems reasonable to suggest that the combinatorial approach could only benefit from incorporation of information about the arrangement of atoms in surface alloys, both

through the identification of promising candidates that were overlooked by the studies described above and the rejection of false positives. The cluster expansion-based simulation strategy described in Chapter 2 is capable of providing this kind of detail. Unfortunately, since each alloy that we might wish to consider would require iterative construction of a sizable training set of DFT results, the computational costs of carrying out a systematic study that included a large number of alloys would quickly become prohibitive.

To provide direction for developing a new, less computationally demanding approach, we might start by reopening the question of why such large training sets were needed in the first place. The chief reason was the inclusion of a large number of long range and multibody interactions in our cluster expansions. While these interactions may have been necessary to resolve many finer details of alloy surface atomic configuration—the strain-dependent populations of 2NN pairs of Pd monomers in AuPd(100), for instance—it may be possible to trade some accuracy for improved speed while nonetheless providing beneficial results.

The approach developed in this chapter is an attempt to successfully negotiate this trade. In the first portion, cluster expansions restricted to 1NN pair interactions are constructed for 12 surface alloys in the fcc(111) surface facet using small DFT training sets. Models developed in this way are compared to our earlier, more sophisticated models of the AuPd and AuPt surface to demonstrate that they are indeed capable of providing acceptable results. Next, we explain how properties of the finite-temperature atomic configuration of any bimetallic surface alloy modeled using a 1NN CE can be predicted on the basis of a dimensionless parameter, the *scaled pair interaction*. Finally, we discuss results from a series of canonical ensemble Monte Carlo simulations that we performed over a range of values of the scaled pair interaction.

7.2 METHODS

Quantum mechanical calculations reported herein were performed on the basis of spin polarized density functional theory (DFT) within the generalized gradient approximation (GGA-PW91)⁸⁸, as implemented in the Vienna Ab-initio Simulation Package (VASP)⁸⁹. The projector augmented wave (PAW) method with a planewave basis set was employed to describe the interaction between ion cores and valence electrons. The PAW method is in principle an all-electron frozen-core approach that considers exact valence wave functions⁹⁰. Valence configurations employed in all cases include the *d* and *s* electrons belonging to the highest numbered shell. An energy cutoff of 350 eV was applied for the planewave expansion of the electronic eigenfunctions.

The slabs we used to model the fcc (111) surface alloys had four 2×2 layers. One component of each alloy was identified as the host, and the other as the impurity. The bottom three layers contained only host atoms, and the topmost layer was a monolayer alloy of host and impurity atoms. The top and bottom layers of each slab were separated from one another through a periodic boundary by a vacuum space corresponding, before relaxation, to seven atomic layers. The upper two layers were fully relaxed using the conjugate gradient method until residual forces on all the constituent atoms became smaller than 2×10^{-2} eV/Å, while the bottom two layers were fixed at bulk positions determined by the host lattice constant. The calculated lattice constants of several host metals appear in Table 7.1 side-by-side with experimental values¹²⁴. As is typical for GGA calculations, most of the predicted values are slightly high.

For Brillouin zone integration, we used a (12×12×1) Monkhorst-Pack mesh of *k* points to determine the optimal geometries and total energies. Previous calculations suggest that the chosen parameters are sufficient for describing the surface properties of the model systems considered.

Table 7.1. Lattice constants predicted by DFT. Experimental values taken from Ref. 124.

	a (DFT), Å	a (Expr), Å	% Diff.
Pd	3.961	3.890	1.82%
Pt	3.986	3.924	1.59%
Ir	3.882	3.839	1.10%
Ni	3.521	3.524	-0.08%
Ag	4.159	4.086	1.79%
Cu	3.635	3.615	0.58%

The Metropolis Monte Carlo (MC) method was used to predict the finite temperature arrangement of atoms in the surface alloys. The simulations were performed in the canonical (constant NVT) ensemble on surfaces with 900 atoms arranged in a 30×30 supercell. The surfaces were annealed at high temperature for 9×10^6 steps to eliminate dependence on the initial configuration, and then the temperature was ramped down to the simulation temperature over another 9×10^6 steps. Data was collected over a final 4.5×10^6 steps.

Cluster expansions truncated to the first nearest neighbor pair interaction were used to model surface alloy energetics. That is,

$$E = J_0 \cdot N_{sites} + J_1 \sum_i \sigma_i + J_2 \sum_{i < j} \sigma_i \sigma_j \quad (7.1)$$

where N_{sites} is the total number of atoms in the lattice, σ_i is the spin of atom at lattice site i , and J_0 , J_1 , and J_2 are the empty, point, and 1NN pair effective cluster interactions (ECIs). Host atoms were spin-down ($\sigma_i = -1$) and impurity atoms were spin-up ($\sigma_i = +1$). For convenience, we will also refer to the sums in eq. (7.1) using the notation Φ_k , where $\Phi_0 = N_{sites}$, $\Phi_1 = \sum_i \sigma_i$, and $\Phi_2 = \sum_{i < j} \sigma_i \sigma_j$.

It is well-known that pair-wise additive terms alone are inadequate to model the energetics of metals^{34,125}. We justify restricting the CE to 1NN pair interactions in three ways. First, as already stated, our goal is not to predict every subtlety in how atoms are

arranged in the surfaces of alloys, but to provide an easily implemented methodology to determine likely arrangements. In catalytically promising cases, it may be worthwhile to adopt a more thorough approach. Second, the inaccuracy that arises from a pair-only model is probably most important in systems in which metal atoms can have varying coordination. This occurs in simulations that include, e.g., vacancies and interstitial defects, surface adatoms, or in which both the bulk and surface are considered. In our simulations, all atoms have the same coordination. The third justification is the substantial agreement between predictions made using a 1NN pair CE and the more complete CE developed in Chapter 3, which will be shown below.

7.3 ESTIMATING THE ECIs

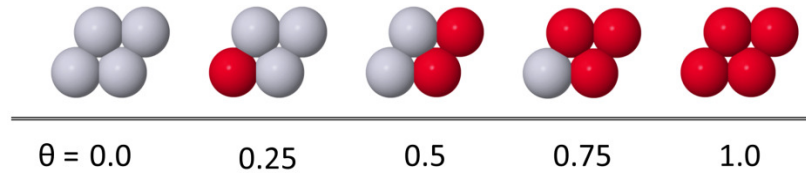


Figure 7.1. Training set surfaces.

The ECIs for the alloys that we considered were determined by fitting to the mixing energies of the five surfaces shown schematically in Figure 7.1, referred to collectively as the training set. The mixing energy was defined as

$$E_{mix} = E_{\theta} - [E_{0.0} + \theta \cdot (E_{1.0} - E_{0.0})] \quad (7.2)$$

The energies on the right hand side of eq. (7.2) are total energies per surface atom calculated using DFT according to the method described in Section 7.2. The subscripts indicate the impurity content, θ .

The fit was made by minimizing the squared errors between the CE and DFT-predicted mixing energies of the $N = 5$ training set surfaces with respect to J_0 , J_1 , and J_2 .

$$\varepsilon^2 = \frac{1}{N^2} \sum_{i=1}^N (E_{mix,i}^{CE} - E_{mix,i}^{DFT})^2 \quad (7.3)$$

Taking the partial derivative of ε^2 with respect to J_0 , J_1 , and J_2 results in a system of three linear equations and three unknowns, each of which have form

$$\begin{aligned} \sum_{i=1}^N \Phi_{j,i} \cdot 4 \cdot E_{mix,i}^{DFT} \\ = J_0 \sum_{i=1}^N \Phi_{0,i} \cdot \Phi_{j,i} + J_1 \sum_{i=1}^N \Phi_{1,i} \cdot \Phi_{j,i} + J_2 \sum_{i=1}^N \Phi_{2,i} \cdot \Phi_{j,i} \end{aligned} \quad (7.4)$$

The sums are over the N surfaces in the training set, and the first and second subscripts on the cluster functions $\Phi_{j,i}$ indicate the associated ECI and the associated surface, respectively. The factor of 4 on the left hand side appears because $E_{mix,i}^{DFT}$ is defined on a per atom basis. The cluster functions appear in Table 7.2 for convenience.

Table 7.2. Cluster functions for each of the surfaces in the training set.

θ	Φ_0	Φ_1	Φ_2
0.0	4	-4	12
0.25	4	-2	0
0.5	4	0	-4
0.75	4	2	0
1.0	4	4	12

Using this procedure, we estimated J_0 , J_1 , and J_2 for the list of alloys shown in Table 7.3. The error between the CE and DFT-predicted mixing energy of each alloy are also shown.

Table 7.3. ECIs and errors for the alloys considered. The first element in each is considered the “impurity”, and is spin = +1 in the cluster expansion. The second is the “host”, which is spin = -1.

Alloy	J_0	J_1	J_2	$\epsilon/\text{atom (meV)}$
AuPd	-0.03495	-0.00133	0.01154	1.006
AuPt	0.01483	-0.00004	-0.00490	0.219
PdIr	0.07886	-0.00037	-0.02624	0.321
PtNi	-0.25173	0.01188	0.08335	8.024
AgPd	-0.01647	-0.00222	0.00541	1.461
AgPt	0.01300	0.00178	-0.00439	1.169
CuPt	-0.00940	0.00146	0.00298	1.204
PdAg	-0.05222	0.00241	0.01728	1.652
PdPt	-0.00104	0.00021	0.00035	0.133
PtAg	-0.01877	0.00579	0.00602	3.851
PtCu	-0.11009	0.00722	0.03633	4.926
PtPd	0.00011	-0.00009	-0.00004	0.056

Figure 7.2. DFT (blue, close symbols) and CE (red, open symbols) mixing energies for each training set surface., which shows the mixing energy curves for all the alloys considered, may provide a clearer indication of the fidelity of the cluster expansions to their respective DFT training sets than the error alone. For some alloys (AuPd, AuPt, PdIr, PtNi, PdAg, PtCu) the fit appears to be quite good, and may well provide quantitatively accurate predictions of atomic configuration. For others (e.g. AgPt or CuPt), this is less true. In these cases, we expect the predictions to still be capable of providing some degree of guidance, but caution is urged. The alloy with visibly the worst fit of all those that we examined is PtPd. Its mixing energy changes signs midway across the composition range. We note, however, that the magnitude of its mixing energy and of its ECIs are extremely small compared to all of the other alloys, indicating that it would behave much like the random alloy.

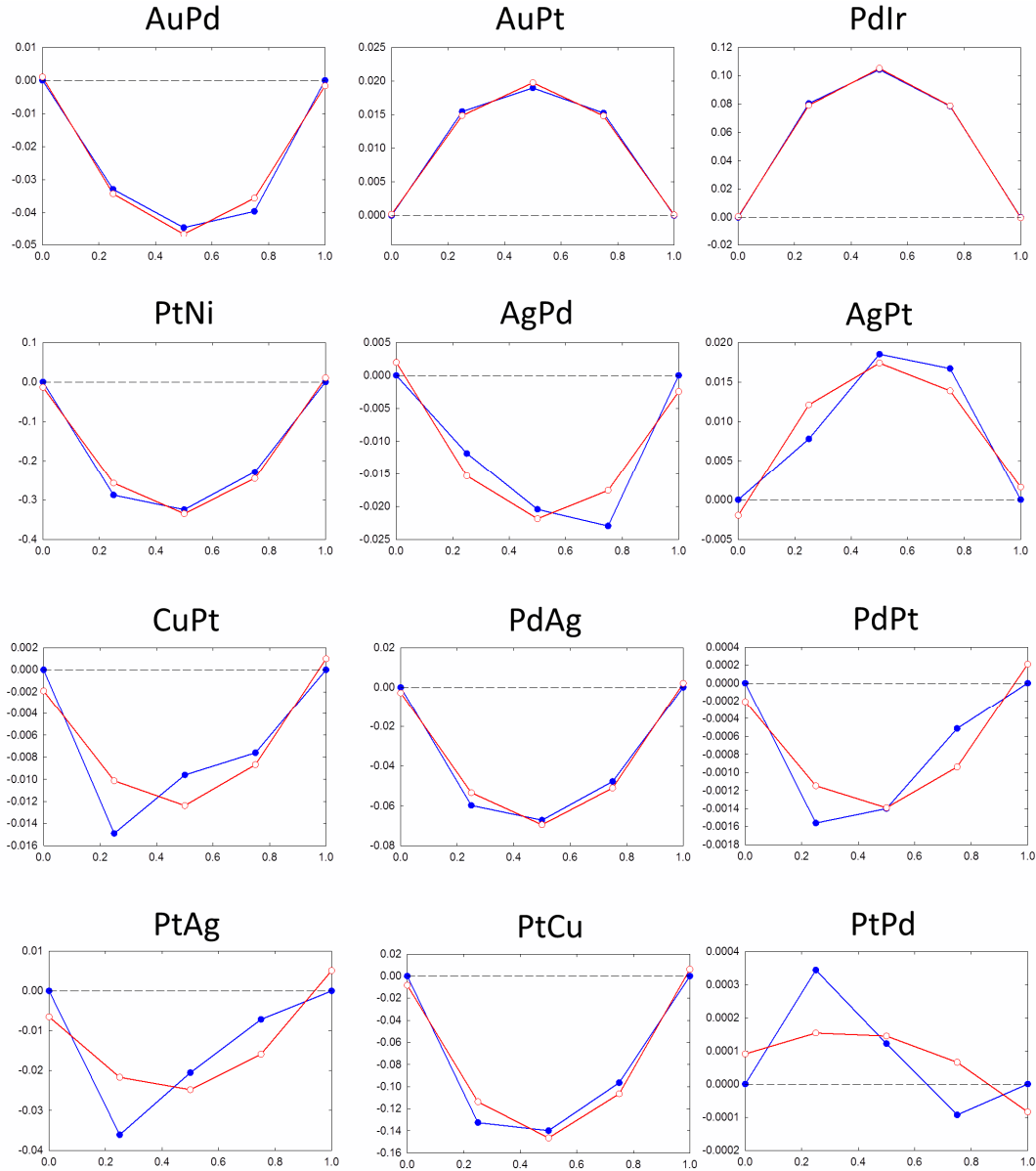


Figure 7.2. DFT (blue, close symbols) and CE (red, open symbols) mixing energies for each training set surface.

In order to evaluate our assumption that 1NN pair interactions are capable of providing a reasonable approximation of surface alloy energetics, we next performed a series of MC simulations of the AuPd(111) and AuPt(111) surfaces using the ECIs

reported in Table 7.3 and then compared the results to those presented in Chapter 3. Recall that the MC simulations discussed in Chapter 3 were based upon CEs constructed from much larger training sets and included pair and multibody interactions out to the 3NN distance.

Figure 7.3 compares the 300K population of Pd and Pt monomers in AuPd and AuPt surface alloys as a function of their overall atomic fraction. While the results based on the 1NN models are not exactly the same as those based on the longer range CEs, their discrepancies from another are small compared to the differences between the alloys themselves.

Using the procedure described above, we also fit the 1NN CE to the AuPd and AuPt training sets from Chapter 3, which included, respectively, 56 and 51 4×4 surfaces. The resulting values of J_2 were 0.01270 eV for AuPd and -0.00525 eV for AuPt, both quite similar to the values derived from the five-member, 2×2 training sets used in this work (See Table 7.3).

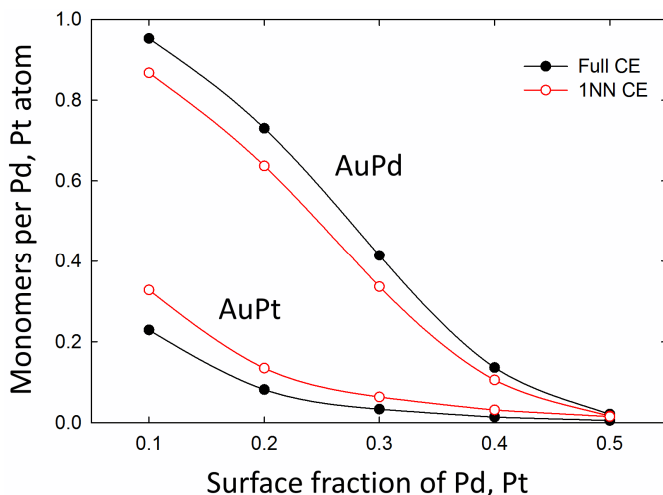


Figure 7.3. Monomer populations predicted using CEs developed in Chapter 3 and the 1NN CEs developed in this chapter.

Both of these results increase our confidence in the ability of 1NN pair models based on the small training set shown in Figure 7.1 to provide reasonable predictions of the arrangement of atoms in fcc(111) surface alloys.

7.4 SCALED PAIR INTERACTIONS

Figure 7.3 shows the results of a set of simulations performed at a particular temperature for two pairs of metals, each with their own cluster expansion. While it would be possible to perform similar simulations for any and every alloy that we desire to consider, this would quickly become cumbersome. Fortunately, the form of the 1NN CE suggests an alternative approach.

In a canonical ensemble (constant NVT) MC simulation, transition from the current microstate, labeled i , to a new, randomly generated one, j , occurs in each step with a probability equal to the ratio of their Boltzmann factors.

$$P_{i \rightarrow j} = e^{-\Delta E_{i,j}/k_B T} \quad (7.5)$$

where $\Delta E_{i,j}$ is the difference in their energies. For a surface alloy whose energetics are modeled by the 1NN CE, this difference is

$$\Delta E_{i,j} = J_2 \cdot (\Phi_{2,j} - \Phi_{2,i}) \quad (7.6)$$

The other two ECIs (J_0 and J_1) and their associated cluster functions vanish due to the constraint of constant composition. Substituting eq. (7.6) into eq. (7.5) results in

$$P_{i \rightarrow j} = \exp[-\bar{J}_2 \cdot (\Phi_{2,j} - \Phi_{2,i})] \quad (7.7)$$

In eq. (7.7), we have replaced the quantity $J_2/k_B T$ with $\bar{J}_2$, the *scaled pair interaction*. By writing the MC criterion in terms of $\bar{J}_2$ rather than T and J_2 separately, we have conceptually eliminated the need to simulate every alloy, each with its own J_2 , over a range of temperatures. Instead, we may perform a single set of simulations over a

range of $\bar{J}_2$, then locate the finite temperature behavior of a particular alloy (i.e. with a particular J_2) within these results.

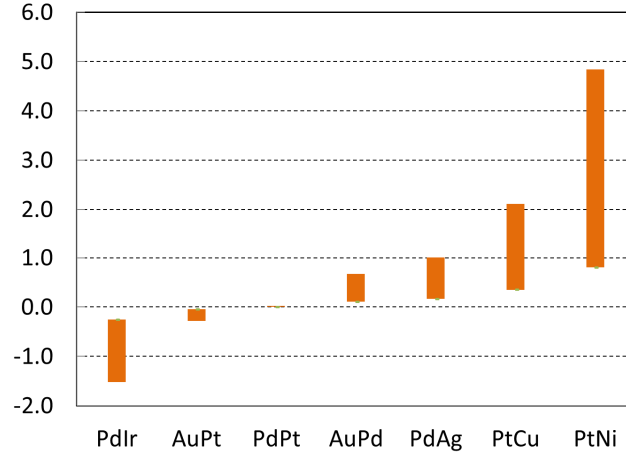


Figure 7.4. The scaled pair interaction over temperatures between 200K and 1200K for several alloys.

The relationship between $\bar{J}_2$ and J_2 is illustrated in Figure 7.4, which shows the values of J_2 for several of the alloys considered above scaled over temperatures between 200 K and 1200 K. For alloys that have negative J_2 values, the top of the bar in Figure 7.4 corresponds to values of $\bar{J}_2$ at 1200 K, and the bottom to 200 K. The reverse is true for alloys with positive J_2 values.

Figure 7.4 makes clear that a broad range of interatomic interactions exists in surface alloys, even in our small sample. Some of the consequences of this will be discussed in the following section, where we present further results of MC simulations. Here we note that although AuPd(111) and AuPt(111) surface alloys are known to possess significantly different atomic configurations (*cf.* Chapter 3), their interatomic interactions are relatively similar compared to those of other alloys.

7.5 HOST-IMPURITY DISTRIBUTION AS A FUNCTION OF $\bar{J}_2$

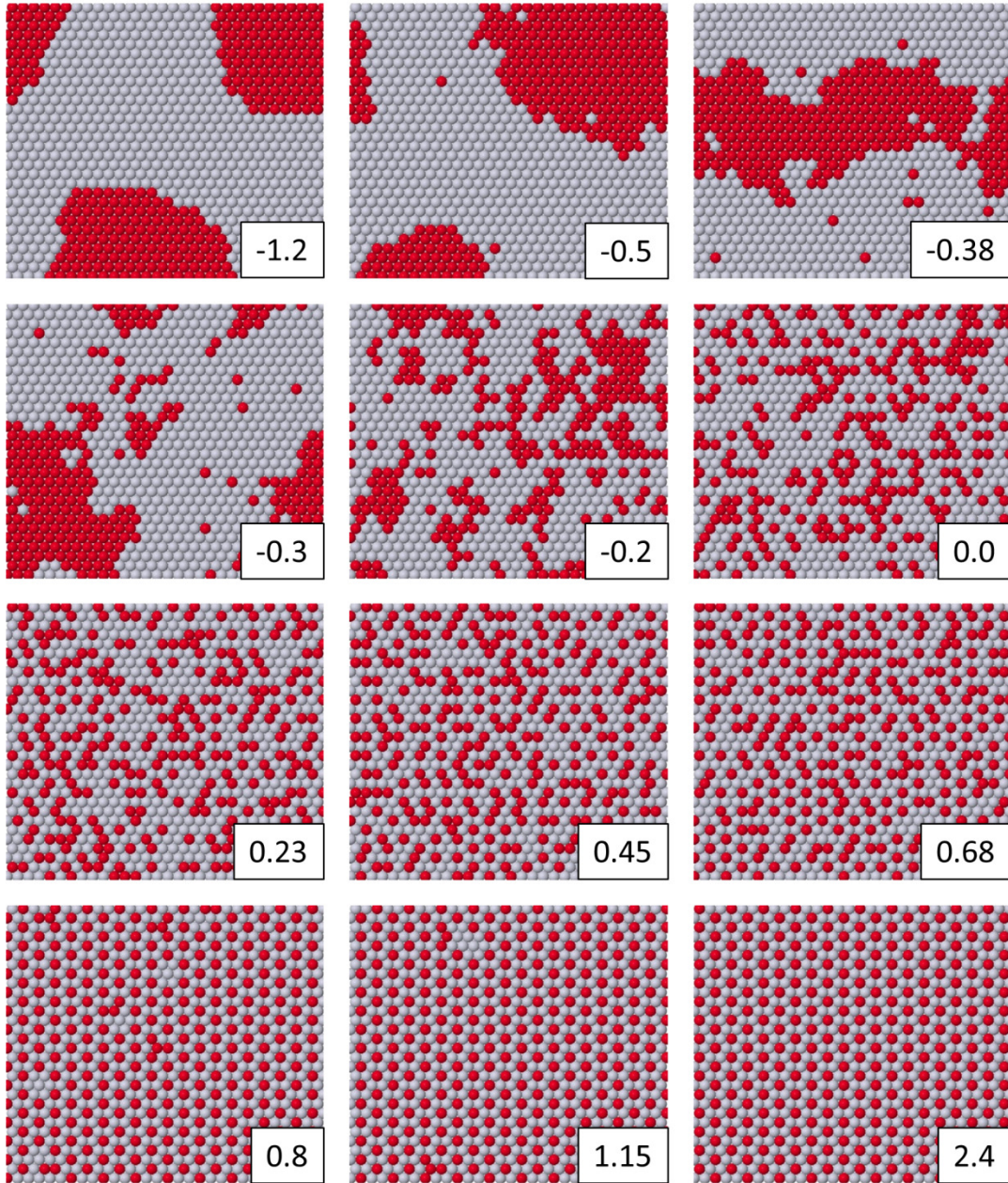


Figure 7.5. Snapshots from simulations of fcc(111) surface alloys with $\theta = 1/3$ at the scaled pair interaction indicated.

In order to explore the effects of $\bar{J}_2$ on atomic arrangement in surface alloys, MC simulations were performed over a range of values from $\bar{J}_2 = -1.2$ to $+2.4$. Impurity compositions between $\theta = 0.01$ and $\theta = 0.50$ were examined.

Figure 7.5 shows snapshots taken from simulations with $\theta = 1/3$.

At $\bar{J}_2 = -1.2$, the impurity atoms (red) fully segregate from the host (gray). This occurs because interactions between like atoms (Impurity-impurity or host-host) make a positive contribution to Φ_2 , and therefore are energetically favorable when J_2 is negative. For the same reason, the island of impurity atoms is roughly circular, which minimizes the number of impurity-host interactions. As $\bar{J}_2$ is increased to -0.5 and -0.38 , impurity monomers and dimers are ejected from the island, and its boundaries become roughened. Larger islands break away at $\bar{J}_2 = -0.3$. At -0.2 , impurity atoms form a mixture of large islands and small ensembles.

As $\bar{J}_2$ changes sign to become positive, host-impurity interactions become more energetically favored, and impurity atoms become increasingly well-dispersed in the surface. At $\bar{J}_2 = 0.23, 0.45$, and 0.68 , a growing number of small impurity ensembles exist in the surface. In addition, the larger ensembles take on branching chain shapes, rather than the more clustered appearance they had at negative values of $\bar{J}_2$. Small patches of $(\sqrt{3} \times \sqrt{3})R30^\circ$ -like order begin to emerge at $\bar{J}_2 = 0.68$, and order clearly dominates at 0.8 . At 2.4 , the surface is completely ordered and free of defects.

The sequence of snapshots in Figure 7.5 demonstrate the strong dependence of atomic configuration on interatomic interactions. They also suggest that if atomic arrangement plays an important role in the kinetics of a reaction, screening studies based solely on ordered surfaces may fail to identify (or wrongly identify) a potentially promising catalyst.

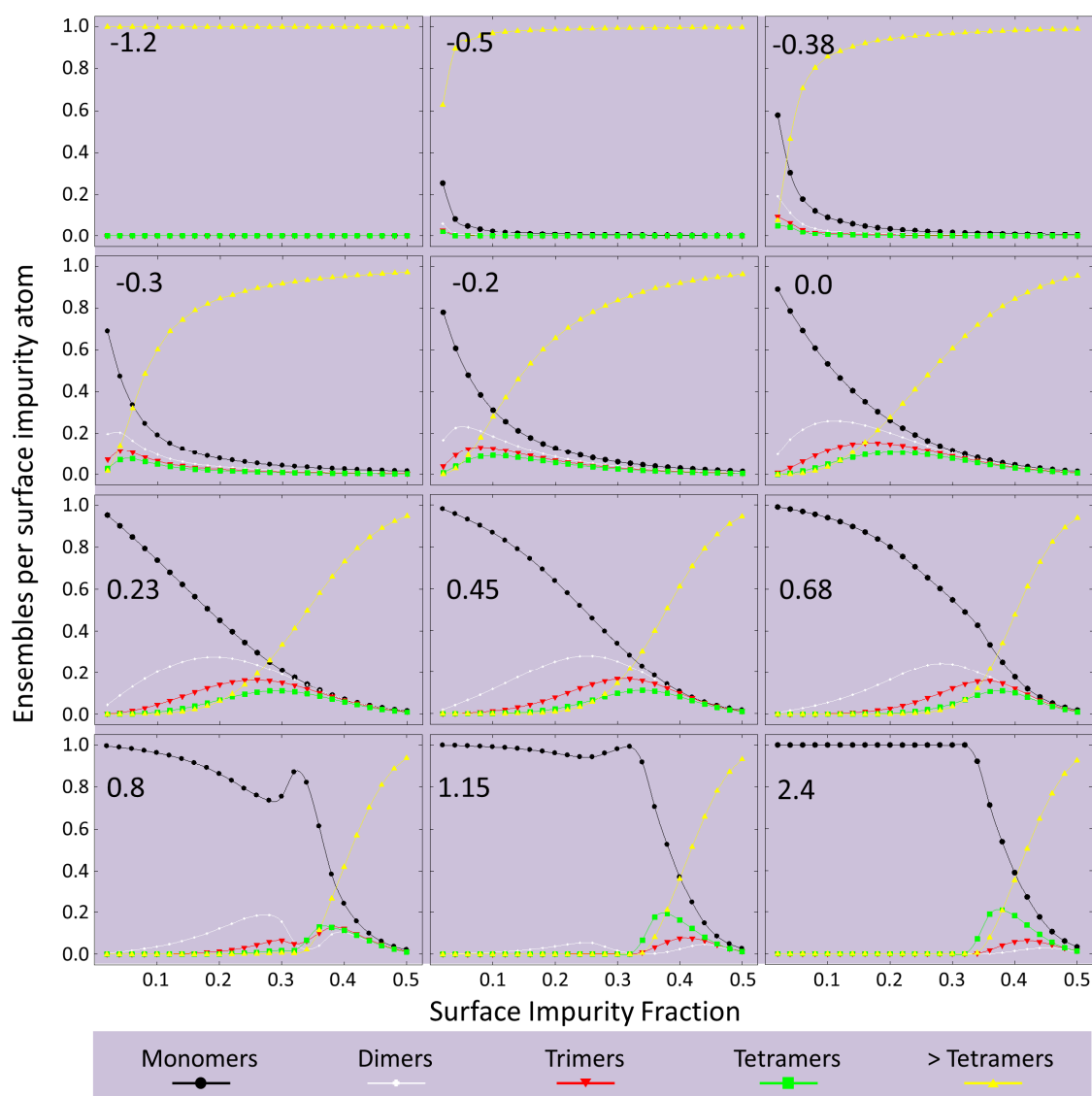


Figure 7.6. Ensemble size distributions for a range of scaled pair interactions.

The series of plots in Figure 7.6 show the size distribution of contiguous impurity ensembles as a function of θ and $\bar{J}_2$. The fractional population of impurity monomers, dimers, trimers, and tetramers are shown, as well as the fraction of impurity atoms belonging to all larger contiguous islands.

For the most negative $\bar{J}_2$ shown (-1.2), all impurity atoms belong to ensembles larger than tetramers, regardless of the impurity fraction in the surface. As $\bar{J}_2$ is increased, impurity atoms increasingly take part in smaller ensembles, especially at lower θ . At $\bar{J}_2 = 2.4$, the population of impurity atoms in large ensembles is essentially 0 until $\theta > 1/3$, whereupon the spaces between impurity atoms in the ordered surface begin to be “filled in.” (See Figure 7.5)

The population of monomers varies with $\bar{J}_2$ and θ in an almost mirror-image fashion to the larger ensembles. At large, negative $\bar{J}_2$, no monomers are present in the surface, while at large, positive $\bar{J}_2$, impurity atoms exist exclusively as monomers until the symmetry properties of the hexagonal lattice no longer permit it (at $\theta > 1/3$).

For most values of $\bar{J}_2$, the populations of intermediate-sized ensembles—dimers, trimers, and tetramers—never rise above the populations of monomers. In the vicinity of $\bar{J}_2 = 0.23$ and 0.45, the fraction of impurity atoms in dimers takes on its absolute largest value, approximately 0.3.

Taken as a whole, the size distributions in Figure 7.6 urge caution in cases where the activity or selectivity of a proposed catalyst depends strongly on the presence of certain contiguous ensembles and/or the absence of others. If a desired reaction has been predicted to occur readily on impurity dimers, trimers, or tetramers in a certain alloy, for instance, the relatively small population of these ensembles that are predicted by our simulations to exist in any surface alloy may be an impediment to its adoption as a catalyst. Similarly, if a reaction pathway depends on the absence of dimers and larger

ensembles for its selectivity, it may be necessary to use a catalyst with low θ , where the majority of impurity atoms are monomers. However, a catalyst with low θ by definition has a small number of impurity sites, which would reduce the rate. One caveat to this warning is that the distribution of atoms in a surface alloy is not only a matter of thermodynamics under vacuum conditions, but has been demonstrated in some cases to also depend on, for example, the presence of adsorbates. Although this phenomenon deserves further attention, it is outside of the scope of this work.

7.6 CONCLUSIONS

A method was developed to predict the energetics of bimetallic surface alloys using a cluster expansion (CE) truncated to include only first nearest-neighbor pair interactions. Restricted training sets composed of only five, 2×2 fcc(111) slabs were used to parameterize the cluster expansion for particular alloys. The energies of the slabs in the training set were calculated using density functional theory. Parameterization was performed using a least squares procedure, and the effective cluster interactions of the 1NN CE model were presented for several example alloys. The errors associated with truncating the CE and using a restricted training set were evaluated in two cases [AuPd(111) and AuPt(111)] by comparing with results from Chapter 3. We determined that in these two surface alloys, the errors were acceptable.

We next demonstrated that because we had limited the cluster expansion to 1NN pair interactions, the finite-temperature, equilibrium arrangement of atoms in all surface alloys was controlled by a single dimensionless parameter, the scaled pair interaction, $\bar{J}_2$.

Finally, we reported the results of a series of canonical ensemble Metropolis Monte Carlo simulations conducted over a range of $\bar{J}_2$ values and degrees of surface impurity fraction. Snapshots of the simulated surface and the impurity ensemble size

distribution were presented to show that surface atomic arrangement is greatly influenced by both variables. Ordered alloys, which are commonly used in combinatorial theoretical catalyst studies, were shown to exist only at $\bar{J}_2$ values greater than approximately 0.8. Based on the ensemble size distributions, we also argued that care must be taken in interpreting the results of theoretical surface chemistry studies that depend strongly on the arrangement of surface atoms.

Chapter 8: Conclusions

Using a simulation scheme that combines density functional theory, the cluster expansion method, and the Metropolis Monte Carlo algorithm (Chapter 2), we explored a number of influences on the atomic configuration of bimetallic catalytic surfaces. In Chapter 3, we examined the consequences of differing interatomic interactions in surface alloys in the (111) crystallographic facet by comparing the results of MC and DFT simulations of AuPd/Pd(111) and AuPt/Pt(111). Chapter 4 extended this study into the (100) surface facet of the same pairs of metals, where it was seen that longer range interactions resulted in the preferential formation of second nearest-neighbor pairs of Pd monomers. Some of the effects of biaxial strain were explored in Chapter 5, and a method to predict the near-surface atomic configuration of bulk alloys was presented in Chapter 6. Finally, in Chapter 7, we developed a computationally inexpensive method to predict the finite-temperature atomic arrangement of bimetallic alloys by reducing their behavior to a single dimensionless parameter, the scaled pair interaction. In each of these cases, we have shown the utility of the DFT+CE+MC approach as a tool for predicting atomic arrangement in alloy surfaces.

Extensions of this work could be pursued fruitfully in a number of directions. To name a few:

- The “pressure gap” that exists between traditional ultra-high vacuum surface science experiments and catalysis under more realistic, high pressure conditions has been at least partially addressed for pure metals¹²⁶⁻¹²⁹. For alloys, the situation is complicated by the fact that many adsorbates interact more strongly with one component than others, which can cause rearrangement of atoms in the surface or enhance segregation to the surface of that

component^{72,126,130,131}. Additional study is needed to elucidate the nature and consequences of these phenomena.

- Similar to the “pressure gap”, a “materials gap” exists between the atomically flat surfaces that commonly have been used in both experimental and theoretical surface science, and more realistic catalytic systems in which metal particles are dispersed on a support. Tremendous effort has been expended developing techniques to determine the morphologies of single-metal and alloy clusters, but the great majority of these have focused on particles in the gas phase^{132,133}. Research into the ways in which particle-support interactions affect the structure and ultimately the catalytic properties of supported catalysts would clearly be of benefit.
- The Metropolis algorithm has enabled us to predict characteristics of the atomic configuration of alloys at thermodynamic equilibrium. However, it is likely that kinetics also plays an important role in determining the structure of alloys. While a few DFT-based, atomistic studies of the diffusion processes occurring in and near the surfaces of alloys have been reported^{134,135}, this area of research is in its infancy.

The prevalence of heterogeneous catalysis, the exponential growth of computing power (and, concomitantly, its increasing availability)¹³⁶, and ongoing improvements in the accuracy and accessibility of modeling techniques virtually guarantee that computational studies such as the ones described in this dissertation and those recommended above will only become more numerous.

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Vita

John Adam Stephens grew up on a farm in Gray County, Texas. After graduating from Pampa High School in 1998, he entered Texas Tech University in Lubbock, Texas, majoring in chemical engineering. He received the degree of Bachelor of Science in December, 2002. During the following years he was employed by Rhodia, a global chemicals concern, in its Vernon, TX manufacturing plant. In August, 2006, he became a graduate student in the John J. McKetta Jr. Department of Chemical Engineering at The University of Texas at Austin, soon thereafter joining the research group of Professor Gyeong S. Hwang.

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