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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE September 1991	3. REPORT TYPE AND DATES COVERED Final 1 Nov 87 - 31 Oct 90	
4. TITLE AND SUBTITLE Microscopic Theoretical Modeling of the Chemical and Tribological Properties of Ceramic Surfaces and Interfaces			5. FUNDING NUMBERS 61102F 2303/B3	
6. AUTHOR(S) William A. Goddard III				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) California Institute of Technology Division of Chemistry and Chemical Engineering Pasadena, CA 91125			8. PERFORMING ORGANIZATION REPORT NUMBER AFOSR-TR-91 0815	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NC Bolling AFB, DC 20332-6448			10. SPONSORING / MONITORING AGENCY REPORT NUMBER AFOSR-88-0051	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution is unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) See Back				
14. SUBJECT TERMS			15. NUMBER OF PAGES 56	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED		18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT SAR

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Through simultaneous examination of all properties of the surface (chemical, tribological, physical, and mechanical) with the same theory, we have the possibility of strong tests on different aspects of the theory. In addition, such a central theory would provide new connections between these properties that would serve to connect what are now orthogonal experiments. These developments should provide a level of understanding useful in designing new materials and such computer-aided materials simulations (CAMS) should provide tools allowing many of the design concepts to be tested on the computer in advance to attempting difficult syntheses and characterizations in the laboratory.

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Justification _____	
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Availability Codes	
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ORIGINAL

Microscopic Theoretical Modeling of the Chemical and  
Tribological Properties of Ceramic Surfaces and Interfaces

Final Technical Report

November 1, 1987 - October 31, 1990

for

Air Force Office of Scientific Research

Grant Number AFOSR-88-0051

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Approved for public release;  
distribution unlimited.

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## SUMMARY

The goal of this research was to develop a microscopic atomic-level understanding of the fundamental surface processes responsible for friction, adhesion, and abrasion. The emphasis is on materials (particularly ceramics) having potential applications in high performance systems and also on systems for which it is possible to design precise experimental tests of the predictions.

There have been five major advances:

- a. **Pseudospectral-Generalized Valence Bond (PS-GVB)** for accurate quantum chemical calculations of large molecules. This is a major breakthrough for calculating electronic states and properties of clusters and crystals. With previous methods, inclusion of electron correlation effects (as in GVB) has generally been limited to about 10 atoms or so (200 basis functions) where costs scales as  $N^4$  or  $N^5$  with size ( $N$ ) of this system. PS-GVB avoids calculating the  $N^4$  electron repulsion integrals which causes this problem. Instead the Coulomb and exchange operators are calculated directly (over a numerical grid) and then combined to form the Fock operators from which the GVB orbitals are obtained. This decreases the computational problem to one that scales as  $N^3$  (dropping to  $N^2$  with cutoffs) and allows systems of 2000 basis functions ( $\sim 100$ -200 atoms) to be computed in the same time as previously for 200 basis functions (10-20 atoms). This approach also allows use of periodic boundary conditions (PBC) for direct calculation of infinite crystals and surfaces. (PBC is still under development.)
- b. **The Cell Multipole Method (CMM)** for calculating forces, structures, and properties of million-atom systems. This is a major breakthrough for atomic-level molecular dynamics simulations of condensed systems. With previous methods, simulations on thousands of atoms generally requires CRAY level computers for studying dynamical properties; however, for modeling tribological systems it may be necessary to treat 100,000 or even a million atoms. (A diamond cube of  $200 \text{ \AA} = 20 \text{ nm} = 0.02 \mu$  per side

has one million atoms.) Although there are  $N^2$  Coulomb interactions for an  $N$  body systems the computational cost for the Cell Multipole Method is rigorously linear in  $N$ . This is done by evaluating multipole fields for each region (cell). We have carried out million atom simulations for finite polymers and for million atoms per unit cell simulations on pseudo periodic amorphous systems. In both cases CMM is  $10^3$  faster than the explicit evaluation of all interactions.

- c. **The Charge Equilibration (QEq) approach for predicting charge distributions in ceramic and polymer systems.** This approach solves a major problem in simulations of ceramics and polymer systems (where electrostatic effects play a dominant role) since there had been no method for actually predicting the charge distributions essential to simulations. The new method has as its input only atomic information (available for all atoms) and predicts the charge redistribution as a function of geometry.
- d. **The Hessian-Biased Force Field (HBFF) method of combining data (the Hessian or second-derivative matrix) from quantum chemical calculations with observed vibrational frequencies to determine accurate valence force fields (describing how the energy and forces depend on bonds, angles, etc.).** This is critical for describing the dynamics of motion as two surfaces interact with each other or with lubricant, and it is also essential in describing the vibrational modes (phonon bands) that couple to surface states in dissipative (frictional) processes. These data are also essential for calculating quantities related to the hardness of materials.
- e. **The Interstitial Electron Model (IEM) for Simulations of Metallic Systems.** We believe that this is a major breakthrough that will allow meaningful simulations of tribological properties of metals. The difficulty in simulating metals is that the electrons respond dramatically to motion of the ions and hence the forces cannot be described solely in terms of ion positions. Our new approach (based on concepts arising from GVB quantum mechanical calculations) treats electrons as classical particles so that the energy is described in terms of electron-electron, electron-ion, and ion-ion interactions. We have tested this approach by calculating elastic constants and phonon

dispersion curves, with excellent results.

In addition we have developed force fields suitable for simulations on graphite, diamond, fullerenes ( $C_{60}$ ,  $C_{70}$  buckyballs),  $Si_3 N_4$ , SiC, Si, Ge, Sn, cubic-BN GaAs, GaP, GaSb, AlAs, AlP, AlSb, InAs, InP, InSb,  $SiO_2$ ,  $Al_2 O_3$ , NiO,  $YBa_2 Cu_3 O_x$ , Al, Fe, Ni, Cu, Pd, Ag, Pt, Au, and other materials of tribological interests.

We believe that these tools and force fields provide the basis for microscopic theoretical modeling of the Chemical and Tribological Properties of Ceramic Surfaces and Interfaces.

## I. Introduction

The major goal to this research was to develop a strategy for establishing a microscopic atomic-level understanding of the fundamental surface processes ultimately responsible for friction, adhesion at surfaces, and abrasion.

Although there have been rapid advances in the experimental techniques for examining composition at surfaces and interfaces relevant for catalysis, tribology, corrosion, and materials synthesis, there has been very little in the way of a microscopic theoretical model suitable for understanding the *chemical*, *physical*, and *mechanical* properties in terms of atomic-level structure and bonding concepts. Our project was a broad-based *theoretical program* aimed at providing the *fundamentals* for constructing such an atomic-level *microscopic model* of the *chemical*, *tribological*, *physical*, and *mechanical properties of ceramic surfaces and interfaces*.

The approach was

- i. to use *quantum chemical* studies to establish the dominant surface species for *clusters* of atoms modeling various ceramics and to elucidate the thermochemistry and detailed mechanistic steps involved in surface reactions of such systems;
- ii. to develop *theoretical force fields* based on the energy surfaces from clusters in *i* that allow predictions of the energies and geometries for infinite surfaces and interfaces;
- iii. to use the force fields from *ii* to predict the *barriers* and *kinetics* for various diffusion and reaction processes relevant for catalysis, corrosion, and materials synthesis processes;

iv. to develop procedures for *molecular dynamics* and *Monte Carlo* simulations of various chemical processes in these systems; and,

v. to interface the results of these simulations onto appropriate graphics systems, allowing the designer to interactively follow a three-dimensional image of the evolving system.

Through simultaneous examination of all properties of the surface (chemical, tribological, physical, and mechanical) with the same theory, we have the possibility of strong tests on different aspects of the theory. In addition, such a central theory would provide new connections between these properties that would serve to connect what are now orthogonal experiments. These developments should provide a level of understanding useful in designing new materials and such *computer-aided materials simulations* (CAMS) should provide tools allowing many of the design concepts to be tested on the computer in advance to attempting difficult syntheses and characterizations in the laboratory.

There have been major advances in each of these areas, as is summarized in the next few sections.

## II. New Developments in Quantum Chemistry

Over the last ten years, the Goddard group has carried out a number of quantum chemical studies on clusters designed to mimic the chemically active sites of metal, semiconductor, and ceramic surfaces. This research has led to the GVB suite of programs which provides powerful methods of including electron-correlation (many-body) effects for accurate predictions of reaction intermediates in transition metal complexes. These studies have led to a number of insights on surface chemistry and have led to new or modified mechanisms for key steps of several important catalytic reactions.

Despite the progress, there remained severe limitations for use of these techniques and tribological systems. We are convinced that *ab initio* methods including a high level of electron correlation are essential to obtain accurate information about the surface chemistry involved in wear and friction (since there is little experimental data to use as guidelines in adjusting parameters). However, with previous techniques inclusive of electron correlation has restricted use to using small clusters as models of catalytic systems, making it difficult

to examine the role of promoters, poisons, modifiers, solvents, and surface structures on catalytic pathways and rates.

A fundamental advance here has been the development of PS-GVB (pseudospectral-generalized valence bond) where the Coulomb and exchange potentials are calculated directly (over a numerical grid) without evaluating or storing the two-electron integrals. Since in PS-GVB the  $N^4$  set of two-electron integrals are never constructed, we eliminate the source of bottlenecks in previous *ab initio* quantum chemistry methods, storing and manipulating  $N^4$  of these integrals. Thus, for 200 basis functions the usual approach involved  $N^4/8 = 2 \times 10^8$  integrals; for 2000 basis functions there are  $2 \times 10^{12}$ ! With PS, the Coulomb and exchange integrals are evaluated over a numerical grid and used as needed. For HF wavefunctions with 200 basis functions, the PS-HF program on a CRAY-YMP is 10 times faster than GAUSSIAN 88 (20 times faster than GAUSSIAN 86), and for 2000 basis functions it should be 100 times faster.

There are four points to the overall PS-GVB development:

- i. PS-GVB-PP allows calculation of structures and charges for large clusters (20-200 atoms) useful in establishing parameters for modeling realistic materials problems.
- ii. GVB-PBC will provide correlated wavefunctions (PP) for infinite periodic crystals (up to  $\sim 50$  atoms per cell), allowing direct prediction of the electronic and structural properties for crystals and surfaces (without corrections due to cluster effects).
- iii. PS-GVB-RCI will provide accurate descriptions of saddle points for reactions (up to  $\sim 30$  atoms), allowing realistic simulation of catalysts and reaction mechanisms.
- iv. GVB-EN2 (second order Epstein-Nesbet perturbation theory for GVB-RCI wavefunctions) should allow very accurate description of bond energies ( $\sim 0.5$  kcal/mol) and van der Waals interactions (to obtain nonbonded potentials for molecular dynamics studies).

We consider PS-GVB to be a genuine breakthrough, providing the means for practical calculations from first principles the chemical and mechanical properties of surfaces and interfaces.

These PS-GVB methods are under active development, and all are expected to be

fully implemented by summer 1992.

### A. Pseudospectral Methods

In PS-GVB the usual  $N^4/8$  set of two-electron integrals  $(\mu\nu|\sigma\eta)$  is never evaluated (where  $N$  is the number of basis functions). It is storing and manipulation of these integrals that causes the current bottlenecks in quantum chemical calculations (for 200 basis functions there are  $N^4/8 = 2 \times 10^8$  integrals, for 2000 basis functions there are  $2 * 10^{12}$ ). Instead, with PS the Coulomb and exchange operators are evaluated directly for a numerical grid. This involves evaluating the  $N^2/2$  quantities

$$A_{\sigma\eta}(r_g) = \int d^3r_2 \frac{\chi_\sigma(2)\chi_\eta(2)}{|r_g - r_2|} \quad (1)$$

directly for a set of grid points  $\{r_g\}$ . With Gaussian type basis functions, the potentials  $A_{\sigma\eta}(r_g)$  are evaluated analytically for each grid point (a sufficiently fast calculation that these potentials can be used and then discarded).

Given the potentials (1), the fundamental Coulomb and exchange matrices could be calculated numerically using

$$\begin{aligned} J_{\mu\nu}^j &= \langle \mu | \hat{J}_j | \nu \rangle = \sum_g \chi_\mu(g) \chi_\nu(g) \sum_{\sigma\eta} C_{\sigma j} C_{\eta j} A_{\sigma\eta}(g) \\ K_{\mu\nu}^j &= \langle \mu | \hat{K}_j | \nu \rangle = \sum_g \chi_\mu(g) \sum_\eta \chi_\eta(g) \sum_\sigma C_{\sigma j} C_{\eta j} A_{\sigma\nu}(g) \end{aligned} \quad (2)$$

However (2) leads to large numerical errors that can be overcome only with huge numerical grids. The reason is that the functions

$$\hat{J}_j \chi_\nu \text{ and } \hat{K}_j \chi_\nu \quad (3)$$

have components *outside* the basis space  $\{\chi_\mu\}$ . With finite grids this leads to large *aliasing* errors,<sup>1</sup> in (2) which manifests itself as noise in the wavefunction.<sup>2</sup> The solution to this difficulty is to expand (3) in terms of a larger *dealiasing* basis  $\{\chi_\sigma^*; \sigma = 1 \dots M^*\}$

$$\begin{aligned} J^j \chi_\nu(g) &= \sum_\sigma^{M^*} \chi_\sigma^*(g) W_{\sigma,\nu}^{j,J} \\ K^j \chi_\nu(g) &= \sum_\sigma^{M^*} \chi_\sigma^*(g) W_{\sigma,\nu}^{j,K} \end{aligned} \quad (4)$$

used only for evaluating (5)

$$\begin{aligned} J_{\mu\nu}^j &= \langle \mu | J^j | \nu \rangle = \sum_{\sigma} S_{\mu\sigma}^* W_{\sigma,\nu}^{jJ} \\ K_{\mu\nu}^j &= \langle \mu | K^j | \nu \rangle = \sum_{\sigma} S_{\mu\sigma}^* W_{\sigma,\nu}^{jK} \end{aligned} \quad (5)$$

where the  $S_{\mu\sigma}^* = \langle \chi_{\mu} | \chi_{\sigma}^* \rangle$  is the overlap between functions of the normal and augmented (dealiasing) basis sets. This set of dealiasing functions filters out the noise due to incompleteness of  $\{\chi_{\mu}\}$ . The coefficients  $W_{\sigma,\nu}^{jJ}$  and  $W_{\sigma,\nu}^{jK}$  in (4) are obtained by a least squares fit over the grid of points.<sup>1</sup>

Critical to the efficiency of the PS method is the multigrid strategy (involving medium, fine, and ultrafine grids) that is used in different parts of the calculation. For HF wavefunctions these procedures have been well optimized by Friesner *et al.*<sup>3</sup> and for molecules with 200 basis functions the current PS-HF program on a CRAY-YMP is 10 times faster than GAUSSIAN 88 (20 times faster than GAUSSIAN 86). For systems above this size computation times for Gaussian 88 scales as  $N^3$  whereas PS-HF scales as  $N^2$ . Thus for 2000 basis functions ( $\sim 100$  atoms) PS-HF should be 100 times faster. Note that 2000 basis functions makes sense for PS since storage and IO needs go as  $N^3$  ( $N^2$  with cutoffs rather than  $N^4$  ( $N^3$  with cutoffs)).

The Goddard group in collaboration with the Friesner group has shown that the PS approach is quite suitable for GVB-PP wavefunctions, where the Coulomb and exchange operators  $J_{\mu\nu}^j$  and  $K_{\mu\nu}^j$  in (5) are used directly in the GVB Fock operators.<sup>4</sup> A new PS-GVB-PP program is operational and has been used for tests on singlet-triplet excitation energies, rotational barriers about double bonds, and bond dissociation.<sup>4</sup> In addition, it has been tested for use with effective potentials.<sup>4,5</sup> In all these cases we find better than 0.1 kcal/mole absolute accuracy and 0.01 kcal/mole relative accuracy, as compared to standard approaches.

We are in the process of completely redeveloping both the GVB formulation and the PS techniques, grids and cutoffs for correlated pairs. Although a challenging goal, we believe that calculations with 2000 basis functions and 100 GVB pairs will become

possible. This would allow accurate studies of ceramic clusters with up to 200 atoms and transition metal systems with up to 100 atoms, and would allow accurate calculations for complexes providing good models of important surface processes.

An important virtue of the PS approach is that the exchange terms needed for GVB-RCI wavefunctions can be calculated directly. The GVB-RCI wavefunction<sup>6,7</sup> (which includes all spin coupling and interpair correction terms) leads to quite accurate potential curves for reactions *if* the orbitals are optimized self consistently. (In this case, the wavefunction contains essentially all important parts of a full GVB-CI or CAS-SCF wavefunction.) However in the past such self consistent GVB-RCI calculations required use of the GVB3 program and hence an  $N^5$  integral transformation every iteration. Fortunately with PS we can evaluate the additional exchange potentials required in GVB-RCI directly (on the fly *without* calculating two-electron integrals). Thus with PS we can generalize the GVB-PP program to calculate the GVB-RCI wavefunction self consistently *without* integral transformations. This requires a modification in how spin couplings are treated, with a slight restriction on the generality of the spinfunctions. Thus for such very accurate wavefunctions, the costs should drop from  $N^5$  to  $N^3$  and with cutoffs to  $N^2$ , for large systems. Timing estimates are more difficult here, but we believe that self-consistent PS-GVB-RCI for up to 1000 basis functions and 50 GVB pairs might be possible ( $\sim 50$  atoms). We are currently developing the theory for PS-GVB-RCI and expect to have a working program (not optimized) by the Summer of 1992.<sup>8</sup>

For tribological problems, it is essential to use periodic boundary conditions (PBC) in calculating the wavefunctions (obviating the need for cluster approximations). For closed shell HF wavefunctions this is straightforward, but the local exchange terms converge slowly with distance, leading to long expansions.<sup>9</sup> By taking suitable Fourier transformations, it is possible to do the slowly convergent integrals in reciprocal space<sup>10</sup>; however this requires a complicated integral transformation. With PS this PBC process is considerably simplified because (1) can be used to calculate the exchange terms as they are needed. Thus using PS it is quite practical to calculate HF wavefunctions using periodic boundary conditions (HF-PBC). For GVB wavefunctions use of PBC is more complicated because the individual

GVB Fock operators do not combine into a single effective multiparticle operator. However for completely filled bands it is straightforward to reformulate GVB-PP wavefunctions for PBC. This requires additional localized exchange terms, but these can be calculated using the PS approach. The restriction to closed shells (filled bands) will be no limitation for many cases (semiconductors and ceramics), although it precludes study of metallic systems (where partially filled bands are necessary). GVB-PBC will allow us to treat the full crystal for many interesting catalysts. We are currently developing algorithms for the GVB-PBC program<sup>11</sup> and expect to have a working version by early 1992. Timing estimates are premature but our goal is to eventually treat systems with 1000 basis functions and 50 GVB pairs per unit cell (50 transition atoms per unit cell).

Such calculations of three-dimensional crystals should be very valuable in extracting charges and force fields that could be used for molecular mechanics and molecular dynamics calculations of tribological systems. By using finite thickness slabs we will use PBC for crystal surfaces, allowing us to consider structures and energetics for various reaction intermediates. (Since PBC is used, the fundamental repeating unit must be large enough that the equivalent catalytic sites do not interact.) For GVB-RCI a general formulation of PBC also seems possible, with the restriction to filled bands, but we have not worked it out. However, including the RCI spin couplings for the two to four pairs that recouple in the transition state should be possible.

With PS it is possible to start with GVB-RCI wavefunctions and calculate Epstein-Nesbet perturbation theory through second order. This should allow bond energies accurate to  $\sim 0.5$  kcal/mol and should allow *ab initio* determination of parameters for van der Waals (dispersion) interactions important for treating lubricants interfacing with solid surfaces. The theory has been partly worked out and the initial GVB-RCI-EN2 programs should be developed by the Summer of 1992.

### III. New Developments in Force Fields

Despite the progress in treating larger clusters with *ab initio* quantum chemistry, the calculations are far too slow for studying the *dynamics* of realistic models of catalysts. Thus

it is essential to replace the electrons with a force field suitable for molecular dynamics and Monte Carlo simulations. Typically<sup>12</sup> force fields are described in terms of short-range valence (bonded) interactions ( $E_{val}$ ) expressed in terms of two-body ( $E_{bond}$ ), three-body ( $E_{angle}$ ), and four-body ( $E_{torsion}$ ,  $E_{inversion}$ ) terms,

$$E_{val} = E_{bond} + E_{angle} + E_{torsion} + E_{inversion} \quad (6a)$$

and long-range nonbonded interactions ( $E_{nb}$ ) composed of van der Waals ( $E_{vdw}$ ) and electrostatic ( $E_Q$ ) terms

$$E_{nb} = E_{vdw} + E_Q \quad (6b)$$

#### A. Electrostatics (Charge Equilibration)

Given a set of charges  $Q_i$  on various atoms, the electrostatic interaction is

$$E_Q = \sum_{i \neq j} \frac{Q_i Q_j}{\epsilon R_{ij}} \quad (7)$$

Traditionally, in molecular simulations of organic molecules, the charges are estimated based on Hartree-Fock (HF) calculations (with the charges chosen to fit the calculated potential energy distribution). There are several serious problems with this approach:

- a. Accurate HF calculations (631G\*\* basis) are possible only for small molecules, up to 10-20 atoms or so (with PS-HF it should become possible for 100 atoms).
- b. The charges should be allowed to change as atoms move about, as bonds are broken, etc., but HF calculations every time step is not practical.
- c. In order to recalculate the charges during the dynamics, the charge calculation must be extremely rapid and cannot involve calculating wavefunctions.
- d. There are no procedures for estimating the charges for crystals of ceramics, metals, etc. important to tribiology.

What is needed is a general approach that can provide charges for large or infinite systems while allowing the charges to polarize and change during the dynamics. We believe that we have solved this critical problem in a recent series of papers.<sup>13</sup>

This new method is called Charge Equilibration (QEq), and the basic idea is to consider each atom as a separate system in a grand canonical ensemble. The energy of each atom ( $A$ ) is considered to depend quadratically upon the charge  $Q_A$

$$E_A(Q_A) = E_0 + \eta_A Q_A + \frac{1}{2} J_{AA} Q_A^2 \quad (8)$$

where  $\eta_A$  and  $J_A$  are related to electronegativity and atomic Coulomb repulsion (electrical capacity), respectively. The interaction between two atoms is written in the form

$$J_{AB}(R) Q_A Q_B \quad (9)$$

where the interaction term  $J_{AB}(R)$  has the Coulomb form ( $1/R_{AB}$ ) for large  $R$ , but includes shielding so that it goes to a finite limit as  $R \rightarrow 0$ . Requiring that the charge distribution be in equilibrium (constant chemical potential) leads then to a set of linear equations

$$A_{ij} Q_j = B_i \quad (10)$$

for the equilibrium charges  $Q$  at a given geometry.

The QEq method is formulated so that there are *no* free parameters. The only data are the experimental ionization potential (IP) and electron affinity (EA) (which determine  $\eta_A$  and  $J_{AA}$ ) and the atomic radii [which determine the shielding of  $J_{AB}(R)$  for small  $R$ ]. The resulting charges are in good agreement with those obtained by fitting electrostatic potentials from good quality HF and MP2 wavefunctions. This represents, we believe, a significant advance in simulations.

The QEq approach requires quantitative electronegativity and self Coulomb terms from experimental data. We found a way to generalize ideas of Mulliken and Pauling to obtain an unambiguous, quantitative measure of these quantities directly from experimental atomic data.<sup>13</sup> This approach is useful for both main group elements and transition metals.<sup>13</sup>

The Charge Equilibration method (QEq) uses only experimental atomic data (ionization potential, electron affinity, and bond radius) and can be used for any atoms up

through Lr (element 103). With current programs, molecules containing 600 atoms are quite practical (there is no hard limit). This QEq method has now been extended to infinite systems (PBC) where crystals with 200 atoms per unit cell are quite practical (no hard limit). In addition, the dynamic charge fluctuations during vibrations have recently been included. This is critical for describing the optical vibrational modes of nonmetals. In addition these dynamical changes will allow infrared and Raman intensities to be predicted. These methods have been extended to allow prediction of dielectric constants and piezoelectric constants.

In addition to the above semiempirical approach for charges, we have been developing a first principles method suitable for large molecules and crystals (up to 200 atoms). Using the PS approach we have now modified the PS-GVB-PP program to calculate the charges based on electrostatic potentials of correlated wavefunctions. [Up to 2000 basis functions ( $\sim 200$  atoms).]

## B. Valence Force Fields

The most common approach to developing valence force fields for molecular simulations has been to start with the experimental geometries and vibrational frequencies for a set of related molecules and to find force field parameters that provide the best fit to these data. Unfortunately, the experimental vibrational data do *not* provide sufficient constraints to ensure that the second derivative matrix (Hessian) is well fit. To illustrate the problem, consider a general nine-atom molecule. A simple spectroscopic quality force field would involve a minimum of 18 parameters to describe the nine different bond stretch terms, 104 parameters to describe the 18 different bond angle terms, and at least 24 parameters to describe the 24 different torsion terms. Thus 146 parameters are needed for the force field. However, the 21 normal modes provide only 21 pieces of data to determine second derivatives, and the experimental structure provides only 21 constraints on the first derivatives (forces). These 42 experimental constraints are far short of determining the 146 FF parameters. Our conclusion is that to generate accurate force fields, one *must* use additional information beyond that available from spectroscopic studies.

An alternative is to use the power of modern quantum chemistry to calculate the full second derivative matrix (Hessian) at any geometry for simple wavefunctions. Unfortunately, simple HF wavefunctions lead to vibrational frequencies that typically disagree with experiment by  $\sim 10-20\%$ . One can obtain greater accuracy with correlated wavefunctions (MP2, GVB, CI); however, full Hessians from such wavefunctions are currently practical only for tiny systems. [The development of PS-MP2 and PS-GVB-RCI may change this situation in another year.] Our current solution to this problem is the *Hessian-biased force field*<sup>15</sup> (HBFF) which combines normal mode *eigenstate* information from theory with *eigenvalue* information from experiment. This force field yields accurate vibrational frequencies, and we have been systematically determining parameters for various molecules.

We have developed a new program (FFPARM) that is used in conjunction with POLYGRAF to determine the optimum force field parameters to fit a set of experimental data. The input data consists of geometry, crystal cell parameters, elastic constants, vibrational frequencies, phonon frequencies, or the full Hessian matrix (from quantum mechanical calculations). These data can come from theory or experiment (whichever is more reliable) and can be incomplete (the data is weighted by its reliability). FFPARM then finds the optimum force field parameters (force constants, well depths, coupling terms) for valence and/or vdw terms to fit the input data.

A number of projects are underway (hydrocarbons, fluorocarbons, diamond, silicon, germanium, silicon-carbide, amino acids, polyenes) for getting accurate force fields using FFPARM.

Unfortunately for transition metal complexes, there is generally not enough experimental data for this approach and use of HF wavefunction is not adequate. The ability to carry out PS-GVB-RCI calculations should solve this problem in 1992. In this case the calculated constants should be sufficiently accurate *without* the use of experimental data.

### C. van der Waals

All molecular systems lead to attractive interactions at large R (dispersion or London forces) and repulsive interactions at small R (Pauli orthogonalization) for all nonbonded

electrons. Referred to as van der Waals interactions, these interactions are generally assumed to be pairwise additive

$$E_{vdw} = \sum_{i>j} E_{ij}^{vdw} \quad (11)$$

and describable with simple exponential-6

$$E_{ij}^{vdw} = Ae^{-BR_{ij}} - C/R_{ij} \quad (12)$$

or Lennard-Jones 12-6 expressions.

Our long range goal in developing force fields is to obtain the van der Waals (dispersion) terms directly from quantum mechanical calculations. Unfortunately the weakness of the interactions, the complications of handling the dynamic correlations consistently and completely, and the need for very complete basis sets have limited reliable calculations to the size of He<sub>2</sub> and Ne<sub>2</sub>. MP2 or EN2 level wavefunctions should lead to acceptable accuracy but the basis sets must be *very* complete, limiting this approach to quite small molecules.

As a result, our emphasis is on determining these parameters *empirically* by using new simulation procedures to predict the thermodynamic and mechanical properties of molecular crystals and polymers for various choices of the van der Waals parameters and then fitting them to whatever experimental data are available. We have now developed programs capable of calculating<sup>16,17</sup>

- a. the full set (all 21) of elastic constants of molecular crystals and polymers,
- b. the vibrational levels and phonon dispersion curves, and
- c. the thermodynamic parameters (Cp, S, H, G) as a function of temperature.

Although the experimental data are incomplete, we find that by calculating all such properties, we can determine the optimal van der Waals parameters.<sup>17</sup>

Thus, to determine the van der Waals parameters for carbon we required that the lattice constants *and* elastic constants be accurately described.<sup>18</sup> Then, to obtain the van der Waals parameters for H, we required that the crystal structure, heat of sublimation, *and* lattice frequencies of crystalline polyethylene be accurately described.<sup>19</sup> This was tested

for the phonon states of polyethylene and for crystals of hydrocarbon molecules where we calculated accurate lattice parameters, lattice frequencies, and cohesive energy.<sup>20</sup> Similarly, new van der Waals parameters have been obtained<sup>28</sup> for N, O, F,<sup>11</sup> P, S, Cl, Se, Br, Te, and I, and others are in progress.

The lowest level wavefunction adequate for nonempirical (ab initio) calculations of van der Waals parameters is second-order perturbation theory (e.g. MP2, EN2). With PS-MP2 and PS-GVB-EN2 this should be possible for systems as large as benzene dimer. Such studies should be practical by mid 1992. In the meantime, we are using FFPARM in conjunction with POLYGRAF (which calculates phonon bands, elastic constants, and lattice parameters) to determine empirical vdW parameters of a number of systems.

#### D. Metals and Alloys (The Interstitial Electron Model)

Most simulations on metallic systems have used two-body force fields, and the results have been quite poor. Recent advances based on GVB quantum chemical calculations have led to the Interstitial Electron Model (IEM) for force fields of metals in which *the electrons are treated as classical particles on the same footing as the ions!*<sup>21</sup> This completely new type of force field for metals will, we believe, lead to accurate simulations for metals.

Based on generalized valence bond calculations of small metal clusters (up to 14 atoms), we learned that metallic systems lead to singly-occupied orbitals localized at interstitial sites. The result is a strong coupling of electronic states with nuclear motion so that one cannot describe the system in terms of ion motions alone. We have now incorporated this concept of interstitially localized orbitals into a force field scheme for metals where the electrons are treated as classical particles!

This force field is then written as

$$E = \sum_{ii'} \phi_{ii'} + \sum_{ie} \phi_{ie} + \sum_{ee'} \phi_{ee'}$$

where potentials are defined for interactions of electrons (*ie* and *ee*) in addition to the traditional *ii* interactions. As a first test we have applied this scheme to the metals Ni, Cu, Pd, Ag, Pt, Au, where we allow two parameters for each interaction and obtain an

exact fit to the lattice constant and the three elastic constants, and an excellent fit to the phonon dispersion curves. For example, for Ni, this leads to an exact fit to the experimental data for lattice constants, elastic constants and phonon dispersion curves (see Figure 1). Note in particular here that the Cauchy discrepancy  $C_{12} - C_{44} \neq 0$  is correctly described (not possible with sums of  $ii$  potentials alone).

We are now expanding these IEM calculations to predictions of surfaces (for Ni, preliminary calculations indicate that the surface layer relaxes by about 3%), grain boundaries, and alloys.<sup>22</sup>

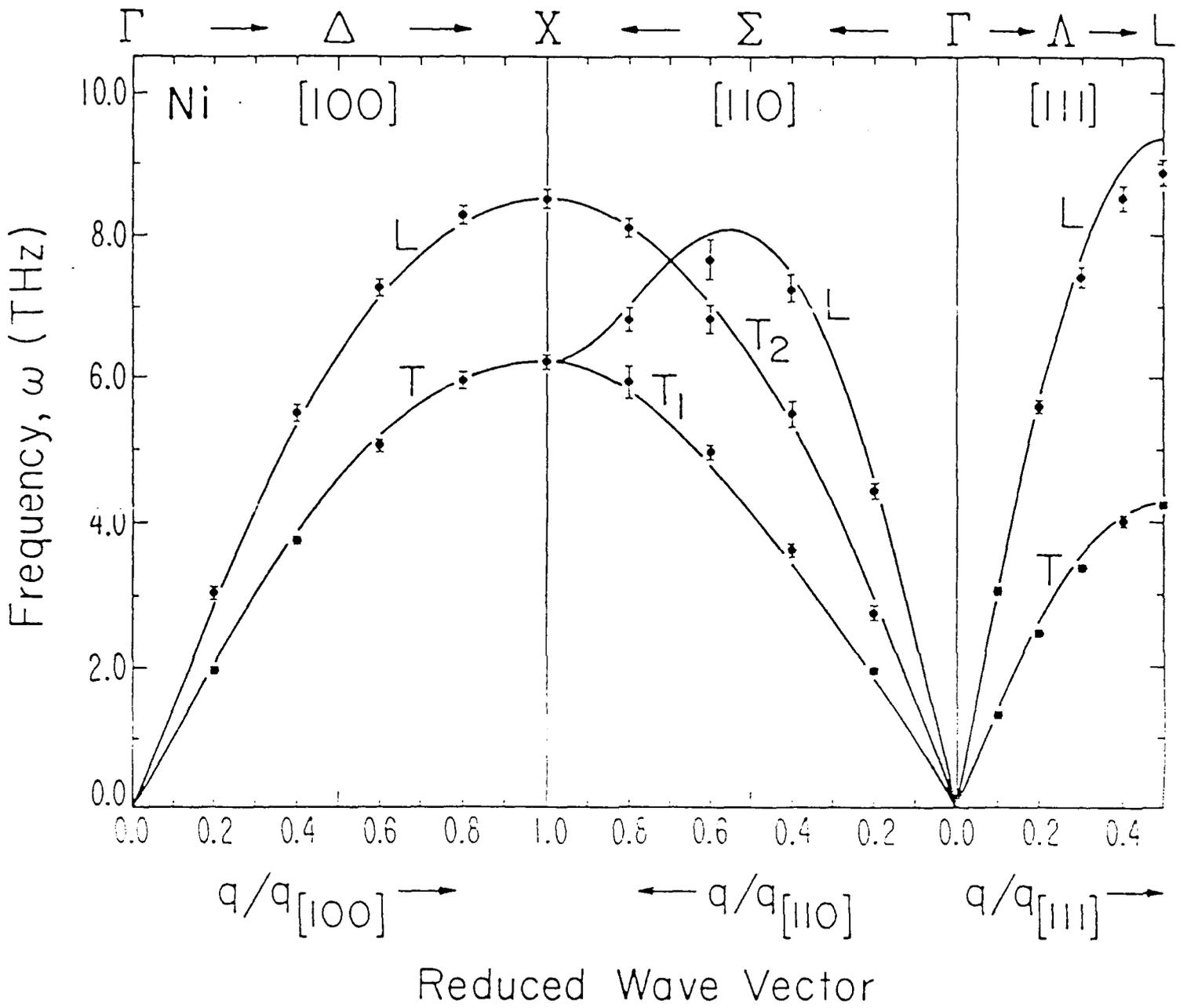


Figure 1.

With GVB-PBC we will be able to get the IEM parameters directly from *ab initio* calculations (rather than experiment).

### E. Force Fields for Inorganic and Organometallic Systems

The standard force fields for organic and biological systems (MM2, MM3, AMBER, CHARMM) have evolved over many years of development. Yet these force fields deal primarily with just four atoms (H, C, N, O). To describe inorganic and organometallic systems, we must deal with the other 100 atoms of the periodic table. Our strategy to doing this is to use generic approaches, where the number of independent parameters are few and vary smoothly as a function of rows and columns in the periodic table.

Our first such force field<sup>12</sup> is DREIDING (developed in collaboration with Dr. S. Mayo and Dr. B. D. Olafson of BioDesign) which handles the 25 elements in the B, C, N, O, and F columns and the Br, C, Si, Ge, and Sn rows of the periodic table. Here there are two parameters per atom  $R^0$  and  $\theta^0$ , where  $R^0$  is the atomic radius and  $\theta^0$  is the equilibrium angle of the hydride (e.g. CH<sub>4</sub>, NH<sub>3</sub>, SH<sub>2</sub>, etc.). In DREIDING, the force constants are determined by very simple rules (e.g.,  $K = 700, 1400, 2100$  kcal/A<sup>2</sup> for single, double, and triple bonds) that are *independent of the atom*. Despite the incredible simplicity, this force field gives quite accurate geometries for a wide variety of structures. Thus, using a random selection of 76 structures from the Cambridge database (including such groups as  $-\text{NO}_2^-$ ,  $-(\text{SO}_2)-$ ,  $-\text{PO}_3^-$ ,  $-(\text{PO}_2^-)-$ ) the RMS error in atom positions is 0.235 Å with average errors of 0.009 Å in bonds, 0.57 degrees in bond angles, and 0.22 degrees in torsions.<sup>12</sup>

Professor A. K. Rappé (Colorado State University) and Goddard have collaborated to develop a Generic Force Field (GENFF) suitable for inorganics and organometallics.<sup>23</sup> In this force field there are *three parameters per atom* rather than two! The new parameter is an *atomic force constant*  $Z_i^0$  defined such that the force constant for bond stretch is (13)

$$K_{ij} = \frac{Z_i^0 Z_j^0}{(R_{ij}^0)^3} \quad (13)$$

where

$$R_{ij}^0 = R_i^0 + R_j^0$$

and the force constants for a bond angle  $i - j - l$  is given by a similar expression involving  $Z_i^0$  and  $Z_l^0$ . These atomic force constants  $Z_i^0$  vary smoothly along rows and columns, allowing them to be interpolated for cases without data. Thus with GENFF one can predict structures for any combination of elements from  $H$  to  $Lr$  (element 103).

Combined with QEq which can predict charges for any element from  $H$  through  $Lr$ , we have a good start for simulating any inorganic compound. To obtain accurate vibrational frequencies will no doubt require additional cross terms (angle-stretch, etc.) from BHFF, however GENFF is an excellent start to making predictions of inorganic structures.

#### IV. New Developments in Molecular Dynamics

##### A. Cell Multipole Method

The calculation of Coulomb energies

$$\sum_{i < j} \frac{Q_i Q_j}{R_{ij}} \quad (14)$$

involves  $N^2/2$  terms for  $N$  particles. Commercial molecular dynamics software all involves processes of order  $N^2$ , limiting the maximum sizes to  $\sim 5000$  atoms. For many problems it is necessary to do an atomic-level simulation on systems with a million atoms. Here the ordinary procedures of MD are just not practical. We have recently developed the Cell Multipole Method (CMM) to solve this problem. The first step is to place the whole molecule in a box (200-500 Å on a side, depending upon the system) which is divided into eight children cells. Each child cell is divided into eight grandchildren cells, etc. until a generation is reached with about 4 atoms per cell (the microcell). For a million atoms there are six levels. For each microcell the multipole moments (charge, dipole, quadrupole) are calculated and these are shifted and added to obtain the multipole moments of the parent cells, grandparent cells, etc. To calculate energies, forces, etc. the total potential of each microcell is written as

$$V_{total}(R) = V_{near}(R) + V_{far}(R) \quad (15)$$

where the interactions with all atoms in the 26 neighboring cells are included in  $V_{near}$  but the interaction with the 1,000,000 - 100 more distant atoms ( $V_{far}$ ) are all evaluated

using the multipole fields. Here the farther atoms use high level (parent) cells while closer cells use the multipole field of low level (child) cells. This procedure is extremely fast and accurate as indicated in Figures 2 and 3.

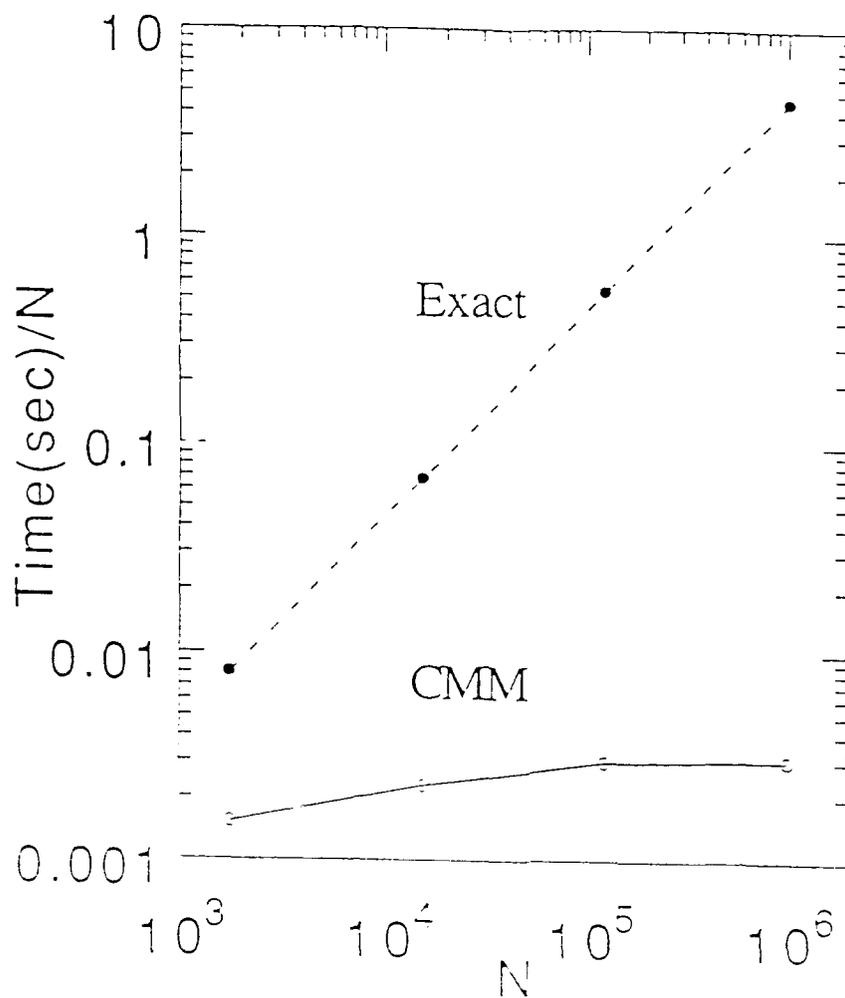
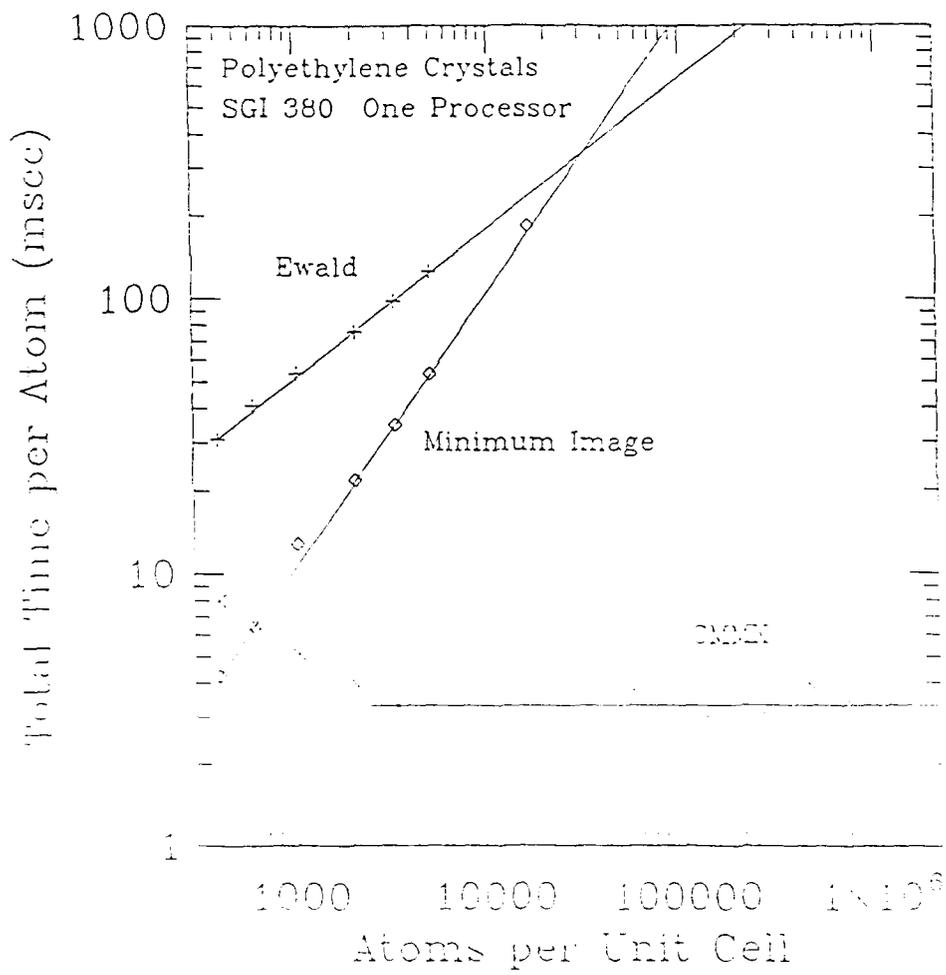


Figure 2. Computational costs for calculation of the Coulomb nonbond interactions for a series of poly(vinylidene fluoride) polymers ( $N = 1792$ ,  $15360$ ,  $122880$ , and  $1013760$  atoms).



## B. Canonical Dynamics

In recent years a number of methods have been proposed to obtain thermodynamic and other properties directly from molecular dynamics. Nosé,<sup>24</sup> Parrinello and Rahman,<sup>25</sup> Nosé and Klein,<sup>26</sup> Andersen,<sup>27</sup> etc. have proposed modified Lagrangians such that the collection of momenta and coordinates from a long dynamics calculation satisfy a Boltzmann distribution for constant pressure, constant temperature conditions. We have implemented the Nosé and Rahman-Parrinello techniques for periodic systems and are testing these methods for various properties, including thermal expansion coefficients and elastic constants. These methods are sensitive to internal "mass" parameters, to initialization, and to total dynamics time.

## C. New Developments with Monte Carlo Methods

Our protein/polymer folding project has led to programs capable of combining Monte Carlo and molecular dynamics techniques for rapid sampling of configuration space to predict optimum conformations. Currently these programs are effective at folding loops with up to 20 amino acids. This is useful in using the experimental structure for one protein to predict the structure of homologous proteins. There are indications that Nosé canonical dynamics will lead to rapid folding.

## V. Molecular Dynamics Calculations of Friction

In carrying out calculations of bulk or surface properties of solids, we use periodic boundary conditions to extend the system in three dimensions and two dimensions, respectively. In this case the calculational effort is proportional to the number of atoms in the unit cell and no artificial surfaces are present. Since the systems are infinite in three or two dimensions, respectively, one must be very careful with electrostatic summations

$$\left( \sum \frac{Q_{ij}}{R_{ij}} \right)$$

and dispersion summations

$$\left( \sum \frac{B_{ij}}{R_{ij}^6} \right)$$

since these generally converge slowly. The general approach for accelerating the convergence of such sums is to convert each sum into two sums, one of which converges quickly in real space and one which converges quickly in reciprocal space. In these procedures there is a parameter  $\eta$  which controls how much of the total sum goes into each part. We have developed<sup>16</sup> an approach for dynamically estimating the total error in the real and reciprocal space parts so that we can choose the  $\eta$  to obtain a prespecified level of accuracy in the minimum calculation time. In addition, we have extended the formulae to include contributions to vibrational frequencies and elastic constants.<sup>16,25</sup>

To use the full apparatus of PBC for problems with surfaces, we treat the system as a finite slab where the thickness  $Z$  is large enough that the surfaces do not interact, see Figure 4.

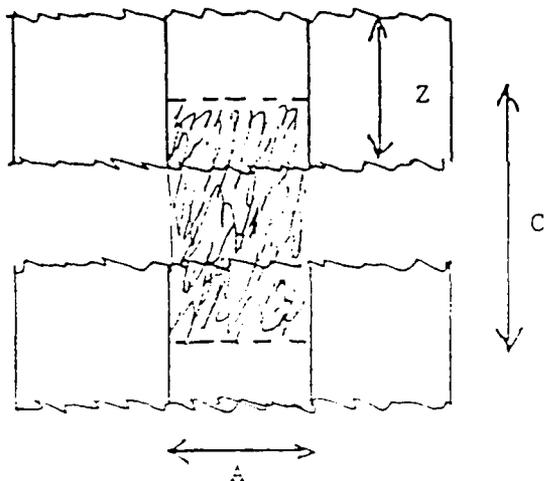


Figure 4

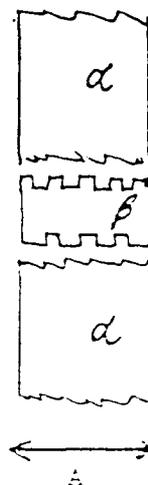


Figure 5

In this case the unit cell parameters (of the two dimensions shown) are  $A$  and  $C$ . The space between the surfaces can be a vacuum, a gas ( $H_2$ ,  $O_2$ , etc.), a liquid ( $H_2O$ ), a lubricant, or a second solid (see Figure 5). The dynamics must be carried out under conditions of constant temperature and constant pressure in order to simulate a system in a normal constant  $T, p$  environment. In addition, we can apply an overall stress, say, in the  $C$  direction, and calculate the lattice parameters and elastic properties for the system in

equilibrium with this external stress. In such situations, the Lagrangian  $L = T - V$  is modified to include additional terms, e.g.,

$$L_T = \frac{\dot{s}^2}{2M_s} - gkT \ln s \quad (16)$$

which ensure that the dynamics trajectories sample phase space appropriately for a canonical distribution for a system in equilibrium with a heat bath at temperature  $T$ .

To study dissipation and internal friction, we consider an oscillating external stress, say,

$$F_X(t) = F_X^0 \cos \omega t \quad (17)$$

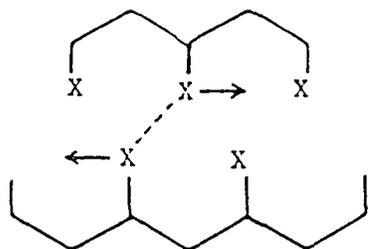
and follow the response in the various cell coordinates

$$H_{\alpha\beta}(t) = H_{\alpha\beta}^0 \cos(\omega t - \delta_{\alpha\beta}). \quad (18)$$

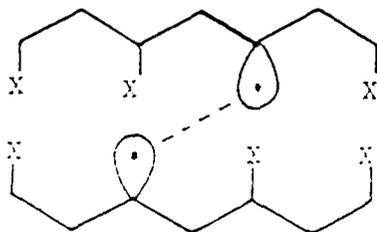
The phase factor  $\tan \delta_{\alpha\beta}$  is directly related to the energy dissipation and can be measured experimentally as a function of temperature for various frequencies. By determining  $\tan \delta_{\alpha\beta}$  from calculations for various applied loads and surface treatments, we can extract information on friction for various surface conditions. Experimental determinations of  $\tan \delta$  are commonplace for polymers where they provide information on the rigidity of the polymer blend as a function of temperature. They have not been useful for studying surface friction because of the difficulties in obtaining sufficiently perfect surfaces. However, for calculations of friction, we believe that prediction of  $\tan \delta$  is the best way to couple with experiment. Our approach is to use the configuration in Figure 8 with an applied oscillating shear (17). Although these calculations will interface only indirectly to current configurations for measuring friction it should be possible to design experiments for studying surfaces such as mica. There may be some gap between the experimental and theoretical frequencies since our current programs are limited by practical considerations (computer time) to frequencies above 10 GHz, whereas 100 MHz is about the highest used experimentally.

For diamond and silicon, the initial focus is on surfaces passivated with H or F. Surfaces where all surface sites are capped with an H or F should have particularly low

friction. Intuitively the fluorine surface might be expected to have the lowest friction since it is smooth and allows little in the way of lateral interactions due to surface-surface contact. the microscopic origin of the friction in such systems is that lateral forces on the surface atoms due to the contact lead to bending of C-C-X bonds that couple with the high energy branches of the bulk acoustic phonon modes. This coupling should be stronger for CCF than CCH because of the lower frequencies, and hence the friction may be higher.



For unpassivated surfaces having broken bonds, additional-dissipation effects will quickly increase the friction



In this case the modulation in covalent bonding that occurs as the surfaces are displaced, distorts the adjacent bonds, leading to coupling into various phonon modes to dissipate energy. Our calculations should be able to quantify these effects.

We expect that the distribution of phonon modes and the coupling with surface states will be particularly important for systems such as diamond and silicon and have developed general procedures for calculating these values, e.g., Figure 8 is for polyethylene, Figure 9 is for silicon,

### Metals

We see very different mechanisms for friction in diamond and metallic systems and intend to carry out parallel studies on clean metal systems. Until recently, we believed that

it was impossible to carry out reliable simulations of metal systems because available force fields are quite inadequate. However, the interstitial electron model described in Section III.D proposed a genuine breakthrough here.

We are now expanding these calculations to predictions of surfaces (for Ni, preliminary calculations indicates that the surface layer relaxes by about 3%), grain boundaries, and alloys. We believe that this work will have progressed sufficiently for studies of friction in about 12 months. In order to define a system for which experiments could best test the theory, we plan to do clean Ag and Ni passivated with S



Interaction of the Ag surfaces with H-terminated diamond should be a good case for comparing experiment and theory since Ag could not react with the H of diamond.

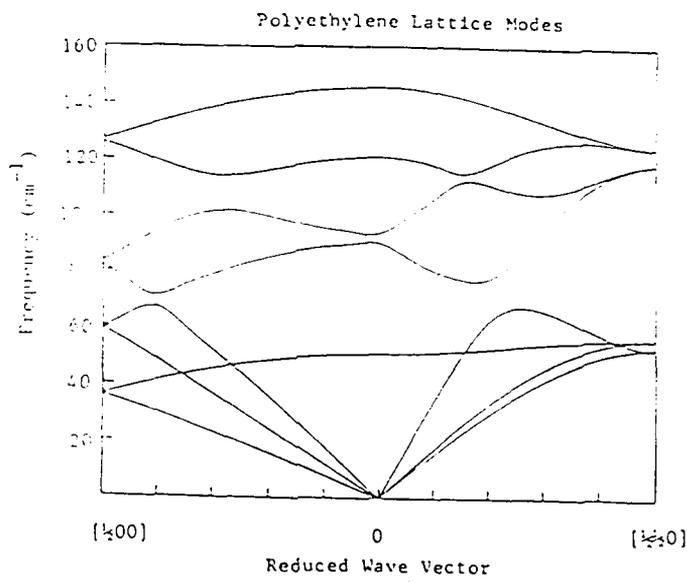


Figure 8.

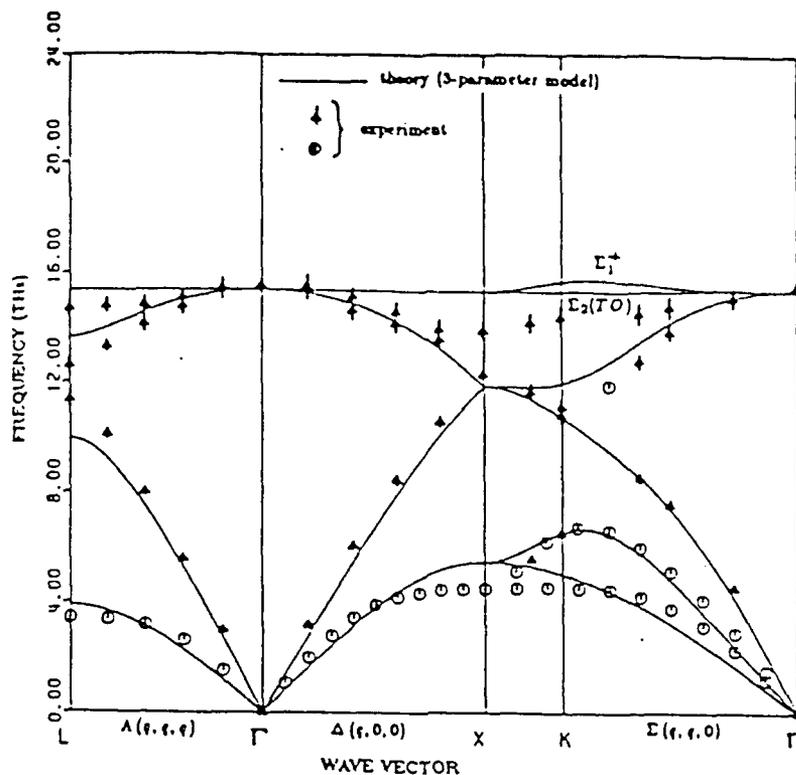
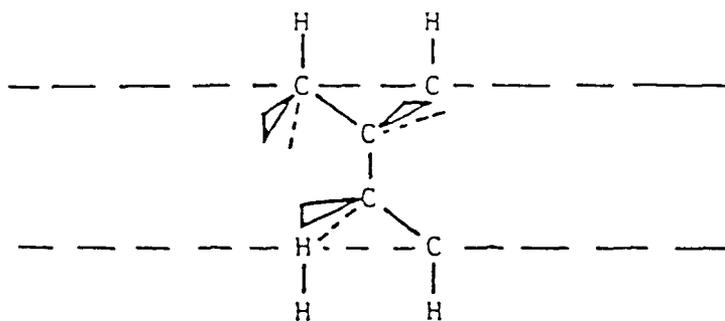


Figure 9. Phonon band structure of silicon. The solid lines are theoretical predictions using parameters calculated from cluster calculations. The triangles and circles are experimental frequencies.

## VI. Calculations of Friction

In order to gain insight into the extraction from microscopic calculations of the quantities (e.g., friction coefficients) useful in describing macroscopic phenomena, we are carrying out a series of calculations simulating friction between two diamond surfaces. The first calculations examined the (111) surface of diamond with each surface atom terminated by a C-H bond. In order to eliminate edge effects, we treated a finite thickness slab with periodic boundary conditions, as in Figure 11.



The lattice constants parallel to the slab were restricted to remain those of the infinite

system; however, each atom was allowed to move an equilibrium position. These slabs were then stacked, as in Figure 12a, to form a three-dimensional infinite system.

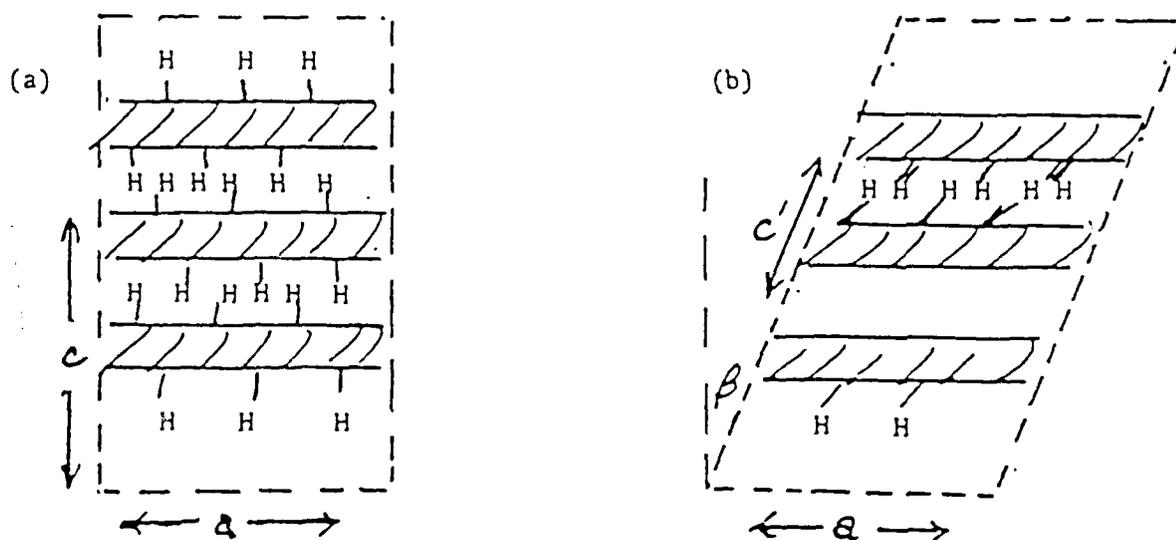


Figure 12.

The spaces between the slabs and the relative location of one slab with respect to the next were optimized to obtain the overall equilibrium system. This system represents two perfect diamond (iii) surfaces in equilibrium. We then calculated the equilibrium structures as each surface is displaced with respect to the next, while simultaneously imposing an external load (10 GPa) on the system. This was carried out by treating the lateral displacement as a shear in the fundamental unit cell of the three-dimensional system, as indicated in Figure 12b. Thus, for each value of shear ( $\beta$ ), we reoptimized all atomic positions, allowing the surface hydrogens to bend out of the wave as the surfaces were displaced, and we allowed the distance between the layers to reoptimize. This was done as a function of external stress. The results are presented in Figures 13 and 14. Figure 13 shows the energy surface (with no imposed load) superimposed on the atom position of the lower surface. The minimum position has the C-H bond of the upper surface symmetrically between the three C-H bonds of the lower surface. The minimum energy path for displacement has the C-H of the upper surface move over an energy barrier of 0.14 kcal/mol to a new equilibrium position with the C-H of the upper surface above a second layer C of the lower system. In

this position, the energy is but 0.01 kcal higher than the original equilibrium position. In the minimum energy pathway, the CH bond of the upper state must next move northeast toward the center of the next hexagon and then east to the next second-layer carbon etc. If the surfaces are constrained to move exactly along a line, the lowest energy pathway would be one that crosses over the sides of each hexagon, leading to a barrier of 0.47 kcal/mol. The highest energy point occurs when the surfaces are displaced so that the lower CH bond points at the CH bond of the upper surface, leading to an energy 1.0 kcal higher than the minimum position.

ENERGY SURFACE  
 MOVING III DIAMOND-H TERM  
 OVER III DIAMOND H-TERM

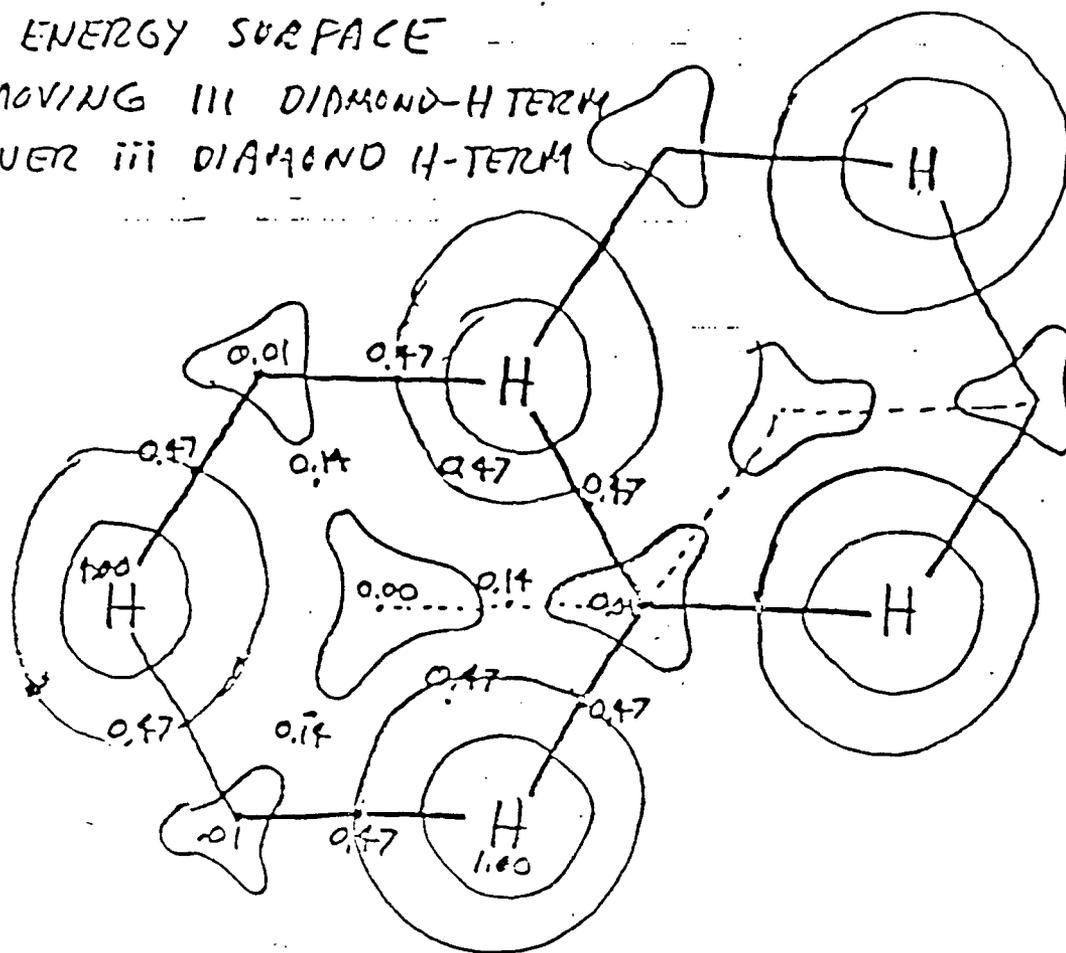


Figure 13.



But how do we go from this optimum energy surface to, say, a coefficient of friction? As one approach, consider the vertical displacements between the slabs necessary for the system to move along the minimum energy pathway (see Figure 14). The slabs are closest for the minimum energy position where the CH bond of the top slab points in the middle of the hexagon of the lower slab. As the slabs are displaced to the right over the 0.14 kcal/mol barrier, the top slab must move away by 0.061 Å and then it comes back to the secondary minimum (above the second layer C) where it is only 0.004 Å above the optimum vertical displacement. Thus, as the system is displaced along the minimum energy pathway, the vertical displacements are as in Figure 15.

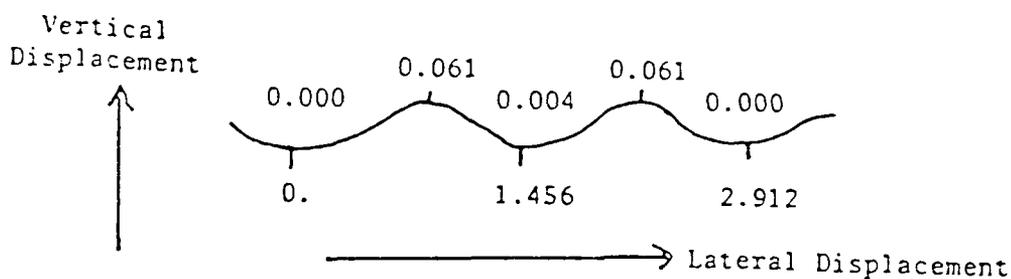


Figure 15.

If there is an external load on the system, we must do work against this bond to displace it back 0.06 Å to go over the first hill, but the bond can do work on the system as we go down the hill again. If this process were carried out with no energy transfer, there would be no friction. That is, the energy cost in going up one hill is returned upon going down and is then available to go up the next hill. However, if the energy is dissipated from the surface as it goes down one hill, it cannot be returned to climb the next and there is friction. To get an idea whether there is time for such dissipation, consider that a velocity of 2 meters/sec converts to 0.02 Å per picosec. Thus, at this velocity, it takes 35 picosec for the system to go back down hill. On the other hand, the characteristic time for energy transfer from the C-C-H bending modes at the surface is likely to be ~1 psec. Thus the energy should be dissipated.

Given the description in Figure 15, we can estimate the maximum coefficient of

friction as the maximum slope of the displacement curve or

$$f = \pi \frac{0.061}{1.456} = 0.132.$$

It is interesting that this value is in the ballpark of experimental measurements of the coefficient of friction in diamond by Tabor who reports  $f = 0.1$  for diamond (111). This does not prove our simple model. The experiments on diamond were carried out with a metal probe in a normal atmosphere. We now know that a well polished diamond surface is covered with C-H bonds. Hence these experiments should be repeated in an inert atmosphere with a diamond probe so that one does not have to worry about the surface H on the diamond being transferred to the metal.

It is also not clear that the coefficient of friction for a completely flat surface is relevant for friction studies since even a single crystal will have steps and other imperfections that may keep parts of the surface from interacting (Figure 16).

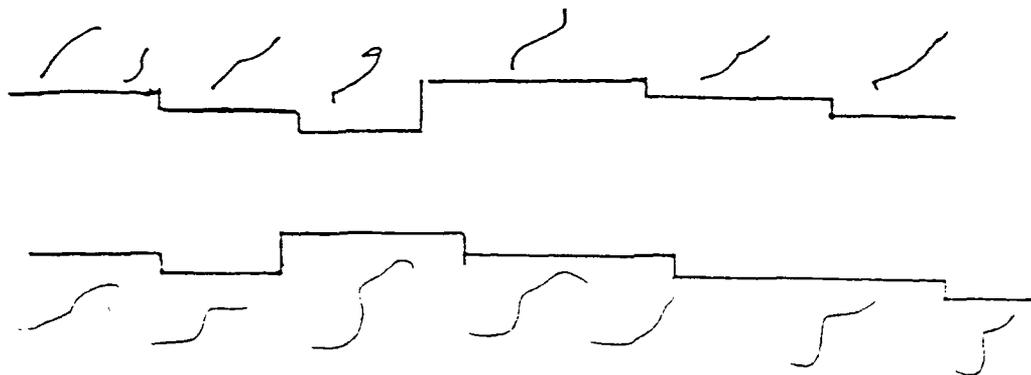


Figure 16.

That is, the experiments on the best quality single surface may be dominated by what happens when two steps come together rather than by the sliding of two surfaces with respect to each other. Of course, similar theoretical calculations can be carried out at the steps; however, there are new questions. Are the step atoms also completely saturated with C-H bonds? We could assume this in the calculations, but this should be tested with appropriate surface science experiments. Using these theoretical approaches, one should be able to simulate friction and wear for systems such as Figure 16.

Over the next year we will be carrying out similar calculations for fluorine-terminated surfaces and for other low index surfaces of diamond. The (110) surface should be particularly interesting since the friction might be very anisotropic.

## VII. Scanning Tunneling Microscopy

A new tool of significant potential for characterizing the surface topography of tri-biologically relevant systems is scanning tunneling microscopy. In this system, a small voltage, say,  $\phi = 100$  mV, is applied between a probe [prepared so as to obtain extremely small (atomic dimensions) points] and the surface and the tunneling current is measured and used with various electronics and piezoelectric elements to maintain atomic-level resolution. The probe is maintained at distances of 5 to 10 Å and the tunneling current [which is assumed to vary exponentially with distance (s)]

$$I_T(s) = \exp \left[ -A s \sqrt{\phi} \right]$$

is measured. In one mode of operation, the current is kept constant as the tip is displaced along the surface, and the voltage applied to the piezoelectric element is monitored to obtain the effective displacement of the tip. Assuming that the work function of the surface  $\phi$  is independent of position, one then gets the topography of the surface. The problem here is that at the atomic level the effective work function and rate of electron transfer *does* depend upon the nature of the orbitals describing the electrons.

There are, however, a number of questions about these experiments:

1. For a given surface, do the peaks of corrugation occur at the atomic centers or between them?
2. For heterogeneous surfaces, under what circumstances can STM distinguish atom types?
3. Under what operating conditions can a particular adsorbate be imaged?
4. What effects does tip structure have? Can we tailor-make more effective tips?

An STM spectrum was taken of molybdenum disulfide by the Caltech Group.<sup>1</sup> A naive interpretation of this would be that the bright spots correspond to the sulfurs, since

---

<sup>1</sup> STM data courtesy of M. Weimer *et al.* of Caltech (1987).

these are farthest from the surface and closest to the tip. The intermediate intensity would be the molybdenums which are one layer down, and the lowest intensities would be the channels that would go entirely through the system.

The way we are currently calculating these systems is to represent the molybdenum disulfide infinite slab using clusters as shown in Figures 17 and 18. We consider that this cluster was cut from the infinite system and that wherever there is a broken bond, we keep the broken bond electrons on the molybdenum coupled high-spin (as if they were coupled to the down-spin orbitals of the missing fragments to obtain bond pairs). This is to prevent these electrons from rearranging to provide stronger bonding within the complex than it would have in the infinite system. For the example under consideration here, there are 30 broken bond orbitals and 28 electrons that should be distributed among these. We replace the other atoms in the infinite system by an estimate of their net charges (say, molybdenum plus two, sulfur minus one) and then calculate this finite cluster until the wavefunctions converge. From this we then evaluate the net charges on the central molybdenum and sulfur atoms and use these to estimate the charges on the atoms that are missing from the system. We repeat this process until it converges. In the current calculations, the tip is modeled with a  $\text{Cs}^+$  at a distance  $R$  from the surface as shown in Figure 19. For each projection of cesium above the surface ( $XY$ ) and for each distance  $R$  above the surface, we calculate two wavefunctions. One denoted  $\Psi_A \Psi_B^-$  has the extra electron on the left (in  $\Psi_A$ ) and the other wavefunction denoted  $\Psi_A^- \Psi_B$  has the extra electron on the cesium. The rate of electron transfer is given by

$$T_{LR} = \frac{2\pi}{\hbar} |H_{LR}|^2 \rho,$$

where the matrix element is given by

$$H_{LR} = \langle \Psi_A \Psi_B^+ | H | \Psi_A^- \Psi_B \rangle,$$

and  $H$  is the *full* many-electron hamiltonian. In these calculations all the orbitals of  $\Psi_A \Psi_B^+$  overlap all the orbitals of  $\Psi_A^- \Psi_B$ . To carry out the calculation for  $H_{LR}$ , we use the

resonance-GVB program (developed by Voter and Goddard<sup>2</sup>) that allows one to rapidly evaluate such matrix elements without additional approximations. Results from these calculations are shown in Figures 20-22.

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<sup>2</sup> *Chem. Phys.*, 57, 253 (1981).

# STRUCTURE OF $2H-MoS_2$

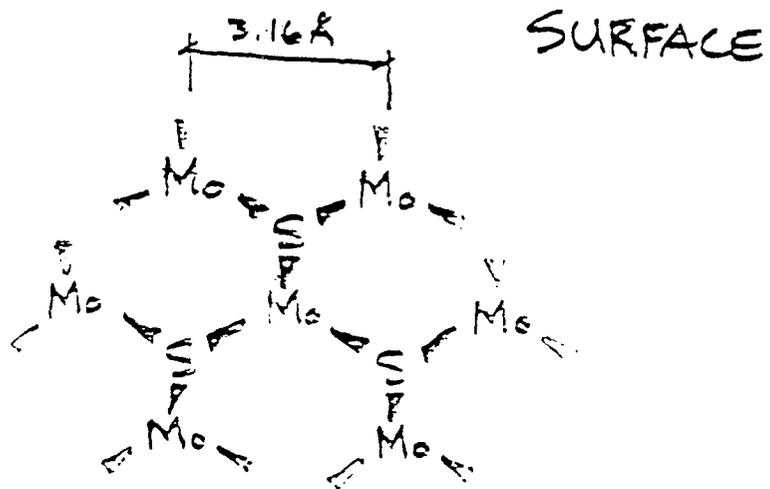
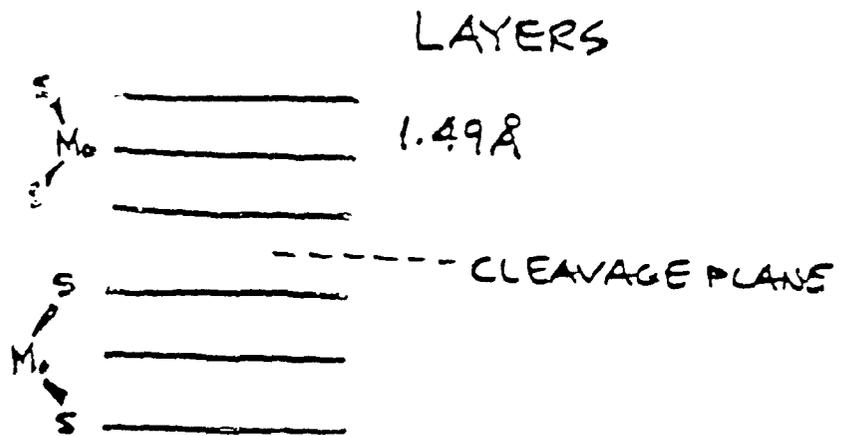


Figure 17.

Mo<sub>7</sub>S<sub>6</sub> CLUSTER

TOP  
VIEW

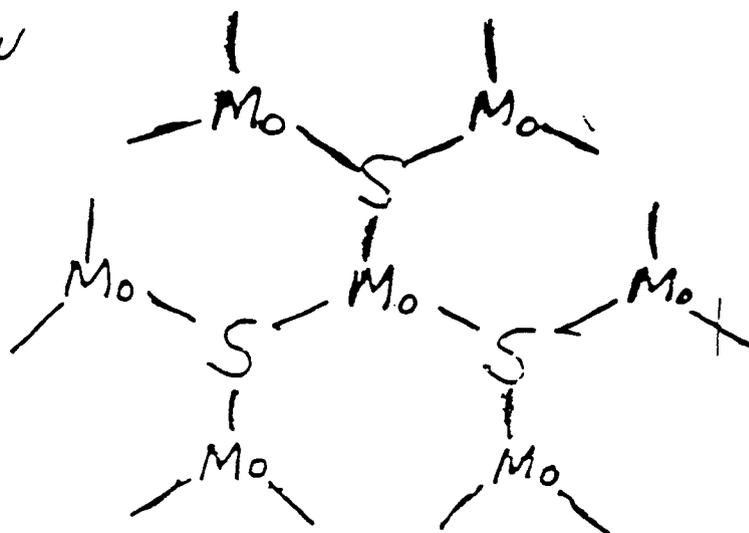


Figure 18.

# ELECTRON TRANSFER RATES

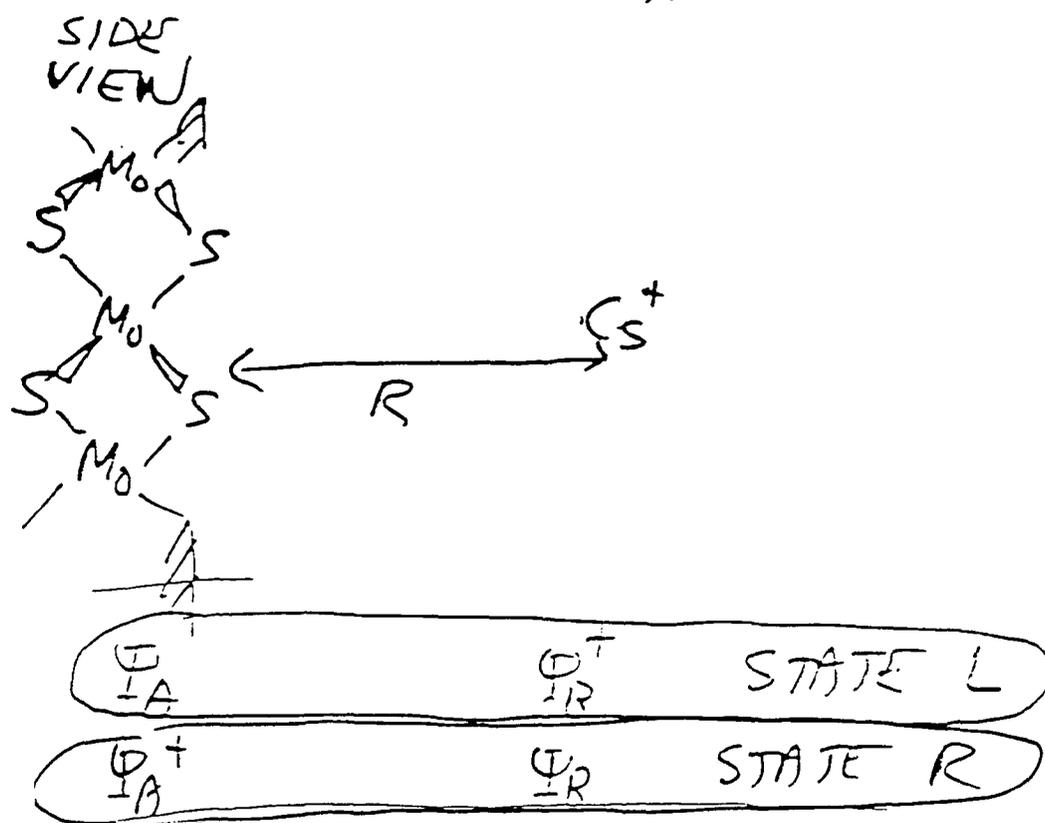


Figure 19.

NEUTRAL  $\text{MoS}_2$  CLUSTER NO PICTURE  
 AMPLITUDE ABOVE S DOMINATES  
 FROM 2-9 Å  
 BUT ABOVE  $\text{Mo}$  MAY DOMINATE ABOVE 9 Å

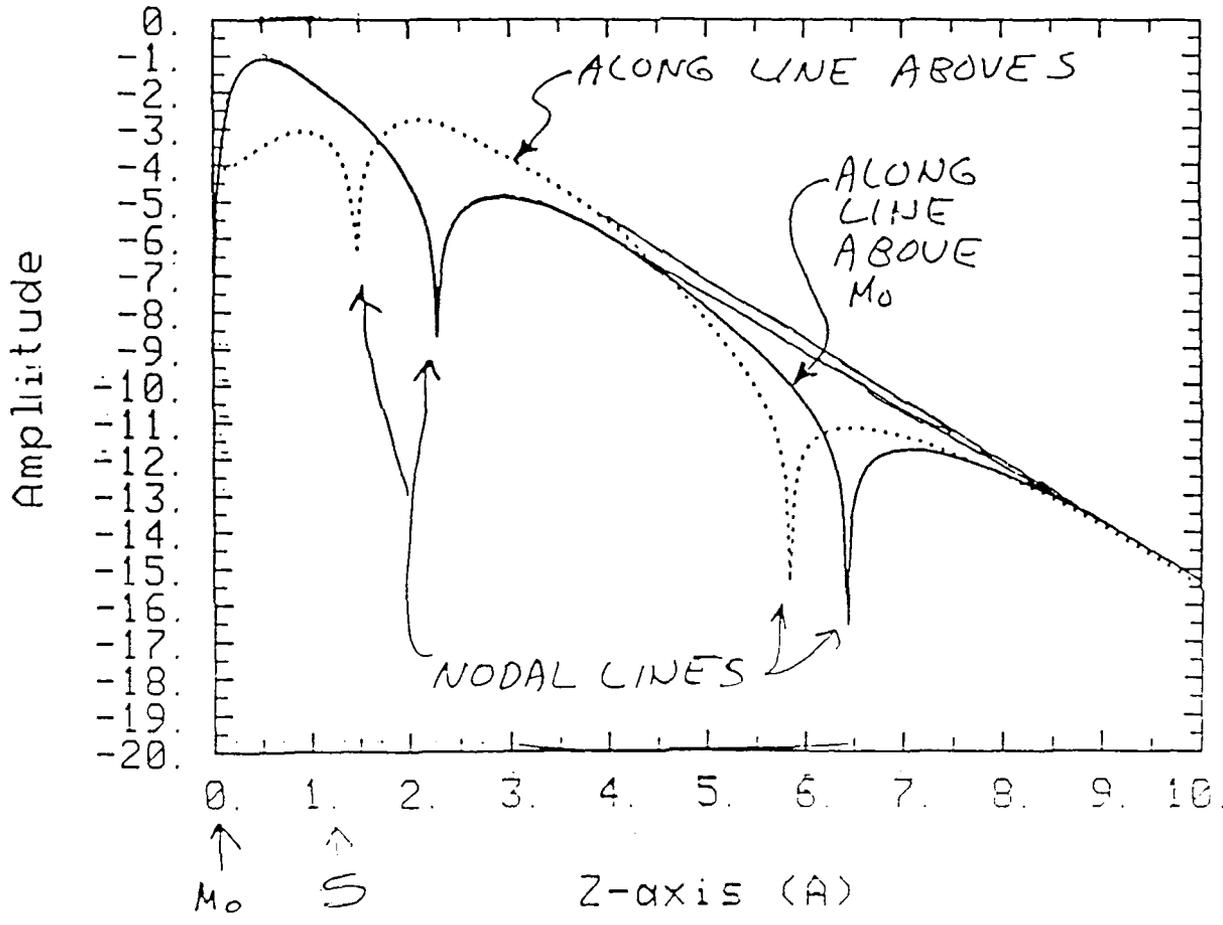


Figure 20.

# ELECTRON OF $MoS_2$

Cluster HOMO along lines through probe atom (Cs)

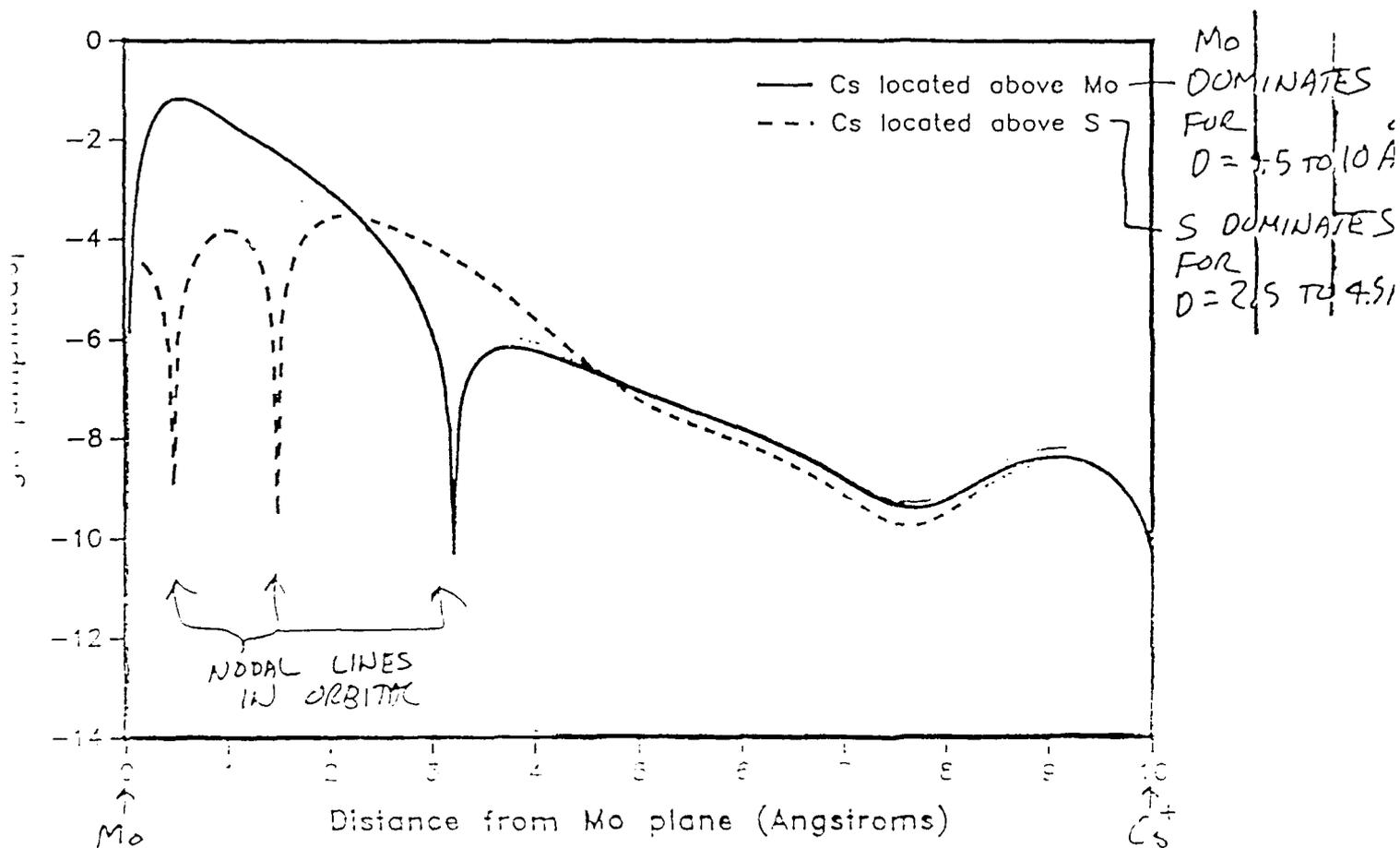


Figure 21. Electron on  $MoS_2$ .

# ELECTRON ON Cs

Cluster HOMO along lines through probe atom (Cs)

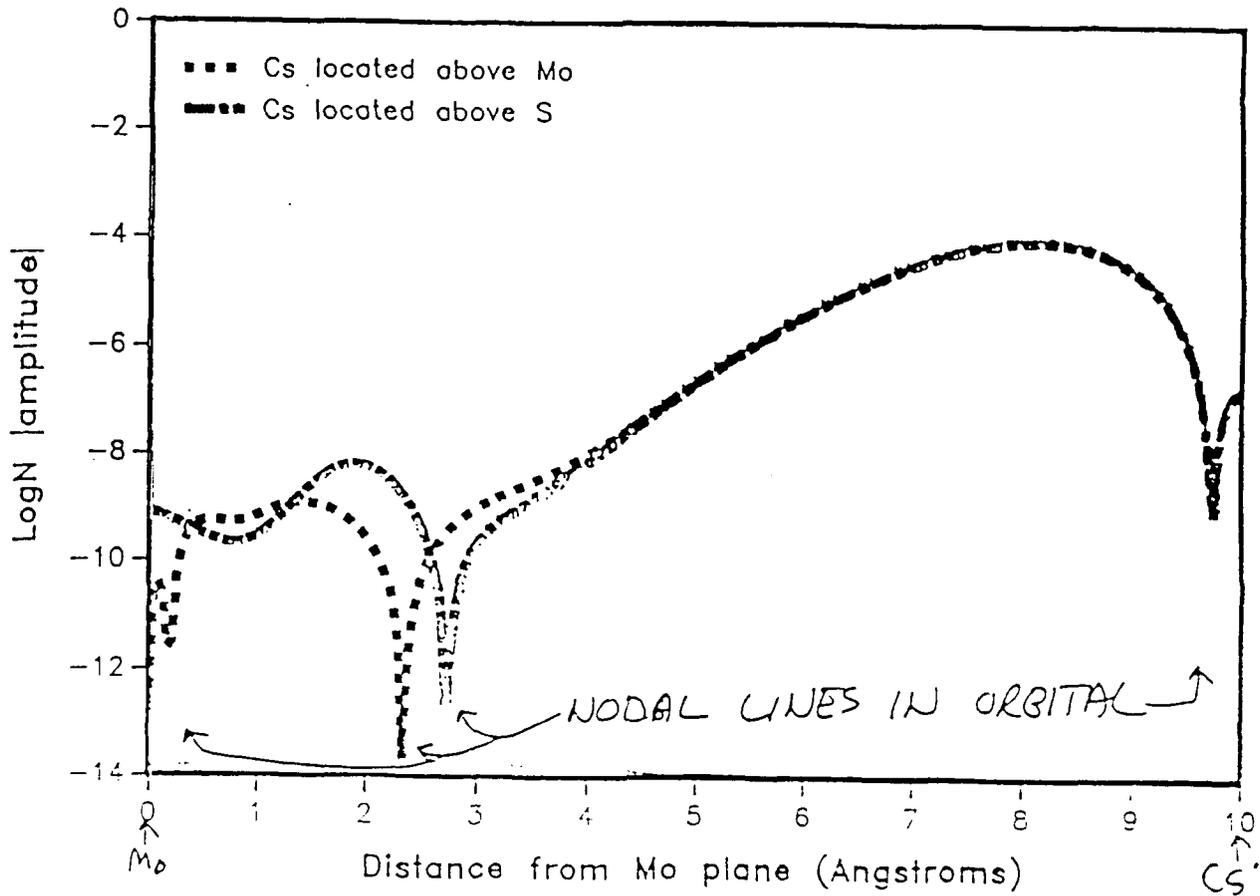


Figure 22. Electron on Cs.

First, in Figure 20 we consider the system without the cesium; that is, we show just the density of the orbital on the  $MoS_2$  that gets transferred to  $Cs^+$  but without the cesium present. These densities are non-monotonic because the amplitude of the orbital goes to zero at around 6 Å from the surface; however, overall, these are higher density above the sulfur than above the molybdenum.

In Figure 21 we show the orbitals for the  $\Psi_A \Psi_B^+$  wavefunction, that is, the wavefunction with the electron still on the  $MoS_2$ . Here we see that when the cesium is *above the molybdenum*, there is *higher* density from about 5 Å out than when the cesium is above the sulfur. Figure 22 shows the case where the electron is transferred to the cesium, that is  $\Psi_A^+ \Psi_B$ . In this case, the amplitudes are essentially the same from about 4 Å out. Thus the electron transfer matrix elements  $H_{LR}$  are dominated by the character shown in Figure 14.

We have now carried out calculations of the relative transfer rates for these two systems and find that indeed when the tip is 8.5 Å from the sulfur (10 Å from the molybdenum), the *highest electron transfer rate* is when the *tip is above the molybdenum!* That is, the measured current does *not* correspond to the surface topography. We are in the process of extending these results in several ways.

We are developing an approach to handle an infinite slab directly so that one does not have to do the iterative cluster calculation described above (which complicates interpretation). In addition, we are using the current approach to map out how the intensity changes as we move the tip around. The next phase of this work will be to carry out similar calculations for various atoms (hydrogen, fluorine, and nothing) sitting on various sites above diamond and silicon. Because the STM experiments are more easily carried out on silicon, and a number of results are already available, we will examine the silicon system first.

Our conclusion from these studies is that STM has a great deal of promise for characterizing tribological systems; however, theory will be critical in extracting the physics from the data.

## VIII. Bibliography

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18. Y. Guo, N. Karasawa, and W. A. Goddard III, "Packaging ..... *Nature*, 1991
19. N. Karasawa, S. Dasgupta, and W. A. Goddard III, "Mechanical Properties and Force Field Parameters for Polyethylene Crystal", *J. Phys. Chem.*, submitted for publication.
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## IX. Personnel Activities

### A. Scientific Personnel on AFOSR Project

1. Professor William A. Goddard III
2. Postdoctoral Fellows:
  - Dr. Siddharth Dasgupta
  - Dr. Chih-mai Kao (departed June 1988)
  - Dr. Jung-Goo Lee (department Mary 1989)
  - Dr. Gilles Ohanessian (departed February 1989)
  - Dr. Kimberly A. Schugart (departed August 1988)
3. Graduate Students:
  - Mark J. Brusich (departed March 1988)
  - Guanhua Chen
  - Terry R. Coley
  - Robert Donnelly
  - Yuejin Guo
  - Jonathan N. Hurley (departed April 1988)
  - Naoki Karasawa
  - Jean-Marc Langlois
  - Mo Li
  - Alan M. Mathiowetz
  - Ann E. Miller
  - Richard P. Muller
  - Jason K. Perry
4. Scientific Staff
  - James E. Kendall

## B. List of Publications Supported by AFOSR

1. Hessian-Biased Force Fields from Combining Theory and Experiment. S. Dasgupta and W. A. Goddard III. *J. Chem. Phys.*, **90**, 7207 (1989).
2. Theoretical Insights into STM Images of Molybdenum Disulfide. T. R. Coley, J. D. Baldeschwieler, and W. A. Goddard III. Abstract appeared in *Royal Microscopical Society Proceedings of Third International Conference on Scanning Tunneling Microscopy*, Oxford, England, 4-8 July 1989.
3. Acceleration of Convergence for Lattice Sums. N. Karasawa and W. A. Goddard III, *J. Phys. Chem.* **93**, 7320 (1989).
4. The Interstitial Electron Model for Lattice Dynamics in fcc Metals. M. Li and W. A. Goddard III. *Phys. Rev. B*, **40**, 12155 (1989).
5. Pseudospectral Generalized Valence Bond Calculations: Application to Methylene, Ethylene, and Silylene, J-M. Langlois, R. P. Muller, T. R. Coley, W. A. Goddard III, M. N. Ringnalda, Y. Won, and R. A. Friesner, *J. Chem. Phys.* **92**, 7488 (1990).
6. Mechanical Properties and Force Field Parameters for Polyethylene Crystal. N. Karasawa and W. A. Goddard III. *J. Phys. Chem.* **95**, 2260 (1991).
7. Charge Equilibration in Molecular Dynamics Simulations. A. K. Rappé and W. A. Goddard III. *J. Phys. Chem.* **95**, 3358 (1991).
8. Packing of Buckyballs; Prediction of Fullerene C<sub>60</sub> and C<sub>70</sub> Crystals. Y. Guo and W. A. Goddard III *Nature* **351**, 464 (1991).
9. Atomic Level Simulations on a Million Particles: The Cell Multipole Method for Coulomb and London Interactions, H-Q. Ding, N. Karasawa and W. A. Goddard III, *Phys. Rev. Lett.*, submitted.
10. Optimal Spline Cutoffs for Coulomb and van der Waals Interactions, H-Q. Ding, N. Karasawa and W. A. Goddard III, *J. Chem. Phys.*, submitted.

11. The Cell Multipole Method for Coulomb Interactions in Periodic Systems with Million-Atom Unit Cells, H-Q. Ding, N. Karasawa and W. A. Goddard III, *Phys. Rev. Let.*, submitted.
12. Generalized Mulliken-Pauling Electronegativities, A. K. Rappé and W. A. Goddard III, *J. Phys. Chem.* submitted.
13. Electronegativities of Transition Metals, A. K. Rappé and W. A. Goddard III, *J. Phys. Chem.* submitted.
14. A Generic Force Field (GENFF) for Simulations of Inorganic and Organic Materials, A. K. Rappé and W. A. Goddard III, *J. Phys. Chem.* to be submitted.
15. Force Fields and Mechanical and Piezoelectric Properties of Polyvinylidene Difluoride Crystals N. Karasawa and W. A. Goddard III, to be submitted.
16. Reconstructed Surfaces of Si(111); Structure and Energetics for Various Models, C. B. Musgrave, S. Dasgupta and W. A. Goddard III, to be submitted.
17. The Interstitial Electron Model for fcc Metals, M. Li and W. A. Goddard III, to be submitted.
18. Relation Between Topography and Intensities in Scanning Tunneling in Microscopy, T. R. Coley, W. A. Goddard III, and J. D. Baldeschwieler, in preparation.
19. Force Fields for Simulation of Group IV and III-V Semiconductors. C. B. Musgrave and W. A. Goddard III, in preparation.
20. Diamond-Diamond Interactions: A Microscopic Model for Friction, N. Karasawa and W. A. Goddard III, work in progress.
21. Force Fields for Simulations of Alkane Polymers, N. Karasawa, S. Dasgupta and W. A. Goddard III, work in progress.
22. Force Fields for Simulation of Fluorocarbon Systems, S. Dasgupta and W. A. Goddard III, work in progress.

23. Potential Functions for Reactions of  $H_2$  with Diamond and Si Surfaces, R. E. Donnelly and W. A. Goddard III, work in progress.
24. The  $2 \times 1$  Reconstructed Surface of Si(100); Structure and Energetics for Various Models, Y. Guo and W. A. Goddard III, in preparation.
25. Surface Energies for Hydrogenated Diamond Surfaces, T. Maekawa, N. Karasawa, and W. A. Goddard III, in preparation.
26. Pseudospectral - GVB, R. P. Muller, M. Ringnalda, T. Coley, J-M. Langlois, and W. A. Goddard III, in preparation.
27. Periodic Boundary Conditions for Hf and GVB Wavefunctions, J-M. Langlois, and W. A. Goddard III, in preparation.
28. Force Fields for  $SiO_2$ , J. J. Gerdy and W. A. Goddard III, work in progress.

**C Invited Talks and Contributed Papers Describing AFOSR-Sponsored Research**

1. *Computation in Polymer Science*, Session on "Interface of Polymer Science with Physics and Computational Modelling", 28th Moretonhampstead Conference on "Interfaces Between Polymer Science and Other Disciplines", sponsored by the High Polymer Research Group of Imperial Chemical Industries, Moretonhampstead, Devon, England, 28 April 1988. (Presented by W. Goddard.)
2. *Role of Theory in Understanding Chemical, Polymer, and Materials, Synthesis*, Union Carbide Corporation, Danbury, Connecticut, 18 May 1988. (Presented by W. Goddard.)
3. *Critical Evaluation of Various Force Fields in Molecular Mechanics*, Symposium on Recent Advances in Experimental and Theoretical Biophysics, Division of Physical Chemistry, Third Chemical Congress of North America and 195th National Meeting of the American Chemical Society, Toronto, Ontario, Canada, 6 June 1988. (Presented by S. Dasgupta.)
4. *Atomic Level Modeling for Tribology*, Air Force Tribology Technical Review, Fairborn, Ohio, 7 June 1988. (Presented by W. Goddard.)
5. *Atomic Modeling of Friction*, Gordon Research Conference on "Frontiers of Tribology", Holderness School, Plymouth, New Hampshire, 20 June 1988. (Presented by W. Goddard.)
6. *Theoretical Insights into STM Images of Molybdenum Disulfide*, Third International Conference on Scanning Tunnelling Microscopy, Royal Microscopical Society, Oxford, United Kingdom, 4-8 July 1988. (Presented by T. Coley.)
7. *Theory of Friction and Adhesion*, 1988 LASST - ACSIS, Joint Workshop on Interface Phenomena, "Adhesion and Friction: Microscopic Concepts", Dalhousie University, Halifax, Nova Scotia, Canada, 25 August 1988. (Presented by W. Goddard.)
8. *Multibody Potentials from Ab Initio Electronic Structure Calculations*, Session I: Atomistic Modeling of Materials; Beyond Pair Potentials, 1988 World Materials Congress, Chicago, Illinois, 27 September 1988. (Presented by W. Goddard.)
9. *Theoretical Studies of Molybdenum Disulfide*, Division of Colloid and Surface Chem-

- istry, 196th National Meeting of the American Chemical Society, Los Angeles, California, 28 September 1988. (Presented by T. Coley.)
10. *Simulation of Materials; From Polymers to Superconductors*, Amoco Research Center, Naperville, Illinois, 17 October 1988. (Presented by W. Goddard.)
  11. *New Developments in Force Fields for Polymer Modeling*, Session I: Polymer-Mechanical Properties, BioDesign Polymer Design and Simulation Consortium, Winter 1988, Princeton, New Jersey, 3 November 1988. (Presented by W. Goddard.)
  12. *Simulation of Materials with Applications to Polymers and High Temperature Superconductors*, International Conference Center, Kobe, Japan, 29 November 1988. (Presented by W. Goddard.)
  13. *Simulation of Materials with Applications to Polymers and High Temperature Superconductors*, Nippon Kaium Club, Tokyo, Japan, 1 December 1988. (Presented by W. Goddard.)
  14. *Simulation of Materials with Applications to Polymers and High Temperature Superconductors*, Sandia National Laboratories, Livermore, California, 17 January 1989. (Presented by W. Goddard.)
  15. *Computer Graphics Simulations of Materials: Polymers to Superconductors*, Research Directors Conference on the '90's and Beyond, Caltech, Pasadena, California, 8 February 1989. (Presented by W. Goddard.)
  16. *Simulation of Materials with Illustrations on Biological, Polymer, and Superconductor Systems*, Research School of Chemistry, Australian National University, Canberra, Australia, 15 February 1989. (Presented by W. Goddard.)
  17. *Simulation of Materials: Applications to Biological, Polymer, and Superconductor Systems*, Chemistry Department Seminar, Yale University, New Haven, Connecticut, 28 February 1989. (Presented by W. Goddard.)
  18. *Simulation of Materials: Applications to Biological, Polymer, and Superconductor Systems*, General Electric Corporate Research and Development Center, General Electric Company, Schenectady, New York, 1 March 1989. (Presented by W. Goddard.)

19. *Simulation of Materials: Applications to Biological, Polymer, and Superconductor Systems*, 1989 Joe L. Franklin Memorial Lecture, Department of Chemistry, Rice University, Houston, Texas, 14 March 1989. (Presented by W. Goddard.)
20. *Simulation of Biological and Materials Systems*, Symposium on Computational Modeling of Molecular Systems, Divisions of Biological Chemistry and Organic Chemistry and Subdivision of Theoretical Chemistry, 197th National Meeting of the American Chemical Society, Dallas, Texas, 12 April 1989. (Presented by W. Goddard.)
21. *Simulations on Polymers — Mechanical, Electrical and Structural Properties*, Imperial Chemical Industries Molecular Simulation Symposium, Wilton, England, 20 April 1989. (Presented by W. Goddard.)
22. *Hessian-Biased Force Fields for Molecular Mechanics*, West Coast Theoretical Chemistry Conference, IBM Almaden Research Center, San Jose, California, 11 May 1989. (Presented by S. Dasgupta.)
23. *Applications of Ab initio van der Waals Potentials of  $H_2-H_2$  and  $CH_4-H_2$  to Large Molecular Systems*, West Coast Theoretical Chemistry Conference, IBM Almaden Research Center, San Jose, California, 11 May 1989. (Presented by J-G. Lee.)
24. *Structure and Bulk Properties of Polymer Crystals*, West Coast Theoretical Chemistry Conference, IBM Almaden Research Center, San Jose, California, 11 May 1989. (Presented by N. Karasawa.)
25. *Molecular Modeling Applied to Problems in Polymers and Surface Science*, Physical Chemistry Department, General Motors Research Laboratories, Warren, Michigan, 15 June 1989. (Presented by W. Goddard.)
26. *Atomic Level Simulation of Materials*, Workshop in Dedicated High-Performance Systems for Visualization and Simulation, Ramo Auditorium, Caltech, Pasadena, California, 20 June 1989. (Presented by W. Goddard.)
27. *Simulation of Materials with Emphasis on Polymers*, Raychem, Menlo Park, California, 28 June 1989. (Presented by W. Goddard.)

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28. *Simulations of Materials: An Update*, General Electric Company, Corporate Research and Development Center, Schenectady, New York, August 9, 1989 (presented by W. Goddard)
  29. *Simulation of Polymers and Other Materials*, Asahi Glass Research Center, Yokohama, Japan, October 4, 1989 (presented by W. Goddard)
  30. *Simulation of Polymers, Superconductors, and Other Materials*, Nippon Steel, Kawasaki, Japan October 5, 1989 (presented by W. Goddard)
  31. Four Lectures on *Theory and Simulation of Chemical, Biological, and Materials Systems*, Visiting Professor of Chemistry, Texas A&M University, College Station, Texas, October 16-19, 1989 (presented by W. Goddard)
  32. *Modeling of Chemical and Tribiological Properties of Ceramic System*, AFOSR Molecular Dynamics Contractors Conference, Session on Tribiological Surfaces, Captiva Island, Florida, November 1, 1989 (presented by W. Goddard)
  33. *Microscopic Theoretical Modeling of Ceramic Interfaces*, Air Force Tribiology Technical Review, Fairborn, Ohio, December 1, 1989 (presented by W. Goddard)
  34. *Simulation of Materials: Applications to Polymers, Metals, and Catalysts*, BP America Research, Cleveland, Ohio, March 12, 1990 (presented by W. Goddard)
  35. *Tutorial on Molecular Modeling*, Exxon Chemical Company Chemicals Research Meeting, Buck Hill, Pennsylvania, May 1, 1990 (presented by W. Goddard)
  36. *Simulations of Surfaces and Interfaces*, at Alcoa Laboratories Technical Symposium on Chemistry and Physics of Surface and Interfaces, Alcoa Center, Pennsylvania, August 20, 1990 (presented by W. Goddard)