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METAL CLUSTERS: DYNAMICS AND STRUCTURE

FINAL TECHNICAL REPORT
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Building 5, Cameron Station
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Dear DTIC Officer:

Enclosed please find twelve copies of "*Metallic Clusters: Dynamics and Structure: Final Technical Report Submitted to the Office of Naval Research (ONR Grant No. N00014-89-J-1492)*" for the Grant Period 15 December 1991-31 December 1993. Enclosed also is one copy of the proceedings for the *14th Annual West Coast Theoretical Chemistry Conference (ONR Grant No. N00014-93-1-0207)* for the Grant Period 1 January 1993 to 31 December 1993. These proceedings consist of an abstract book, a list of names/addresses of attendees, etc.

Sincerely,

Emily A. Carter

Emily A. Carter
Associate Professor

Enclosures

During the tenure of this grant, we have examined the dynamics and structure of metal clusters in the gas phase and on surfaces. We have extended the concept of cluster to also examine metallic interactions in two-dimensional islands and thin films. We have used both quantum mechanical approaches and classical Monte Carlo/Molecular Dynamics simulations. In addition, we have continued our development of a new first principles dynamics scheme specifically designed with atomic clusters in mind. The projects we have completed include: (i) the electronic structure and metal-metal bonding in low-lying states of Pt_2 and Pt_3;[1] (ii) structure and growth mechanisms of Pd two-dimensional clusters (islands) on bcc(110) substrates as a function of coverage;[2] (iii) structure, growth, and interdiffusion of Ni films on Ag(100);[3] (iv) development of a systematic guide to choosing the size and shape of a simulation cell using periodic boundary conditions for use in studying interfaces between crystalline solids of different density and symmetry;[4] (v) development of a general mean field theory for predicting thermodynamically preferred structures and growth mechanisms of thin metal films;[5] (vi) development of first principles dynamics and simulated annealing algorithms for localized wavefunctions (Gaussian-based) to predict structures and dynamics of atomic clusters;[6-10] and (vii) development of a new optimization algorithm for first principles predictions of cluster geometries that allows an $O(N^3)$ scaling of the two-electron integrals.[11] (The footnotes refer to the list of publications in Section E.) Progress made in each of the areas are summarized briefly below.

A. Quantum mechanical studies of metallic bonding

For most metallic materials, the interactions are poorly understood at this point. This prompted us to initiate a series of projects starting from the simplest metals, alkali metals, all the way up to mixtures of transition metals (TM's), in order to begin understanding metallic bonding from first principles. The goal is to use the quantum mechanical information to characterize the nature of various types of metallic interactions. Ultimately, we plan to design first principles-based interaction potentials for metals, for use

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in molecular dynamics and Monte Carlo simulations of bulk, surface, and interfacial phases. In particular, there is a dearth of potentials for describing alloys involving mixtures of fcc and bcc metals, because the character of such interactions is poorly understood. We believe that by studying small aggregates or clusters of these metals with quantum mechanics, we will be able to develop a detailed understanding of metallic bonding. So far, we have studied Pt, Na, and Ni clusters. We are interested primarily in studying TM's, not only because of their technological importance, but also because of the fundamental complexity introduced by the presence of partially-filled d-shells. We discuss here only the Pt cluster work, since the other clusters were examined with our ab initio molecular dynamics (AIMD) method, which is discussed in a separate section.

The major result of the work on pure Pt clusters,[1] which was somewhat surprising, is that the s-electrons play the dominant role in metallic bonding for the noble metals. We had initially expected more d-electron participation since the d-shell is not filled, but the s-electrons appear to dominate, even for Pt. Employing both generalized valence bond (GVB) and configuration interaction (CI) methods combined with a relativistic effective core potential and a more than double-ζ quality valence basis set, we calculated the equilibrium structures of all low-lying states of Pt dimer and trimer. Our preliminary work assumed equilateral triangle geometries with bulk M-M distances for Pt_3. We find a very dense Pt_3 electronic state spectrum, with all nine states that were close in energy when the bulk geometry was imposed still staying close in energy for the optimized structures (within 7 kcal/mol of the ground state). In addition, we find a linear $^5\Delta_g$ state that is also very low-lying (6.3 kcal/mol up from the ground $^3A_1$ state). The physical reason for the high density of states of different spin lying so close to the ground state is that all of these low-lying states have only one strong ($\cong$50 kcal/mol) 6s-6s bond holding the cluster together. By contrast, d-d bonds are essentially worthless, as evidenced by the near degeneracy (within 0.002 eV) of the $^3A_1$ (s-s plus d-d bonding) and $^5B_2$ (s-s bonding only) states and the negligible orbital overlap in the d-d bond ($S_{d\text{-}d} = 0.03$ vs. $S_{s\text{-}s} = 0.78$).

We find that the equilibrium geometries of the cluster in all these low-lying states have bond lengths greater than or equal to the bulk metal, but greater by no more than 0.21 Å. The structures we calculated are in good agreement with scanning tunneling microscopy determinations of the Pt dimer and trimer structures on graphite.[1] Most of the structures are within ±5 degrees of an equilateral triangle configuration, dictated by the predominance of the s-s bond. The linear state is obviously an exception, with the bonding consisting of a three-center two-electron bond involving s-electrons on the outer Pt's and a dz^2-electron on the central Pt, making this linear state competetive with the triangular states. Our calculations offer a simple explanation for the photoelectron spectrum of Pt_3^-, where transitions are observed within a 0.2-0.3 eV window. We believe these transitions, previously unassignable because it was unclear as to whether these were vibronic transitions or transitions to a dense electronic manifold of neutral Pt_3, have a strong component of the latter type. The nearly filled d-shell on Pt makes it impossible for the metal-metal bonds to shorten, because of interatomic repulsive interactions. This makes d-d coupling energies very small, leading to the dense manifold of states.

B. Structure and growth mechanisms of thin metal films

Isothermal (NVT) Monte Carlo simulations[2,3] have been used to characterize the structure and growth mechanisms of ultrathin transition metal films on transition metal substrates, as a function of substrate structure, interfacial strain, temperature, and coverage. Such films have promising technological applications in such areas as magnetic recording media (because of unusual magnetic properties of Fe, Co, and Ni in 2-D films) and heterogeneous catalysis (because of dramatically altered chemisorption properties), and as high temperature coatings (for mechanical properties, e.g., engine design).

We carried out simulations of the growth of clusters (islands) of a face-centered cubic (fcc) metal, Pd, on a body-centered cubic (bcc(110)) substrate, using pseudo-many-body embedded atom method (EAM) potentials.[2] These were carried out as a function of both coverage and temperature, to understand when two-dimensional islands or threedimensional crystallites may dominate dispersive structures. We find that large two-dimensional islands growing anisotropically along the [001] direction are preferred over any other structure. We have calculated barriers to diffusion of adatoms within the context of the EAM potential and find low barriers for reshaping the island to propagate along the preferred direction. The growth along the [001] direction can be rationalized in terms of maximizing the number of nearest neighbor and next nearest neighbor interactions within the adlayer. These channels of Pd should be visible using ion scattering spectroscopy.

We also examined the adsorption of an fcc metal on an fcc substrate, in order to determine the conditions under which alloys are formed versus stable metal overlayers (i.e., stable phase separation). In particular, we have simulated the adsorption of Ni on Ag(100), which is of particular interest because of the potential for unusual magnetic properties in low-dimensional films.[3] We find that Ni grows in a layer-by-layer, pseudomorphic fashion at room temperature up to at least 3.2 ML. This film has a tetragonal structure, consisting of a compressive interlayer stress that compensates for the expansive intralayer strain (Ni/Ag has a 13.9% lattice mismatch). Interdiffusion of Ag atoms to form a capping Ag monolayer on top of the Ni film is found to be thermodynamically favorable. Consistent with the fact that bulk Ni is immiscible in bulk Ag, no stable alloy formation is observed nor is a commensurate-incommensurate transition ever seen.

In the process of carrying out these simulations of strained metallic films on metallic substrates, it became clear that one needed to have a systematic approach to choosing the simulation cell size, in order to avoid predicting structures that were mere artifacts due to constraints imposed by the cell size coupled to periodic boundary conditions. As a result, we came up with a scheme that systematically minimizes periodic-boundary-induced strain necessarily present in simulations of crystalline interfaces of different density and symmetry.[4] The method involves constructing a discrete strain sequence that evaluates the strain as a function of cell size, where the discretization parameter is given by the substrate lattice constant. We show that this can be used to unambiguously choose a cell size for any interface simulation and will virtually eliminate possible artifacts due to periodic-boundary-condition-induced strain.

Most recently, we have developed a mean field statistical mechanical theory to examine more generally both the growth mechanism and structures of fcc metallic films on fcc(100) substrates using the Finnis-Sinclair pseudo-many-body analytic potential function (fit to properties of alloys and pure metals).[5] The goal was to determine in a more general sense which (and whether) bulk properties of these metals could be used to predict structures and growth mechanisms of ultra-thin metallic films. Eleven hetero-interfaces with bulk cohesive energy differences as large as 4 eV and lattice mismatches ranging from -21% to 16% were studied. For small (up to ≅5%) mismatched interfaces, pseudomorphic Stranski-Krastanov (one complete layer followed by 3-dimensional clustering) growth is found to be competitive with pseudomorphic layer-by-layer growth. When the lattice mismatch is 10% or higher, the growth mechanism always involves incommensurate, 3-dimensional (Volmer-Weber) growth, where growth of (111) clusters is energetically competitive with growth of (100) clusters on (100) substrates. The overlayer structures and growth modes correlate most closely with only one property: the lattice strain between the substrate and the adlayer. By contrast, the trends in the bulk cohesive energies do not allow even any qualitative prediction of the overlayer structures. We do find that surface energies can dictate minor changes in the film growth modes. Lastly, over the 300-800 K temperature range examined, we find no change in film morphology. We expect at lower temperatures (work in progress) to see some alterations in the growth mechanisms and film structures.

In sum, we are able to predict real space structures as a function of growth conditions that will aid the interpretation of both ion scattering and electron diffraction data, as they become available. The structures we calculate may help guide the design of thin films on certain substrates, based on the surface free energies, the interfacial strain, and the temperature at which the film is grown and is expected to operate.

C. Ab initio molecular dynamics

We have developed the first ab initio molecular dynamics/simulated annealing theory for both Hartree-Fock and Generalized Valence Bond (GVB) molecular wave functions.[6-9] Prior to this development, such theories were limited to density functional theory (DFT) dynamics. This method has two advantages over DFT approaches: (i) it incurs no large errors in the energy for molecular systems, unlike DFT, which was originally designed to model 3-dimensionally infinite systems rather than finite systems, where the gradient of the electron density changes drastically and (ii) it can be used to study excited electronic states. Electronically excited states would be accessible via spin-polarized DFT, but such wave functions are not eigenfunctions of spin. Our approach, which includes electron correlation at the GVB level, can be used to study the dynamics and structures of ground and excited spin eigenstates. The method is most simply described as following the classical motion of the atomic nuclei, but where the forces on the nuclei are calculated *analytically* directly from the electronic wavefunction.

This method will be extraordinarily useful in our study of metal clusters, where we have an aggregate of atoms that are all identical or very similar. These similarities cause nightmares for traditional quantum chemical approaches for optimizing structures of such clusters, since normally one calculates the gradient of the energy given some initial configuration of the atoms and moves toward the nearest minimum. Such an approach is almost guaranteed to fail because of the many local minima bound to be present in such a situation. Our method utilizes a "simulated annealing" algorithm, which allows us to heat up the nuclei and then slowly cool them down to find the minimum energy structure (i.e., the global minimum). By using simulated annealing, we can search for global minima in an unbiased manner with ab initio forces. We can predict structures of ground and excited states of these aggregates and see how they change with temperature. The electronic and vibrational structure can also be examined as a function of temperature. We have demonstrated the power of this method in several ways: (i) examining the short-time dynamics of a distorted, stretched Na_4 cluster;[6] (ii) annealing of the Na_4 cluster starting from a random 3-D geometry;[7] and (iii) annealing of a Ni_5 cluster starting from two very different random 3-D geometries with different amounts of initial kinetic energy.[10] For the short-time dynamics of Na_4,[6] we observed completely different behavior for the singlet and triplet states, starting from exactly the same geometrical configuration and velocities. In particular, we observed spin-eigenstate dependent dynamics, in which the singlet, with two bonding pairs of electrons tend to pull the nuclei closer together, while in the triplet, the two high spin electrons repel each other, forcing a pair of nuclei to repel each other (the bond stretches further). Such dynamics would never be seen in a classical simulation and are a beautiful illustration of the Pauli Principle in action. For the annealing of Na_4,[7] we found that we could start from a random 3D structure, and the ab intio quantum mechanical forces quickly induced a structural transition from 3D to 2D. The global minimum structure is known to be a planar rhombus, and we were able to access via this algorithm that structure, along with another one low lying in energy that was T-shaped. Most impressive, however, is our demonstration for a Ni_5 cluster,[10] that beginning with two entirely uncorrelated initial conditions of positions and momenta and following their annealing trajectories led to the same minimum energy structure. This demonstrates that for reasonably corrugated potential energy surfaces, we are able to predict in an unbiased manner the global minimum structure. For Na_4, the problem remains that the surface is very flat and therefore it is difficult to cool the cluster and reliably access only the global minimum. Thus, our method is expected to perform best for corrugated potential surfaces and perform worst for flat potential surfaces.

This method of AIMD is exceedingly expensive because one has, in principle, to evaluate the forces on the nuclei at every time step, where, if one is also propagating the wavefunction classically via an extended Langrangian,[6,7] then the time step length is determined by the shortest time scale in the problem in order to conserve energy properly. In this case, this limits the time step length to that of the motion of electrons (via the propagation of the wavefunction) rather than the nuclei. Thus, one is evaluating the forces on the nuclei much more often than is really needed, since the nuclei move much slower than the electrons. This motivated another thrust of our work, which involved implementing two multiple time step algorithms that would take advantage of the natural separation of time scales between nuclear and electronic motion (i.e., the Born-Oppenheimer approximation) and hence save computer time by evaluating the nuclear forces less often. Our first method translated into a savings of about a factor of 7, however, the form of the equations in fact was unstable when larger time step ratios than 10:1 (nuclear: electronic) were used.[8] This motivated our latest algorithm that was adapted from the work of Berne and co-workers (as was the first algorithm).[9] This algorithm is time-reversible, unlike the first one, and is much more stable than the previous one. We can conserve energy adequately for up to a 60:1 time step ratio, and obtain a factor of 20 savings over the single time step scheme. We are encouraged by this scheme, however, we are also considering other algorithms to increase the speed even further at this time.

D. O(N^3) Scaling of Integral Evaluations During Geometry Optimization

We have developed an optimization technique for ab initio geometry optimization that should greatly enhance the prediction of metallic and mixed metal cluster structures. This gradient-based technique is a modification of the quadratically convergent quasi-Newton method, and although it requires more energy evaluations than conventional approaches, each of these energy evaluations is much cheaper due to O(N^3) scaling of the two electron integral evaluation.[11] Essentially, the method optimizes the position of one atom in the cluster at a a time, which requires only mN^3 new integrals to be evaluated (m = the number of basis functions on the atom that is moving) instead of the N^4 integrals that would be required if all atoms moved at once. We demonstrated that this method is just as likely as a method that moves all atoms at once to find the same set of low energy structures.

Statistics obtained from numerous optimization runs with Lennard-Jones clusters of up to 27 atoms shows that the number of energy and gradient evaluations are only 1.5-5 times greater than conventional methods. Given the $O(N^3)$ scaling advantage, this can result in substantial savings in the cost of geometry optimization at the ab initio level.

In sum, we have completed a number of projects during the past two years, many of which we continue to work on. We have learned about metallic bonding, dynamics, and structure in small metal clusters, about structure and growth mechanisms of metallic thin films, and we continue our methods development related to ab initio molecular dynamics and cluster geometry optimization.

E. Publications Acknowledging Current ONR Grant

1. H. Wang and E. A. Carter, "Metal-Metal Bonding in Transition Metal Clusters with Open d-Shells: Pt_3," *J. Phys. Chem.*, **96**, 1197 (1992).

2. B. C. Bolding and E. A. Carter, "Two-dimensional Metallic Adlayers: Dispersion versus Island Formation," P. J. Reynolds, ed.; in "On Clusters and Clustering, From Atoms to Fractals," (Elsevier, Amsterdam, 1993), 167.

3. B. C. Bolding and E. A. Carter, "Effect of Strain on Thin Film Growth: Deposition of Ni on Ag(100)," *Surface Sci.*, **268**, 142 (1992).

4. B. C. Bolding and E. A. Carter, "Minimization of Periodic-Boundary-Induced Strain in Interface Simulations," *Molecular Simulation*, **9**, 269 (1992).

5. T.-M. Chang and E. A. Carter, "Mean Field Theory of Heteroepitaxial Growth of Thin Metal Films," *Phys. Rev. B*, submitted (1994).

6. B. Hartke and E. A. Carter, "Spin Eigenstate-Dependent Hartree-Fock Molecular Dynamics,"*Chem. Phys. Lett.*, **189**, 358 (1992).

7. B. Hartke and E. A. Carter, "Ab initio Molecular Dynamics with Correlated Molecular Wavefunctions: Generalized Valence Bond Molecular Dynamics and Simulated Annealing,"*J. Chem. Phys.*, **97**, 6569 (1992).

8. B. Hartke, D. A. Gibson, and E. A. Carter, "Multiple Time Scale Hartree-Fock Molecular Dynamics," *Int. J. Quantum Chem.*, **45**, 59 (1993).

9. D. A. Gibson and E. A. Carter, "Time-Reversible Multiple Time Scale Ab Initio Molecular Dynamics," *J. Phys. Chem.*, **97**, 13429 (1993).

10. B. Hartke and E. A. Carter, "Ab Initio Molecular Dynamics Simulated Annealing at the Generalized Valence Bond Level: Application to a Small Nickel Cluster," *Chem. Phys. Lett.*, **216**, 324 (1993).

11. I. V. Ionova and E. A. Carter, "$O(N^3)$ Scaling of Two-Electron Integrals During Molecular Geometry Optimization," *J. Chem. Phys.*, in press (1994).

F. Seminars Presented Acknowledging Current ONR Grant

Invited Lectures

August 25, 1992	"Spin Eigenstate-Dependent Ab Initio Molecular Dynamics of Clusters," in the Symposium on Frontiers of Molecular Simulation at the American Chemical Society National Meeting, Washington, DC.
June 3, 1993	"Generalized Valence Molecular Dynamics of Clusters," in the Symposium on Clusters at the Canadian Society for Chemistry Conference, Sherbrooke, Quebec, Canada.

July 23, 1993	"Ab Initio Molecular Dynamics and Simulated Annealing of Atomic Clusters," at the Third World Congress of Theoretical Organic Chemists, Toyohashi, Japan.
August 24, 1993	"Solid State and Surface Chemistry from First Principles: Structure and Dynamics," Exxon Award talk at the American Chemical Society National Meeting, Chicago, Illinois.
August 26, 1993	"Sequential and Simultaneous Ab Initio Molecular Dynamics for Clusters and Surface Chemistry," in the Symposium on Computational Methods in Inorganic Chemistry at the American Chemical Society National Meeting, Chicago, Illinois.

Invited Seminars

January 21, 1992	"Theoretical Studies of Metallic and Semiconductor Surface Chemistry," Chemistry Department Seminar, California State University at Los Angeles, Los Angeles, California.
May 11, 1992	"Simulations in Materials Science: Mechanisms for Thin Metal Film Growth and Etching/CVD Chemistry of Silicon," Chemical Research Center Seminar, General Electric Company Research and Development Center, Schenectady, New York.
May 12, 1992	"Sequential and Simultaneous Ab Initio Molecular Dynamics," Physical Chemistry Seminar, Massachusetts Institute of Technology, Cambridge, Massachusetts.
August 31, 1992	"Using Theory to Understand Chemistry on Surfaces," Seminar at Olin Chemical Corporation, Cheshire, Connecticut.
September 1, 1992	"Using Theory to Understand Chemistry on Surfaces," Chemistry Department Seminar, University of Connecticut, Storrs, Connecticut.
October 6, 1992	"Sequential and Simultaneous Ab Initio Molecular Dynamics," Physical Chemistry Seminar, University of Washington, Seattle, Washington.
December 8, 1992	"Sequential and Simultaneous Ab Initio Molecular Dynamics," Physical Chemistry Seminar, University of Wisconsin, Madison, Wisconsin.
February 11, 1993	"Using Theory to Understand Chemistry on Surfaces," Chemistry Department Seminar, California State University, Northridge, California.
September 17, 1993	"Ab Initio Molecular Dynamics in Materials Science," Physical Chemistry Seminar, Iowa State University and Ames Laboratory, Ames, Iowa.
October 12, 1993	"Ab Initio Molecular Dynamics," James Franck Institute Seminar, University of Chicago, Chicago, Illinois.

October 18, 1993	"Ab Initio Molecular Dynamics," McKoy Award Lecture, University of California, Los Angeles, California.

Contributed Talks and Presentations

March 17, 1992	"Generalized Valence Bond Molecular Dynamics," poster at the Sanibel Symposia, St. Augustine, Florida (presented by Bernd Hartke).
May 21, 1992	"Multiple Time Step Algorithms for Ab Initio Molecular Dynamics," poster at the 13th Annual West Coast Theoretical Chemistry Conference, Richland, Washington (presented by Douglas Gibson).
May 22, 1992	"Generalized Valence Bond Molecular Dynamics for Small Metal Clusters," talk at the 13th Annual West Coast Theoretical Chemistry Conference, Richland, Washington (presented by Bernd Hartke).
August 24, 1992	"Effects of Periodic-Boundary-Induced Strain on Thin Film Growth," talk in the Symposium on Theoretical Aspects of Materials Related Surface Chemistry at the American Chemical Society National Meeting, Washington, DC (presented by Barry Bolding).
March 2, 1993	"Generatlized Valence Bond Molecular Dynamics and Simulated Annealing for Small Metal Clusters," poster at Femtosecond Chemistry - The Berlin Conference (presented by Bernd Hartke), Berlin, Germany.
June 17, 1993	"Ab Initio Molecular Dynamics with Reversible RESPA," poster at the 14th Annual West Coast Theoretical Chemistry Conference, Los Angeles, California (presented by Douglas Gibson).
June 18, 1993	"Effect of Temperature and Lattice Mismatch on Structures of Metallic Thin Films," poster at the 14th Annual West Coast Theoretical Chemistry Conference, Los Angeles, California (presented by Tsun-Mei Chang).
June 18, 1993	"Monte Carlo Simulations of Metallic Thin Films," poster at the 14th Annual West Coast Theoretical Chemistry Conference, Los Angeles, California (presented by Michelle Radeke).
June 19, 1993	"$O(N^3)$ Scaling of Two-Electron Integrals During Molecular Geometry Optimization," poster at the 14th Annual West Coast Theoretical Chemistry Conference, Los Angeles, California (presented by Irina Ionova).
June 29, 1993	"$O(N^3)$ Scaling of Two-Electron Integrals During Molecular Geometry Optimization," poster at the Eighth American Conference onTheoretical Chemistry, Rochester, New York (presented by Irina Ionova).

June 30, 1993	"Effect of Temperature and Lattice Mismatch on Structures of Metallic Thin Films," poster at the Eighth American Conference on Theoretical Chemistry, Rochester, New York (presented by Tsun-Mei Chang).