

Annual Report for Period: 09/1999 - 09/2000

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Principal Investigator: Bartlett, Rodney J.

Award ID: 9980015

Organization: University of Florida

KDI: Multi-scale Simulation Including Chemical Reactivity in Materials Behavior Through Integrated Computational Hierarchies

Project Participants**Senior Personnel****Name:** Bartlett, Rodney**Worked for more than 160 Hours:** Yes**Contribution to Project:****Name:** Zerner, Michael**Worked for more than 160 Hours:** No**Contribution to Project:**

Prof Zerner died in January, 2000.

Name: Trickey, Samuel**Worked for more than 160 Hours:** Yes**Contribution to Project:****Name:** Simmons, Joseph**Worked for more than 160 Hours:** Yes**Contribution to Project:****Name:** Cheng, Hai-Ping**Worked for more than 160 Hours:** Yes**Contribution to Project:****Name:** Harris, Frank**Worked for more than 160 Hours:** Yes**Contribution to Project:**

Senior Investigator

Name: Dufty, James**Worked for more than 160 Hours:** Yes**Contribution to Project:**

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Name: Yip, Sidney**Worked for more than 160 Hours:** Yes**Contribution to Project:**

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Contribution to Project:

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Worked for more than 160 Hours: Yes
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Worked for more than 160 Hours: No
Contribution to Project:

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Contribution to Project:

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Contribution to Project:

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Contribution to Project:

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Contribution to Project:

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Worked for more than 160 Hours: Yes

Contribution to Project:

Organizational Partners

Motorola Inc

IBM

Hypercube

ACES QC

ACES QC is a contract research organization.

The College of New Jersey

Planning to submit an RUI for more formal collaborative research. This collaboration is looking at the novel use of energy landscapes to

identify major deviations from equilibrium in MD simulations. These regions may require improvements in the interatomic force functions.

Other Collaborators or Contacts

The following faculty from predominantly undergraduate institutions are collaborating with us on various aspects of this work:

Dr. John Watts, Associate Professor of Chemistry at Jackson State University.

Dr. Charles Weatherford, Professor of Physics, Florida State University.

Dr. Janet DelBene, Professor of Chemistry, Youngstown State University.

Dr. Brian L. Wiener, Associate Professor of Physics, Penn State University-DuBois, DuBois, PA

The following Fulbright Fellow has participated:

Dr. Afaf Al-Derzi, Associate Professor of Chemistry, Al Al-Bayt University, Mafraq, Jordan

The following staff from National Laboratories have participated:

Dr. James Rustad, Battelle, Pacific Northwest National Lab, Richland, WA.

Dr. L. Rene Corrales, Battelle, Pacific Northwest National Lab, Richland, WA

Activities and Findings

Project Activities and Findings: (See PDF version submitted by PI at the end of the report)

The award of this grant established a multi-disciplinary research effort centered at the University of Florida on the topic of 'Multi-Scale Simulations from Molecules to Materials (MSSMM).' This embraces, at successively larger scales, quantum chemistry(QC), molecular dynamics (MD), surface and solid physics(SSP), kinetic Monte Carlo(MC), and finite element(FE)/continuum theory, all tied together by novel software; and tested by carefully chosen experimental results. The project involves nine investigators at four Universities, with input from industry, the national laboratories, computer hardware and software companies, and other universities.

The problem addressed is fundamental: our objective is to invent NEW theory and algorithms and implement them into state-of-the-art software to make it possible to accurately describe real materials including the chemistry they undergo. Today, with classical potentials, MD simulations of tens of millions (even up to billions!) of atoms can be made for short time periods. However, such results can be no better than the potentials governing the interactions among the atoms. It is well known that such classical potentials cannot adequately describe the long range parts of molecular interactions reliably and bond breaking, in particular. Hence, fracture, its associated electron ejection and chemical reactions (transient and final states), polishing, or essentially any phenomena that involve bond breaking or formation and their associated spectroscopic fingerprints, require a quantum mechanical description. But the QM description has to be coupled into a framework that permits real materials to be simulated, which involves SSP, MD, MC, and FE all working together in concert.

We discuss this further in the following Research Findings section, where we focus on the research objectives and accomplishments in the first twelve months of this work, followed by a survey of progress in the coordinated experimental efforts. Prior to that, we can summarize other Research Activities.

The first meeting of the full team after the award was on Oct. 2, 1999 in Jacksonville, FL. There we held an intense, all-day effort on detailed research plans after reviewing research capabilities plus developments since writing the proposal.

The second major activity was to organize a workshop entitled 'Scale-parity, Multi-scale Simulation of Chemo-mechanical Processes', Feb 25-26, in St. Augustine, FL. In this two and one-half day workshop, (partly supported by the DOE), we assessed the state of the field with the help of eight speakers and on-site reports from four workgroups ('Parameterized Potentials', 'Embedded Quantum Mechanics', 'Mesoscale Molecular Dynamics', 'Full-system Simulations'). There were 35 participants. We continued this focus into the 40th Sanibel Symposium, where two additional sessions were devoted to Materials Modeling. The

attendees, speakers, and schedule are shown in Contributions to Education and Human Resources. It is our plan to hold such a workshop annually during the course of this effort.

In the summer, June 12- August 15, we supported five undergraduate students to participate in this study. The schedule included a far-reaching short course on the topic of Materials Modeling, with lectures given on the various aspects by several of our senior investigators, 'hands-on' computer exercises, and research problems. This will also be done annually. The participants and schedule are shown in Contribution to Education and Human Resources. A copy of the full text will be sent under separate cover.

Over the year we ran a series of research topics seminars for the Florida participants, with the dual goals of (a) integrative briefing of the graduate students and postdocs on research not in their immediate specialty and (b) hearing the work of potential postdocs.

A list of speakers and topics is appended to the Contribution to Education Section.

Other research activities include the following invited presentations at meetings, universities, and laboratories:

BARTLETT INVITED PRESENTATIONS:

July 2000 'Ab Initio Density Functional Theory,' 4th Canadian Computational Chemistry Conference, Bishop's University, Lennoxville, Quebec, Canada, July 28-Aug 3.

May 2000 'Predicted NMR Coupling Constants Across Hydrogen-Bonds: A Fingerprint for Specifying Hydrogen Bond Type,' SETCA 2000, University of Georgia, Athens, GA, May 17,18.

May 2000 'Ab Initio Density Functional Theory,' Twelfth Annual Workshop on Recent Developments in Electronic Structure Theory, ES200, Atlanta., GA, May 19-21.

April 2000, Fifth Annual European Workshop on Quantum Systems in Chemistry and Physics, Uppsala, Sweden, April 13-18.

February 2000, 'Ab Initio Density Functional Theory,' Fortieth Annual Sanibel Meeting, St. Augustine, FL, Feb 27- March 3.

February 2000 'Coupling Constants Across Hydrogen Bonds in NMR: The Role of Predictive Theory,' Bircher Lecture, Vanderbilt University, Nashville, TN

December 1999 'Survey of Theory and its Application to Molecules and Materials,' Motorola, Inc., Mesa, AZ

December 1999 'Materials Science: Ab Initio DFT,' Arizona State University

November 1999 'Correlation in Molecules and Solids' The Third Congress of the International Society of Theoretical Chemical Physics, Mexico City, Mexico

October 1999 'Excited States in Molecules and Solids: Interplay between Experiment and Theory,' ESMS Conference, Tarragona, Spain

TRICKEY INVITED PRESENTATIONS:

February 2000 'Dielectric Functions in LiF,' 20th Werner Brandt Workshop on Energy Deposition Phenomena, University of Florida, Gainesville, Florida

November 1999 'Jellium Blob Chemistry: Predicting and Understanding Trends in Molecular Response Anisotropy from Simple Models,' The Third Congress of the International Society for Theoretical Chemical Physics, Mexico City, Mexico

HARRIS INVITED PRESENTATIONS:

January 2000 'Numerical Aspects of RHF Calculations on Surface Systems,' Facultes Universitaires Notre-Dame de la Paix, Namur, Belgium

August 2000 'Numerical Problems in Extended-System Calculations,' IBM, Zurich, Ruschlikon, Switzerland

Project Training and Development: (See PDF version submitted by PI at the end of the report)

A. QUANTUM CHEMISTRY (Rodney J. Bartlett)

QM means that the electrons must be described together with the nuclei to obtain the potentials of interaction required by the MD and MC simulations. However, to transfer the electronic potential information to MD, preferably 'on the fly', demands that the potential be generated

very quickly. Furthermore, even some of the best quantum chemical methods often have difficulty with bond breaking. Coupled-cluster (CC) theory, for example, which is effectively exact near the equilibrium region of a molecule, has some difficulty farther out on the potential curve and in describing the breaking of multiple bonds, in particular, although not usually for single bonds--our objective. However, CC theory or multi-reference configuration interaction (CI) calculations are far too demanding to directly use in MD simulations of many particles, forcing us to pursue other, faster alternatives.

There are five possibilities in order of increasing sophistication and reliability:(1) tight binding (TB); (2) semi-empirical quantum chemistry;(3) Hartree-Fock self consistent field (SCF) theory;(4) density functional theory (DFT); and (5) SCF based second-order perturbation theory, MBPT(2) (also known as MP2). For current multi-scale materials applications only the TB approach has been used. For some types of simulations, such as those for smaller numbers of atoms as in biological applications, others are possible, with DFT frequently being the choice.

Semi-empirical quantum chemistry, although faster than all but TB, has seldom been used in simulations because of many well-known failures. However, to quantify this observation, we have performed a series of simulations of C60 colliding with a wall, to watch its fragmentation as a function of choice of potentials. Note this fracture of nonstructures as well as carbon fiber composites are highly relevant issues. It is known experimentally that of the energies of interest, C60 tends to fragment into C2 and other C2n fragments. It is certainly true that the INDO approximation (intermediate neglect of differential overlap) fails to allow C60 to fragment because of the method's misbalance of molecules' attractive and repulsive forces. However, once we go to the NDDO Hamiltonian (neglect of diatomic differential overlap) in either the PM3 or AM1 parameterization, we obtain a proper fragmentation pattern for C60[Hsaio, et. al.] (See Figures 1-5) (References are in Journal Publications.) Depending upon the parameterization, these results are in contrast to that obtained by TB, which in this case was parameterized for the solid, which has been the de facto standard in the field. This study attests to the essential role of a proper description of the essential features of the electronic structure to get a potential that yields correct results. Ab initio and DFT simulations are planned to provide reference results for this prototype system.

Armed with the apparent success of using an NDDO Hamiltonian to generate a potential for C60, in a major new effort, we are creating a hybrid approach we call the 'transfer Hamiltonian' that is meant to 'distill' the essential information from ab initio quantum chemistry into the form of a semi-empirical NDDO Hamiltonian. Because this is a very low rank operator, it can be used to rapidly generate the energies and forces for MD, hopefully retaining the accuracy of the underlying ab initio method.

To illustrate, for C there are nine purely atomic quantities that define all the results at any geometry for C60. The nine quantities can be specified by doing a series of ab initio calculations involving small clusters of C, since the forces rapidly fall off with distance, from which either the forces or the energies, or a combination of both, can be used to fix the nine values. This is typically achieved using a genetic algorithm. In this way the NDDO Hamiltonian itself is entirely specified. It is also checked against the ab initio values in all the critical regions of the potential. To do the same for SiO2, requires a slightly larger number of parameters to be determined for Si because of the need for d orbitals, plus nine for O. We can readily add H2O to the simulation, too. Hence, for a rather small number of quantities, all of which are atomic, we have an NDDO Hamiltonian that can rapidly generate the forces required for MD. Furthermore, because of their atomic nature, we might expect that these values will also come close to being transferable. Insofar as the reparameterized NDDO Hamiltonian correctly describes the ab initio results, we expediently obtain the quality of ab initio potentials but within a computationally viable MD procedure.

We have also explored using this idea for reaction dynamics, where the critical information is the transition state. However, like MD, we require considerable information about the energy surface and the forces (gradients) on it, which makes purely ab initio applications prohibitive. Here, we have generated ab initio results from the G2 extrapolated MP2 method to specify the NDDO parameters for OH extracting H from ethane and its halogenated analogues. We fit the forces (gradients) along five points on the G2/MP2 reaction path and the curvature (Hessian): the reactants, products, the transition state, and the reactant and product Van Der Waals structures. We then use this potential with a quasi-classical flux-flux auto correlation approach to obtain rate constants in excellent agreement with experiment [Runge, et al]. (See Figures 6-8) We applied the same intermolecular potential technique, assisted by coupled-cluster theory, for the OH abstraction of H from dimethyl sulfide [Sekusak, et al].

There is also a purely ab initio approach to the transfer Hamiltonian. This is offered by the CC correlated Hamiltonian, $\exp(-T)\text{Hexp}(T)=K$, where the T operator is the CC cluster operator determined in a CC calculation. In second-quantized form in the atomic orbital basis set, K will look quite similar to the NDDO Hamiltonian once K is truncated to one and two particle terms, but unlike the NDDO operator, which is limited to a minimum basis set, a larger polarized basis might be used for K. This allows us to assess how important the effects of d orbitals on C might be, eg, leading us to even better, but still low rank, simplified Hamiltonians. Of course, K itself is a much richer operator to match than that obtained from fitting NDDO parameters to energies or forces. In fact, if K could be represented adequately, we would be able to obtain the relevant excited and ionized states too, yet in a very simple structure. The latter might be particularly relevant if multiple surface information is required in simulations.

In another longer term effort, we would like to improve upon the rigor and feasibility of DFT calculations in 'on the fly' simulations. This has caused us to pursue on the one hand, what we call 'ab initio' DFT for rigor [see RJB presentations above], while on the other, seek simplified

forms of potentials that might provide good, but quickly evaluated approximations.

B. MOLECULAR DYNAMICS (H.P. Cheng, J.H. Simmons, S. Yip, F. Harris)

Molecular dynamics (MD) allows studies of physical phenomena and processes at the atomistic level with high spatial and temporal resolution. On MD method development, the objective of the KDI program is to develop and implement sophisticated computational methodologies that enable accurate descriptions of the interatomic interactions in large-scale MD simulations.

We (HPC) currently perform MD simulations at various levels including classical MD, first-principles MD (on-the-fly), as well as all quantum mechanical (AQ) MD that combines the quantum path integral (PI) method with first-principles MD. These techniques are being used to study materials such as silica (bulk, surfaces and clusters), alumina, and their interactions with water molecules/clusters. We aim at developing simulation methods that combine first-principles MD, based on density functional theory within the framework of pseudo-potentials in conjunction with plane-wave expansions, and classical MD (CMD), with emphasis on the computation of mechanical properties at the interface. In addition, progress has been made in developing an interface between the classical MD and the finite element (FE) method (e.g. SiO₂ system) to link simulations at different scales.

In CMD with empirical potential energy functions, we are adding the Mintmire potential energy functions (for aluminum oxide crystals and alumina) to our CMD code that is equipped with two-body potentials (any type), Tersoff potentials, and embedded-atom potentials. The Mintmire functions provide a framework in which charge transfer can be described as dynamics progresses in the classical MD simulations. The goal is to incorporate information from quantum chemistry calculations to describe chemical reactions in large-scale CMD simulations.

In FPMD for finite-sized systems, Born-Oppenheimer local spin density molecular dynamics (BO-LSD-MD) is being used to study interactions between water and SiO₂ in clusters. Substantial progress has been made on two related projects that emphasize water-SiO₂ interactions as the number of SiO₂ molecules and the number of water molecules increase. All calculations are carried out with inclusion of the generalized gradient correction (GGA, PBE) and with cut-off energy (~70 Ryd) which gives an accuracy better than 0.5 kcal/mol for hydrogen bonding in water clusters. Our results indicate that previous calculations on the reaction barrier for dissociation of water molecules are different from those predicted by semi-empirical calculations (AM1). Isomeric states also exist in (H₂O)_(n)-(SiO₂)_(m). Important processes such as hydrogen atom transfer are observed via the FPMD simulations and information on the dynamics of the processes are obtained for the first time.

The previously mentioned prototype system, the C₆₀ molecule, is chosen as an example to study the nature of bond breaking in covalent bond systems using FPMD (BO-LSD-MD with GGA). The simulations of C₆₀ at 4000 K are still in progress because of the high computational demand. Results at 130 fs depict a physical picture of a melting process in which bond breaking opens the pentagon and hexagon rings. The formation of carbon double bonds is also observed. Simulations at longer times will provide necessary information to understand the fragmentation of C₆₀ molecules at the microscopic level. The DFT simulations will be compared with CMD and MD and all semi-empirical MD (see the Quantum Chemistry section of this report).

For Extended systems, we have been investigating two first-principles MD algorithms based on DFT and plane-wave expansions in conjunction with pseudo-potentials. Both methods use periodic boundary conditions (PBC). The first one propagates Newtonian equations on the Born-Oppenheimer ground state electronic surface similar to BO-LSD-MD in which PBC are not applied. The second is a Car-Parrinello MD (CPMD) method that uses an effective Hamiltonian that includes the time derivative of the electron wavefunctions to accelerate the convergence of the Kohn-Sham equations during the MD steps. Comparative studies of systems such as SiO₂ surfaces and Al₂O₃ surfaces are underway.

As one of the major components in the KDI program, we are developing methods that properly treat the quantum DFT MD and classical MD interfaces. Unlike most of the existing approaches (often known as QM/MM) in which the continuation of the mechanical properties at the interface is not guaranteed, we have formulated a theoretical method that enables an appropriate description of large structural deformations in the interface. BO-LSD-MD is chosen to describe the quantum region because of its unique features that enable fast and accurate simulations of finite-sized systems. In our approach, the interface will be built sufficiently distant from the reaction center such that the chemical processes occur at the tip of the crack.

JHS has been studying classical MD simulations to prepare for the interface with HPC's quantum mechanical simulations. In the classical MD simulations, both crystalline and non-crystalline SiO₂ systems have been examined using a screened Born-Mayer interatomic potential. The simulated structure is then subjected to a uniaxial strain until fracture. These studies have shown that the major features of fracture are reproduced by the MD simulation. For example, we find that the fracture surface exhibits a characteristic roughness, essentially equal to that measured on real systems by AFM. We also find that the fracture process differs with crystallinity or lack thereof, and rate of strain application. By changing the rate of strain application, we find that the MD simulation reproduces the differences in surface structure found experimentally between the mirror, mist and hackle regions.

The major modification to be examined in this grant is the effect of surface chemistry on the fracture process. Since it is not possible to adequately represent chemical reactions using classical interatomic potentials, we need to turn to HPC and RB's quantum mechanical systems

to introduce the chemistry. As a first step, we plan to simulate the chemical reactions by use of classical empirical events in the MD, such as dissociation rates and chemical reactivity coefficients borrowed from experiment. In this respect we are collaborating with Rene Corrales (PNNL Labs) in the development of an adequate set of water-silica potentials.

One of the key steps in this combination of classical and quantum mechanical MD is to determine at what point to make the transition between the two. Clearly, near equilibrium interatomic distances, classical interatomic potentials are adequate. Far from equilibrium, this is not the case, and electronic states play a major role, consequently quantum mechanical interactions must be used. Visual examination of the interatomic positions does not readily produce a good evaluation of the bonds that will potentially be strained out of equilibrium. Therefore, we plan to apply a novel energy landscape method which plots the potential energy surface around each atom to determine which bonds are strained and offer an easy path to diffusion or deformation. Once determined the strained region will be exposed to molecular water.

SY has addressed molecular dynamics studies of strength and deformation of alpha-quartz as a prototypical model system using an existing classical interatomic potential. SiO₂ have been of much interest for the potential application of producing pressure induced amorphized structures. Oddly, uniaxial compression, however, has never been explored. We have carried out a molecular dynamics simulation study of the stress-strain response of single crystal/alpha-quartz under uniaxial compression using the interatomic potential of van Beest, Kramer, and van Santen. Our simulation at 8000C shows the onset of yield at 16Gpa and subsequent time-dependent evolution of an 'amorphous' planar microstructure. We believe this behavior corresponds to the experimental observations in geophysical studies pertaining to the hydrolytic weakening of quartz, where evidence of evolution of planar isotropic material and 'deformation lamellae' also have been reported [Subramanian and Yip].

In a related but separate study of tensile deformation of alpha-quartz we have observed a stress-induced structural transition from alpha to beta quartz which is known to occur at 847K. By means of an order parameter (the Wyckoff position parameter for Si) we propose a distinction between a dynamic and a static beta phase which clarifies the different experimental observations. By considering shear deformations we are able to combine the simulation results with the transition data driven by temperature and construct an Ising-type phase diagram, with shear stress playing the role of the external magnetic field [Liao and Yip].

In the coming year SY will continue with the study of strength and deformation of alpha-quartz, linking his work to that of JHS. Yip, J. Simmons, J. Dufty, F. Harris, and H.P. Cheng will work on developing a simulation code with molecular dynamics and finite-element capabilities. They will also introduce a water environment; this is necessary for an attempt to probe hydrolytic weakening. This is likely to involve collaboration with colleagues, J. Rustad and R. Corrales, at the Pacific Northwest National Laboratory.

We have constructed an interface to connect CMD and the FE method which is based on the elastic theory of continuum mechanics. The code is ready to be tested for multi-scale simulations of SiO₂ systems.

C. SURFACE and SOLID PHYSICS (S. B. Trickey, F. E. Harris, J. Dufty)

(ST) Relatively little first-principles computational work has been done on cleavage and deformation energies of many technologically important ordered ceramics. Such calculations are an important input for this project as a way to provide information on the structure, energetics, and elastic properties to (a) calibrate more realistic potentials, (b) move beyond fixed potentials to 'reactive' potentials as shown in [Apell, et. al.1] In both cases the unusual asset we have is a gaussian orbital code ('GTOFF', by J.C. Boettger and S.B. Trickey) that allows us to calculate ultra-thin film and crystalline DFT structure-energy relationships in a completely consistent way using the same kind of basis sets as in molecular calculations. [Boettger and Trickey]

The focus system is Si₃N₄ because of the lack of information relative to Si, SiO₂, and SiC; the latter three are test cases. We are preparing for full-scale calculations on homogeneously deformed crystals and cleaved thin slabs, with the new graduate student now evaluating basis sets. The results will be used to fit potentials for use in MD simulations by Prof. Cheng. A related part of the student's project will be to develop and implement techniques to calculate the DFT local softness and electronegativity ('reactivity indices') and transfer that information to potentials, for example, of the Streitz-Mintmire type. [Apell, et., al., 2] [Sabin, et., al.] During this period ST worked out most of what is needed to do that transfer in at least one practical way and began work on ways to model the electron density during the simulation so that approximate DFT reactivity indices can be determined on the fly in the MD simulations.

In related work, a sabbatical visitor from an undergraduate campus of Penn State University, Brian Weiner, worked with ST on Density Functional Theory. As with Prof. Bartlett's DFT effort summarized above, the goal is to improve DFT calculations regarding chemical and physical realism particularly in reactive situations, and to raise the maximum number of particles treatable in a simulation. We are developing new, constructive methods for building approximate functionals for the time-dependent case [Weiner and Trickey]. Based on explicit symmetry operators for density operators, the method also can be applied to the time-dependent case. A three-part series of papers is being written [Weiner and Trickey]; the second part specifically displays the construction of new functionals.

A less widely used, but potentially valuable complement to DFT studies will be bona fide RHF (and ultimately correlated) calculations on these extended systems. To avoid ambiguity, we emphasize that these are not density-functional or approximate-exchange calculations, but are at the

same level that has become a standard for molecular calculations. We (FEH) are making progress in the following areas of this kind:

(a) Evaluation of exchange matrix elements

When electron repulsion matrix elements are calculated exactly using gaussian-type orbitals (GTO's) and Ewald-type convergence acceleration is used, there arise incomplete Bessel functions for which satisfactory numerical methods have not been fully developed. We have continued our work in this area, have found more efficient numerical procedures, and have corrected errors arising in earlier work in this area by other investigators. Our work during the current grant period has been submitted for publication (F. E. Harris, 2).

(b) 2D Brillouin-Zone integrations

One of the most demanding parts of RHF calculations on extended systems is integrating contributions of occupied energy bands (Brillouin-Zone integrations). Building on work in this area by the Amsterdam group and others, we have developed a completely analytical method for doing such integrations for two-dimensional bands (needed for surface systems) at a level where both the Fermi surface and the quantities to be integrated are described at a quadratic level of approximation. Others had already found that these integrations are done at greatly higher efficiency using quadratic, as opposed to linear interpolations, but the methods proposed for doing so were weakened and slowed down by the lack of analytical formulas. Our work in this area is reported [F. E. Harris, 3].

(c) Complete RHF calculations of polymer systems

This work does not directly solve problems addressed by this grant, because it deals with systems that are only extensive in one dimension. However, it is nonetheless relevant because it serves as a benchmark to show what can be expected from similar calculations on surface systems. We have found that careful theoretical and numerical work can make visible the properties of the density of states at the Fermi level at the RHF level, thereby providing a starting point for a rigorous analysis of the effects of electron correlation in extended systems. This is an ongoing effort, the portion of which done under grant auspices is reported [F. E. Harris, 1].

(d) Complete RHF calculations of surface systems

Work in this area directly relates to the grant objectives, as it supplements the ab initio work aimed at determination of optimum parametrization of approximation methods. In general it has been found that parameters optimum for molecular systems may not be the best choice in extended systems, and passing to the macroscopic limit is an important alternative to studying clusters of increasing size. During the grant period we have started the work needed to make good RHF calculations on surface systems. This work utilizes the progress we have described under item (b) above, and has reached the point where a preliminary report is in preparation [F. E. Harris, 4].

Our efforts in this area are designed to provide quantum-mechanical studies on surface systems which can supplement the ab initio work discussed in part A of this report. A necessary component of this work is the refinement of the methods to be used to increase their reliability and efficiency.

JD was on sabbatical this past year, but in his work two problems have been considered: 1) how to embed a quantum cluster in classical statistical mechanics, and related questions regarding effective classical potentials for molecular dynamics simulation; 2) the proper formulation of the local stress tensor for heterogeneous systems, particularly those with quantum clusters, and associated definition of elastic properties. Some results on these and related problems have been presented at conferences and colloquia listed above in Research Activities (J. Dufty).

Research Training:

This research project currently involves 12 graduate students and 6 postdoctoral associates. They are involved in all aspects of the programs, meetings and presenting joint seminars, participation and assistance in workshops and short courses, and in exchanging information between the various universities and partners involved. The scope of theory required for modeling materials should ensure that these students and postdocs are well trained in a variety of theoretical and computational approaches enhancing their future employment prospects.

Outreach Activities:

Besides the extensive research presentations at major meetings listed in Research Activities, our workshop On Scale-Parity Multi-Scale Simulations of Chemo-Mechanical Processes on February 25-27 communicated our objectives to the most relevant community and solicited their input. Also in the larger forum of the Sanibel meeting, where there are ~300 scientists in attendance, we reiterated our effort via presentations and via addressing the topic with several outstanding speakers.

The summer short course is also the first of its kind, in that we introduce undergraduate science majors to the spectrum of theory and computational tools that are being used in materials modeling, and that need to be improved.

So far we have only had two faculty members from an undergraduate school participate in the project, but with the help of the NSF's programs for undergraduate faculty, we expect to greatly increase this participation in the future. This will further disseminate our results to undergraduates and for use in their courses.

The Project Web page <http://www.qtp.ufl.edu/kdi> is described under the section on Publications and Products.

Journal Publications

- W. Cai, M.de Koning, V.V. Bulatov, S. Yip, "Minimizing Boundary Reflections in Coupled-Domain Simulations", *Physical Review Letter*, p. , vol. , (.) Accepted
- S. Subramanian, S. Yip, "Yield in Alpha-Quartz: Amorphous, Planar Microstructure Evolution", *Computational Materials Science, Special Issue devoted to the proceedings of the Symposium on Multi-Scale Materials Modeling, IUMRS-ICAM*, p. , vol. , (.) Accepted
- D. Liao, S. Yip, "Stress-Induced Structural Transitions in Alpha-Quartz", *Philosophical Magazine*, p. , vol. , (.) to be submitted
- Y.W. Hsiao, K. Runge, M.G. Cory, R.J. Bartlett, "Direct Molecular Dynamics Using Quantum Chemical Hamiltonians: C60 Impact on a Passive Surface", *Chem. Phys. Letters*, p. , vol. , (.) Submitted
- K. Runge, M.G. Cory, R. J. Bartlett, "The calculation of Thermal Rate Constants gas phase reactions; The Quasiclassical Flux-Flux Autocorrelation Function (QCFFAF) Approach", *Chem. Phys.*, p. , vol. , (.) Submitted
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- J.G. Fripiat, I. Flamant, F.E. Harris, and J. Delhalle, "Computational Aspects of Polymer Band Structure Calculations by the Fourier Space Restricted Hartree-Fock Method", *International Journal of Quantum Chemistry*, p. , vol. , (.) Accepted
- F.E. Harris, "On Kryachko's Formula for the leaky Aquifer Function", *International Journal of Quantum Chemistry*, p. , vol. , (.) Submitted
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- S. Sekusak, P. Piecuch, R.J. Bartlett, and M.G. Cory, "A General Reaction Path Dual-Level Direct Dynamics Calculation of the Reaction of Hydroxyl Radical with Dimethyl Sulfide", *Journal of Physical Chemistry*, p. , vol. , (.) Accepted

Books or Other One-time Publications

Web/Internet Sites

URL(s):

<http://www.qtp.ufl.edu/kdi>

Description:

The site was begun specifically to provide (a) communication about the award to the broader scientific community and (b) a means of efficient internal sharing among the geographically dispersed members of the KDI team. The site currently is undergoing substantial revision.

Other Specific Products

Product Type: INTERNAL REPORT on UML

Product Description:

INTERNAL REPORT (Supervised by Trickey after Zerner's Death)

'An Introduction to Object Oriented Programming for Computational Scientists: FORTRAN 90 and the Unified Modeling Language,' by Charles W. Martin and Dan W. De Kee. We developed this as a way of distilling the more important aspects of UML for design and construction of large, heterogeneous scientific codes. Development continues.

Sharing Information:

Our plan is to revise and extend this document into a primer on UML and its use in modern scientific computation; whether it will be published conventionally or on the web is not yet decided.

Contributions**Contributions within Discipline:**

- * We have demonstrated that simplified Hamiltonians can be created to retain most of the essential information obtained from high level ab initio quantum chemistry, especially for bond breaking. In this way, reliable potentials of interaction, which are the critical element in all simulations, can be greatly improved. These techniques can have a dramatic effect on materials modeling and their failures.
- * We have developed MD approaches using a variety of classical potentials (Stillinger-Weber, Born-Mayer, Van Beest et al, Tersoff, etc. to simulate the behavior of solids under stress. We have observed stress-induced fracture that closely simulates real systems in terms of surface roughness and strain rate dependence. We have developed an energy landscape approach with a promise for extremely high sensitivity to mechanical deformation.
- * We have discovered synergisms between application of chemical and localized mechanical stress to generate new nanometer surface modification and discovered that water-containing single inorganic crystals can produce exotic, self-organized surface structures of nanometer dimensions when exposed to electron beams and UV lasers. Both of these contributions have potential for generating nanostructures with unique optical, mechanical, and chemical properties.
- * We have suggested that our observed stress-strain response of alpha quartz accounts for the experimental observation of the hydrolytic weakening of quartz.

Contributions to Other Disciplines:

- * The potentials of interaction we are introducing, that combine accuracy with extreme efficiency, are equally critical to the description of large biological molecules, particularly when bonds are formed or broken. The current highly parameterized molecular mechanics type potentials as in AMBER, CHARMM, and other programs, cannot be used in bond breaking situations.
- * The energy landscape methodology is applicable to many disciplines. It has promise for simulations of diffusion and reaction processes.
- * Our observations on the hydrolytic weakening of quartz is pertinent to geophysical observations.

Contributions to Human Resource Development:

As discussed above, our project is a forum for educating undergraduate students in the wide range of computational and theoretical methods that are used in materials modeling. Participants in our summer course included a student from Florida A&M University, and we expect to maintain our strong association with this institution through both students and faculty, the latter participating in our research program for faculty from predominately undergraduate institutions. We have a similar association with Jackson State University.

In addition, our short course has generated lecture notes, laboratory exercises, and computer orientation manuals that we will disseminate to

interesting parties.

Workshop On Scale-Parity Multi-Scale Simulation of
Chemo-Mechanical Processes
Ponce de Leon Resort
St. Augustine, Florida

Schedule

Friday, February 25, 2000

9:00-10:45	Rod Bartlett Sam Trickey Noam Bernstein Thomas Beck Robin Selinger	Welcome Goals
10:45	Coffee Break	
11:15	Pierre Deymier Diana Farkas John Mintmire	
1:00-3:30	Lunch	
3:30-6:30	Joe Simmons Mike Marder Group Discussions	Overview
7:00	Dinner in the Club Room, Fairways Grill	
Saturday, February 26, 2000		
9:00-10:30	Group Discussions	
10:30-11:00	Coffee Break	
11:00-12:00	Group Representatives in Final	Discussion

List of Participants:

Farid Abraham, IBM Research Center
Janice Barner, University of Florida
Rodney J. Bartlett, University of Florida
Thomas Beck, University of Cincinnati
Noam Bernstein, Harvard University
Ariana Beste, University of Florida
Hai-Ping Cheng, University of Florida
L. Rene Corrales, Battelle, Pacific Northwest National Laboratory
Pierre Deymier, University of Arizona
James Dufty, University of Florida
Diana Farkas, Virginia Tech
Kim F. Ferris, Pacific Northwest National Laboratory
Yehiel Gotkis, LAM Research
Ireneusz Grabowski, University of Florida
Frank E. Harris, University of Florida
Thomas M. Henderson, University of Florida
So Hirata, University of Florida
Ya-Wen Hsiao, University of Florida

Kenneth Jackson, University of Arizona
 Anatoli Korkin, Motorola, Inc.
 Michael Marder, University of Texas, Austin
 John W. Mintmire, Naval Research Laboratory
 Ajith S. Perera, University of Florida
 Simon Phillpot, Argonne National Laboratory
 Jeffrey Rickman, Lehigh University
 Keith Runge, University of Florida
 James Rustad, Batelle, Pacific Northwest National Laboratory
 Hideo Sekino, Nonlinear Technology
 Robin Selinger, Catholic University
 Joseph Simmons, University of Florida
 Carlos E. Taylor, University of Florida
 Motoi Tobita, University of Florida
 Samuel B. Trickey, University of Florida
 Peter L. Ventzek, Motorola, Inc.
 Sidney Yip, Massachusetts Institute of Technology

KDI Summer 2000 Program for Undergraduate Students

June 8: Materials Problems: The Role of Computer Models
 Joseph Simmons, University of Florida

June 13: Quantum Chemistry I: What's It All About?
 Rodney J. Bartlett, University of Florida

June 15: Quantum Chemistry II: Wavefunction Methods
 Rodney J. Bartlett, University of Florida

June 19: Quantum Chemistry III: Density Functional Theory:
 an Alternative, Rodney J. Bartlett, University of
 Florida

June 21: Electronic Structure in Periodic Solids I
 Samuel B. Trickey, University of Florida

June 22: Electronic Structure in Periodic Solids II
 Samuel B. Trickey, University of Florida

June 27: Role of Symbolic Computing and FORTRAN-90 I
 Frank E. Harris, University of Florida

June 29: Role of Symbolic Computing and FORTRAN-90 II
 Frank E. Harris, University of Florida

July 4: HOLIDAY - NO CLASS

July 6: Role of Symbolic Computing and FORTRAN-90 III
 Frank E. Harris, University of Florida

July 11: Moving the Nuclei: Basics of Dynamical Simulations
 Samuel B. Trickey, University of Florida

July 12: Molecular Dynamics I
 Joseph Simmons, University of Florida

July 13: Molecular Dynamics II
 Joseph Simmons, University of Florida

July 14: Kinetic Monte Carlo;
Joseph Simmons, University of Florida

Participants included:

1. Willie Merrell - Junior in Physics at Florida A&M University
2. Joseph DuPuis - Senior in Fall, 2000 at the University of Florida
3. Michael VonNiederhausern - Junior in Fall, 2000 at the University of Florida
4. An Nguyen Le - Graduate of the University of Florida, Summer 2000
5. Todd McCaskey - Sophomore in Fall, 2000 at the University of Florida

In-House NSF/KDI Seminar Program:

July 18, 2000 - Saeid Davatolhagh, Ohio State University, 'Bond-Ordering Model for Glass Transition'

June 21, 2000 - Norbert Flocke, Texas A&M University, 'Hubbard and PPP Study of the Ground and Lowest Excited States of C60'

June 12, 2000 - Mahin Hammati, Arizona State University, 'Resolution of FeF₂ Viscosity Anomaly in Terms of Density Maxima and Other Water-like Features'

April 27, 2000 - Joe Simmons, 'Structure vs. Reactivity in Simulations of SiO₂'

April 6, 2000 - Michael Pykhtin, 'Density Functional Theory of Dynamical Processes at Surfaces with Novel Geometries'

March 28, 2000 - Maohua Du, 'BOMD Simulation of SiO₂ Clusters with Water'

March 9, 2000 - Round Table on 'Test Cases for Transfer Hamiltonians and Consequent Parameterization of Potentials'

February 3, 2000 - Dominic Alfonso, PNNL, 'Applications of Empirical-based Molecular Dynamics, Tight-binding and Periodic DFT Methods to Properties of Technologically Important Materials'

January 25, 2000 - Chuck Martin, 'Object-oriented Programming in FORTRAN 95 and the Universal Modeling Language - IV'

January 14, 2000 - Sam Trickey, 'Toward Inclusion of Reactivity in Potentials-The Streitz-Mintmire Approach'

January 13, 2000 - 'Chuck Martin, 'Object-oriented Programming in FORTRAN 95 and the Universal Modeling Language - III'

January 6, 2000 - Jan Broeckhove, University of Antwerp, 'Object-oriented Programming in FORTRAN 95 and the Universal Modeling Language - II'

December 30, 1999 - Jan Broeckhove, University of Antwerp, 'Object-oriented Programming in FORTRAN 95 and the Universal Modeling Language - I'

December 10, 1999 - Hai-Ping Cheng, 'Survey of Modern Simulation Methods - III'

November 19, 1999 - Hai-Ping Cheng, 'Survey of Modern Simulation Methods - II'

November 12, 1999 - Tom Swiler, Advance Materials Lab, University of New Mexico, 'MD Simulations of Reactive Wetting of Metal Ceramics'

November 5, 1999 - Hai-Ping Cheng, 'Survey of Modern Simulation Methods - I'

Contributions to Science and Technology Infrastructure:

* The primary resource we are developing is unified software that permits all aspects of materials modeling to be done conveniently. The development of such software was the primary recommendation of our Workshop in February, since at this time, the introduction of each new interatomic potential into a simulation is a major undertaking, prohibiting the ease of exchange of such potentials to move toward predictive methods.

Beyond Science and Engineering:

* In the longer term, the software developed in this project might have a commercial role.

Special Requirements

Special reporting requirements: None

Change in Objectives or Scope: None

Unobligated funds: less than 20 percent of current funds

Animal, Human Subjects, Biohazards: None

Categories for which nothing is reported:

Any Book

THOMAS DICKINSON'S INVITED PRESENTATIONS:

October 1999 - "Laser Materials Studies of Ionic Compounds," Washington State University

October 1999 - "The Origin of Localized Laser Induced Plasma Formation on Single Crystal Ionic Solids," FACSS International Meeting, Vancouver B.C.

January 2000 – “Synergisms of Laser Irradiation, Electron Beams, and/or Mechanical Stimulation,” SPIE Conference, San Jose, CA

February 2000 – “Corrosive Nano-Tribology: Generation of Atomically Flat Surfaces with an AFM in Controlled Solutions,” Washington Sec. Am. Ceramics Soc., Richland

February 2000 – “Nanometer Scale Environmentally Driven Fracture at Interfaces,” Adhesion Society Annual Meeting

February 2000 – “The Role of Defects in Laser Desorption and Ablation from Dielectrics,” NIF-LLNL

March 2000 – “Fundamental Studies of Laser Desorption and Ablation from Modified Surfaces of Ionic Single Crystals,” APS Meeting, Minneapolis, MN

April 2000 – “The Role of Surface and Near Surface Defects in Laser Desorption,” Keynote Lecture, International conference on Defects in Insulating Materials, Johannesburg, South Africa

April 2000 – “The “one-Two Punch” Approach to Laser materials Interactions with Transparent Materials,” MRS Spring Meeting, San Francisco, CA

JAMES T. DUFTY'S INVITED PRESENTATIONS:

May 2000 – “Fundamental Studies of Laser Desorption and Ablation from Modified Surfaces of Ionic Single Crystals,” Foundation for Research and Technology-Hellas (FORTH), Heraklion, Crete, Greece

July 2000 – “Nanometer Scale Studies of Wear, Re-growth, and Asperity-asperity Interactions in Aggressive Solutions on single Crystal Surfaces,” Gordon Conference on Tribology

KENNETH JACKSON'S INVITED PRESENTATIONS:

July 1999 – “Atomic Scale Crystal Growth Processes,” Korean Association for Crystal Growth, Seoul, Korea

August 1999 – “Monte Carlo Modeling of Crystal Growth Processes,” ACCGE Conference, Tucson, AZ

June 2000 – “Non-Equilibrium Phase Transformations,” Microgravity Materials Science Conference, Huntsville, AL

July 2000 – “CMC Packaging for Microelectronics,” Taiyo Yuden Seminar, Takasaki, Japan

August 2000 – “Optical Communication Systems,” ACCGE Conference, Vail, CO

SIDNEY YIP’S INVITED PRESENTATIONS:

February 2000 – “Atomistic View of Mechanical Behavior of Crystals: Strength, Deformation, Toughness,” Sanibel Symposium, St. Augustine, FL

June 2000 – “Toward Understanding Strength,” Computational Materials Science Network Workshop, Argonne National Laboratory

August 2000 – “Atomistic Modeling of Mechanical Behavior of Materials,” Symposium of Multi-Scale Simulations: Mechanics of Materials from the Nano-to the Meso-Scale, International Conference on Engineering Science, Anaheim, CA

FIGURE CAPTIONS

Figure 1: Snap shot at time = 8200 au, TB Hamiltonian, 300 eV

Figure 2: Snap shot at time = 8200 au, AM1 Hamiltonian, 300 eV

Figure 3: Snap shot at time = 8200 au, PM3 Hamiltonian, 300 eV

Figure 4: Snap shot at time = 8200 au, MNDO Hamiltonian, 300 eV

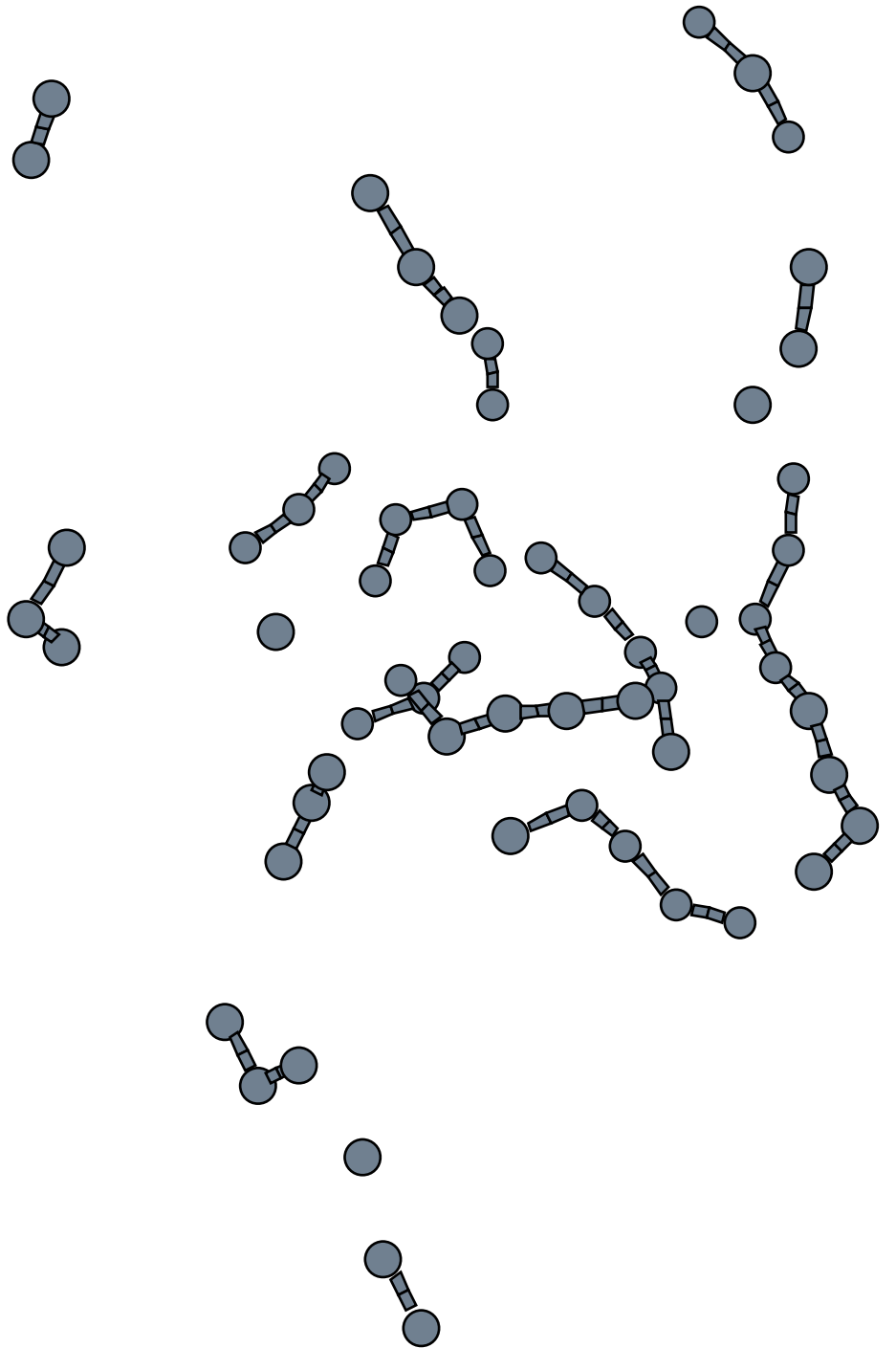
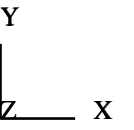
Figure 5: Snap shot at time = 8200 au, INDO Hamiltonian, 300 eV

Figure 6: QCFFAF predicted rate constants for OH abstraction of H from ethane

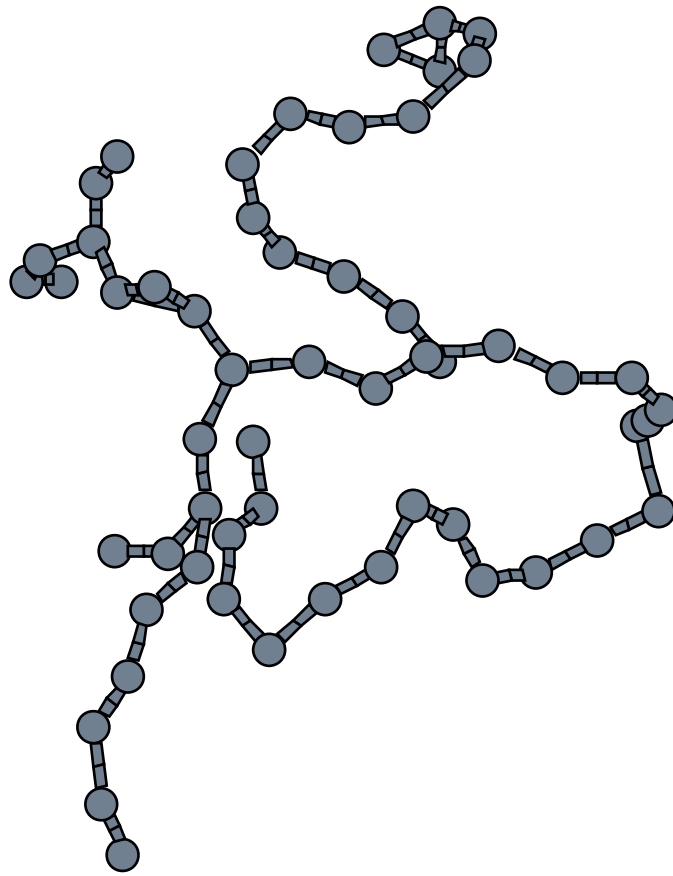
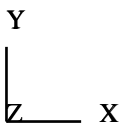
Figure 7: QCFFAF predicted rate constants for OH abstraction of H from chloroethane

Figure 8: QCFFAF predicted rate constants for OH abstraction of H from fluoroethane

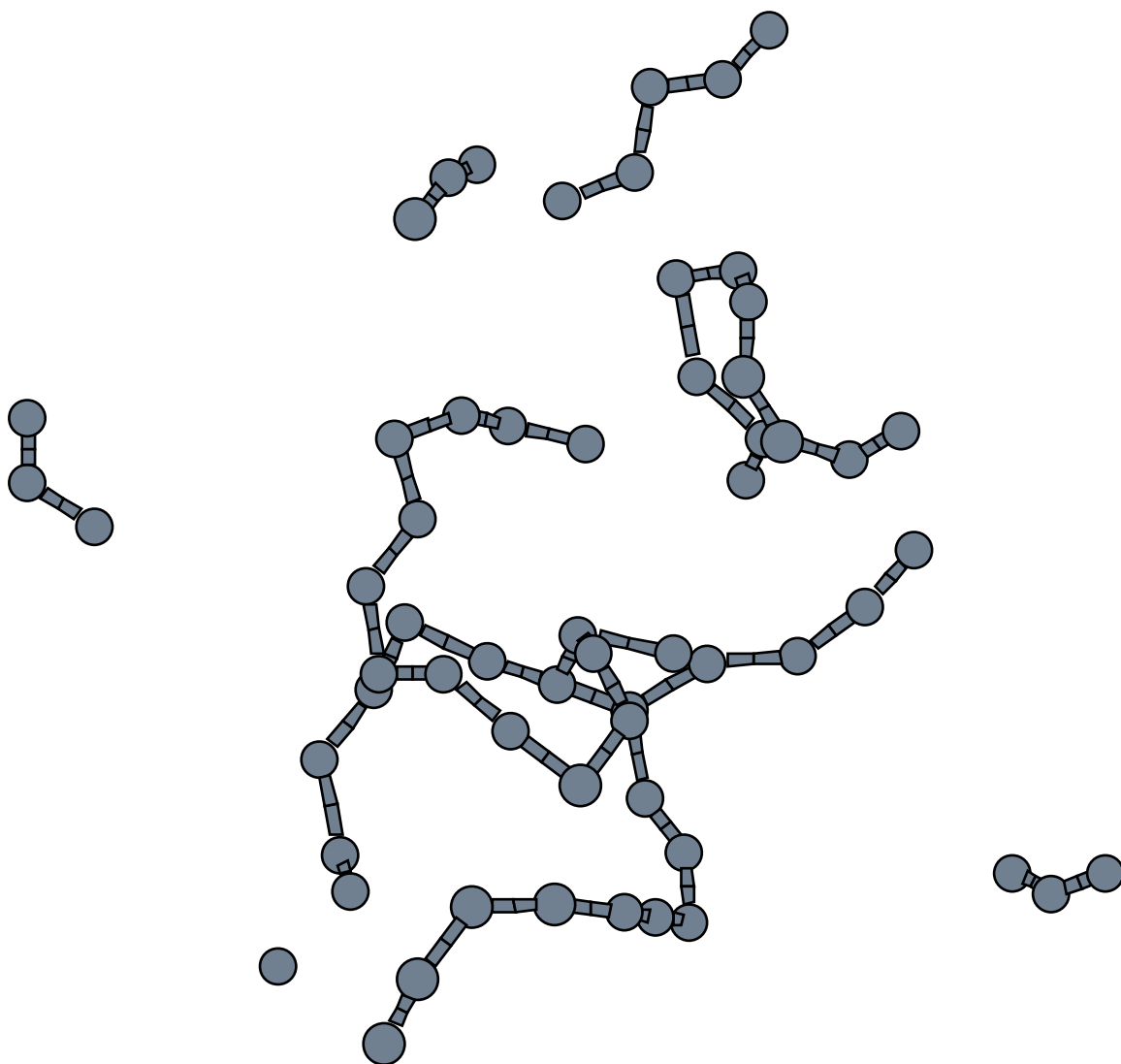
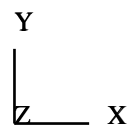
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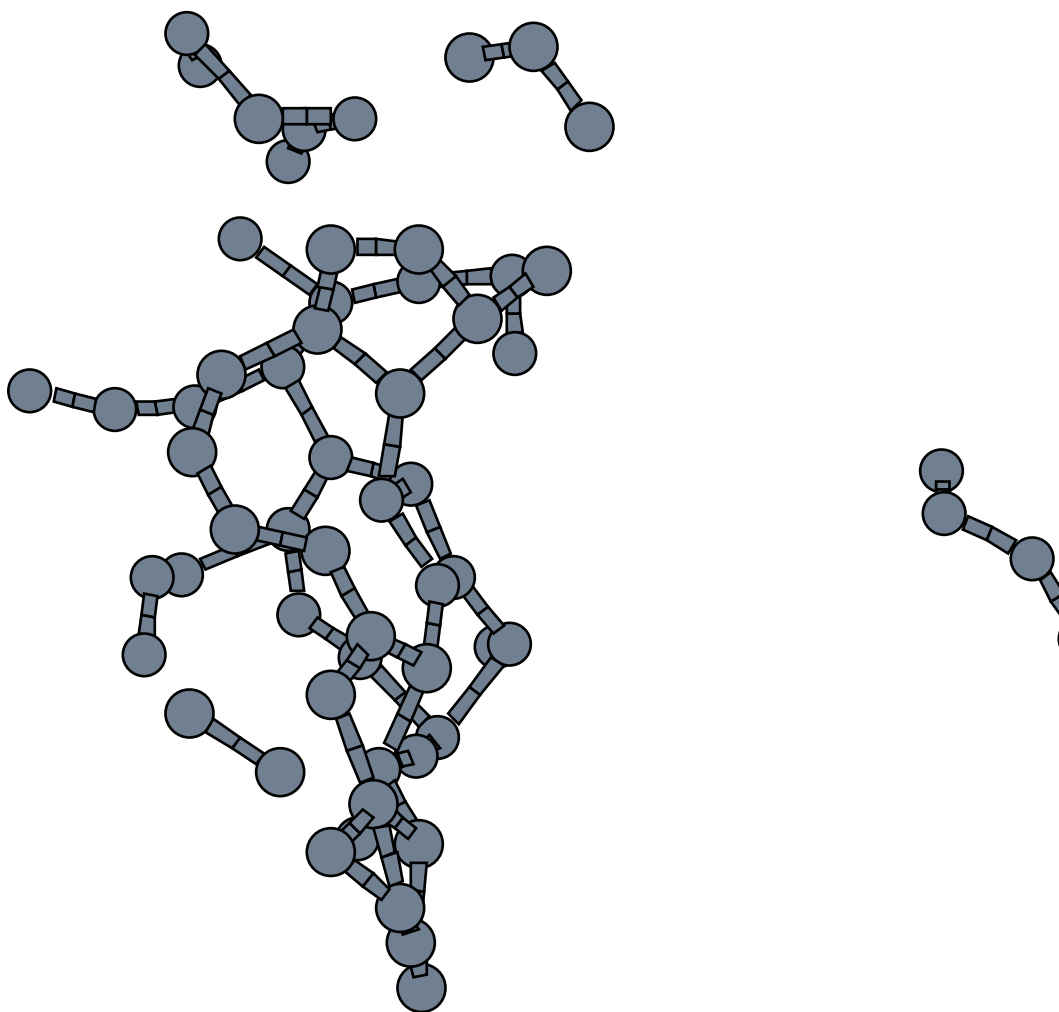
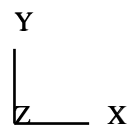
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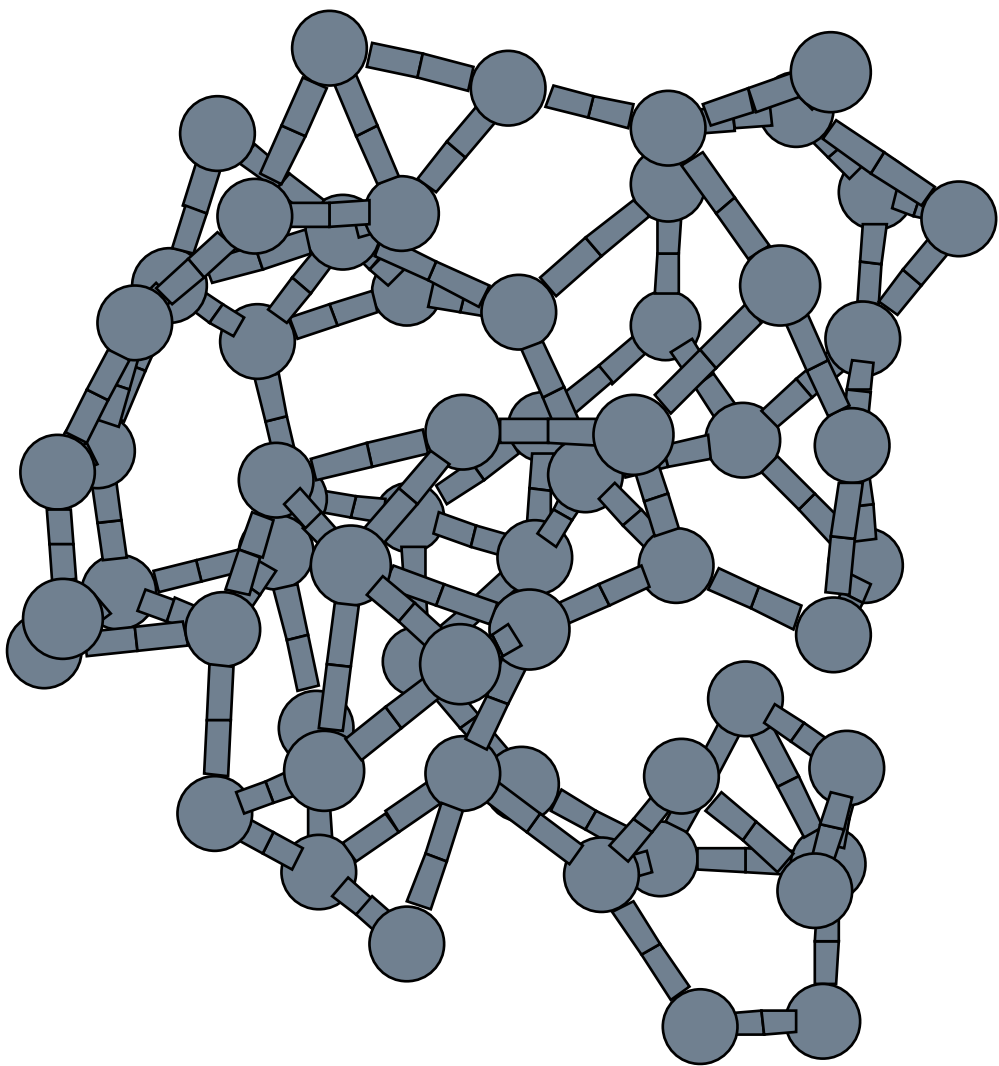
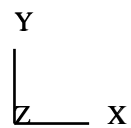
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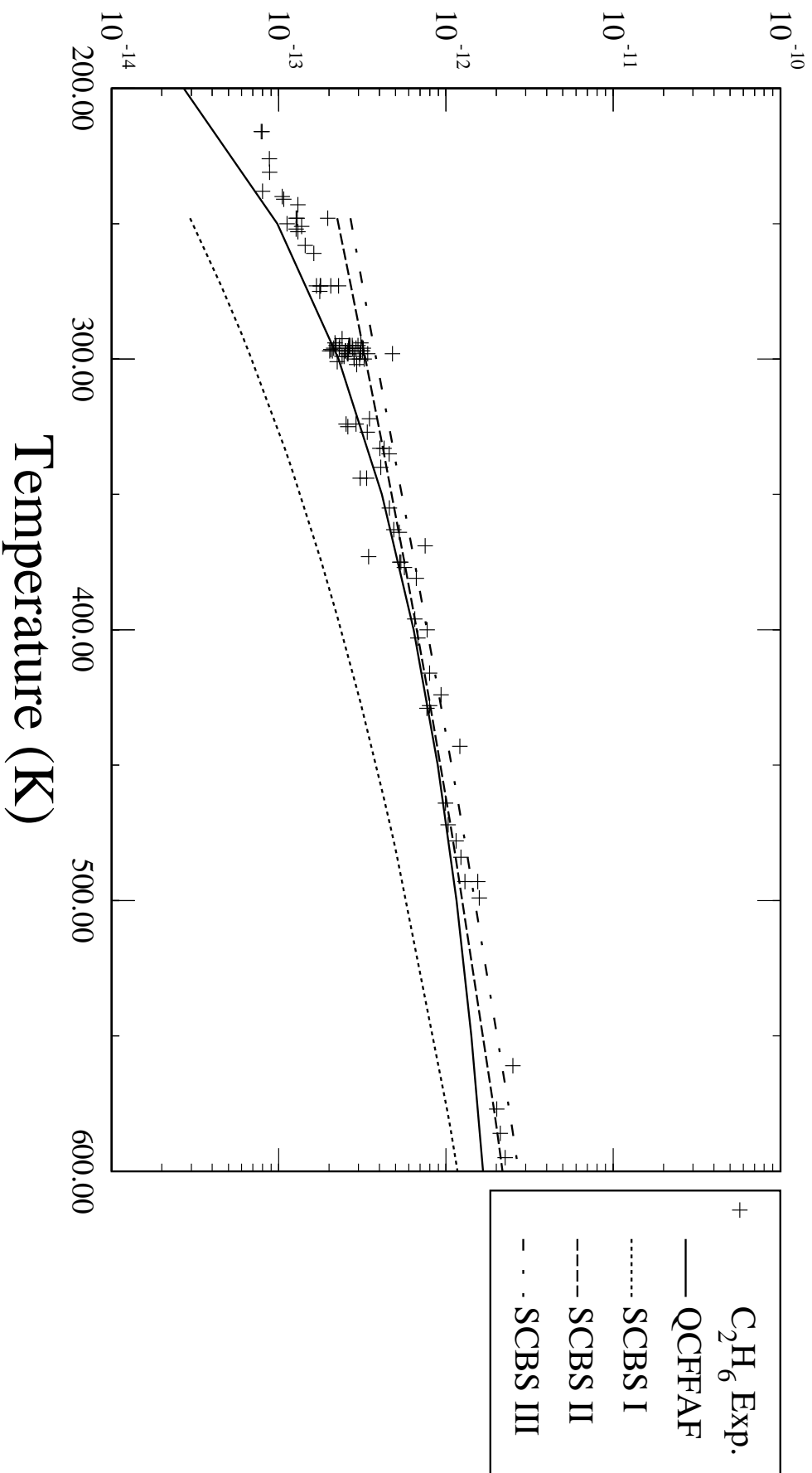
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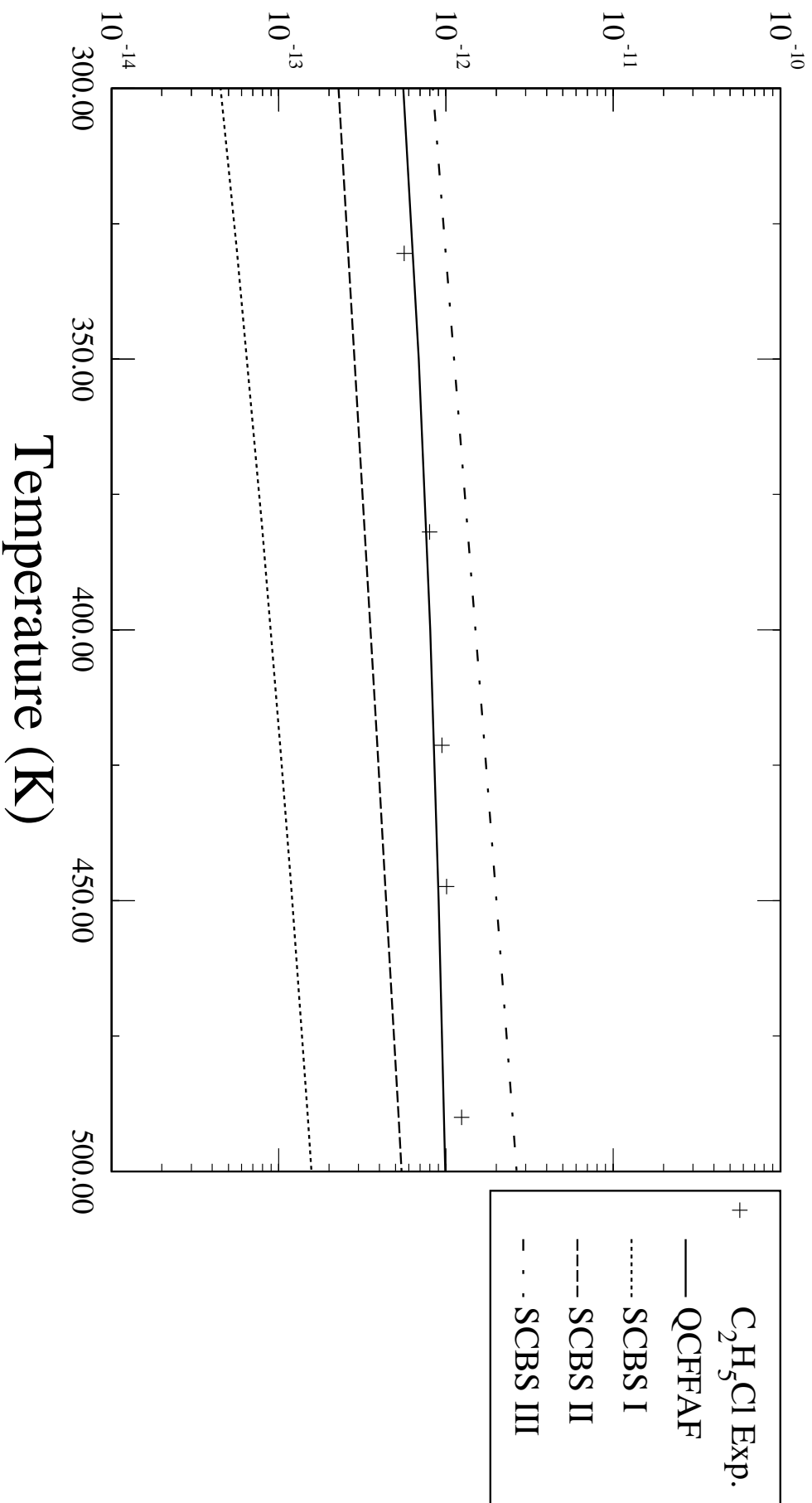
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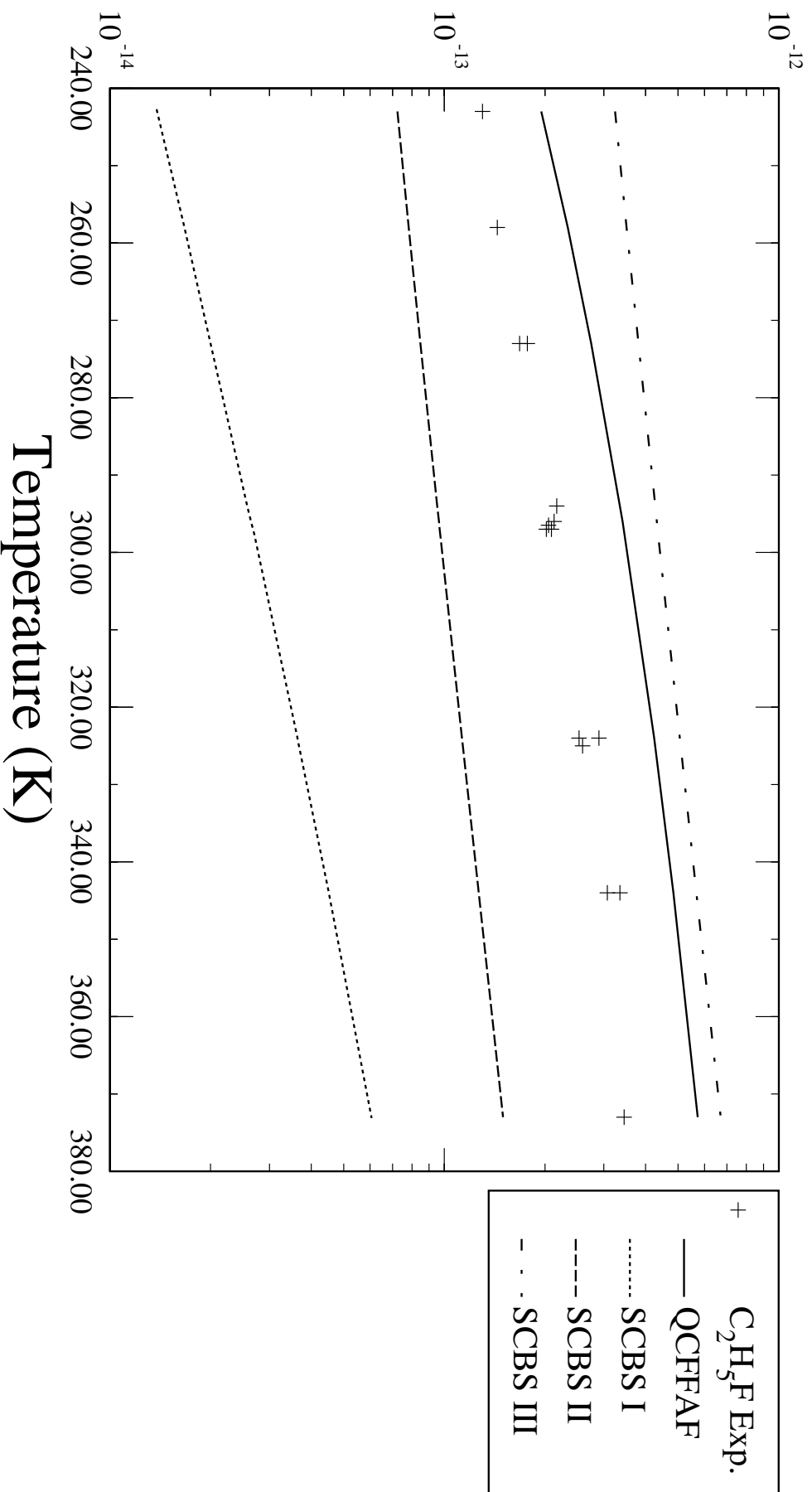
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Rate Constant



D. KINETIC MONTE CARLO (K. Jackson)

During the first year we have been adapting our Kinetic Monte Carlo code to explore the formation of dislocation etch pits. The primary issue to be addressed is the relative roles in the formation of etch pits of the crystal structure around the dislocation and the stress field around the dislocation. The discontinuity in the crystal structure created by the dislocation is responsible for enhanced crystal growth on surfaces where the rate of nucleation of new layers is slow. Similarly, some dislocation etch pits exhibit strong crystallographic features, suggesting that this is the dominant mechanism. Other dislocation etch pits, such as those formed on silicon using a Sirtl etch, are rounded, and exhibit no crystallographic features, suggesting that the selective etching in this case is due the strain field around the dislocation. We have been modifying our Monte Carlo computer code to incorporate both of these effects. The input stress fields around the dislocation will be coupled to calculations of the dependence of the sensitivity of bonds to chemical attack, which is derived from quantum calculations. Our Monte Carlo code incorporates the availability of the etchant at the defect in the fluid phase, the variations in the stress field around the dislocation, and the geometry of the crystal structure at the dislocation. The separate effects of the strain field and geometry will be isolated using simulations in which either or both of these effects are present.

E. FINITE ELEMENT THEORY (S. Yip)

The main objective of this work is the formulation of an overall framework for the multi-scale simulation of mechanical behavior of covalent and ionic solids under conditions far from equilibrium-large-strain deformation and/or elevated temperatures.

A general problem in the domain decomposition approach to modeling discrete systems with localized inhomogeneities (crystal defects) is the spurious reflection of elastic waves due to a change in system description across a domain boundary. Such effects are seen, for example, in the atomistic modeling of dislocation motion, crack propagation, and energetic particle-solid collisions; they are also of concern in the development of hybrid techniques involving multiple length and/or time scales. Coupling schemes or boundary conditions have been proposed, mostly in the form of ad hoc viscous damping. To date, however, none can claim to be free from empiricism and the attendant limitation on general applicability. We have formulated a time-dependent boundary condition coupling an atomistic simulation system to linear surroundings such that reflection of elastic waves across the boundary is minimized. Inter-domain interactions expressed in terms of memory kernel functions within linear response theory are treated in a natural dynamical manner, albeit numerically. This approach promises to provide an effective link between molecular dynamics simulations and finite-element calculations in the context of applications relevant to the KDI project [CIA, et al].

F. SOFTWARE (F.E. Harris, S. Trickey, M. Zerner)

Over the report period, we undertook an intense study of the use of Universal Modeling Language to drive the development and integration of complex software. An internal review paper (Martin & DeKee) that focused on UML in the context of Fortran 90/95

was developed and a prototype full-configuration-interaction code written as a test of the concepts. The code development halted with the death of Prof. Zerner and the subsequent departure of the student and postdoc who were involved. Pursuit of UML as a major tool for integrating the disparate software continues.

G. EXPERIMENT (T. Dickinson)

We (TD) have focused on the following two areas of research: 1) Fundamental experimental studies of the consequences of the combined application of mechanical and chemical stimulation to materials. In the first, in several mechanical wear situations, e.g., in chemical mechanical polishing of substrates, a surface experiences simultaneous tribological loading and chemical exposure. The combination can greatly increase wear rates. We examine the nanometer scale tribo-chemical wear of model single crystal surfaces in carefully buffered aqueous solutions mechanically stimulated by the tip of a Scanning Force Microscope (SFM)[Dawes, et. al]. Quantitative data on nanometer-scale wear of single atomic layer steps are readily obtained. Stress-enhanced dissolution of steps is readily observed along distinct crystallographic directions with striking differences in rate and highly non-linear dependence on contact force. This enables us to develop mechanisms for the corrosive wear and the vulnerability of steps in terms of the bonding along these particular steps. Exploiting this effect, we produce atomically flat surfaces many microns in dimension and generate nanometer-sized structures. We also examine tip-manipulated redeposition of material on surfaces where, for example, atomic dimension 'pits' can be refilled, again forming atomically flat surfaces. We use SFM as a means of detaching nanometer sized particles that strongly adhere to flat substrates using again simultaneous exposure to stress and 'corrosive vapor' (water), to study slow crack propagation on the nanometer size scale. This work relates directly to the modeling efforts by J. Simmons and Sidney Yip for slow crack growth in glass. [Hariadi, et.]. Finally, extensions to polymers that are simultaneously exposed to solvents and mechanical stimulation, results in localized nanometer scale swelling of the polymer. Together these processes are seen as potentially useful low temperature, low energy routes to nanometer scale modification of surfaces; and 2) The use of lasers and electron beams to modify surfaces of inorganic single crystals and polymer surfaces in the presence of water or solvents [Ibsen, et. al]. In the second area, we have discovered a synergism that generates very unique structures, often nanometer size scales, due to combined heating and induced bond breaking from the applied radiation. The liquids provide a means for ion and molecular mobility that greatly enhances modification. Modeling techniques that others are in the project are developing involving stress and chemical attack may be applicable to the phenomena we are observing here [Bandis, et. al].

In the coming year the plan is to extend experiments in both these areas applying additional instrumentation to reveal more details of the appropriate mechanisms. We will pursue, in single crystal growth, the use of tip oscillations as a means of stimulating localized growth of 3-dimensional structures. The materials of interest include a number

of bio-related materials such as Ca-phosphates and polymers such as PMMA, PS, and PC. Stimulating materials with lasers while under solutions will be pursued to determine if unique synergistic interactions can be generated. There are close ties with theory and modeling pursued through scheduled visits between institutions. Collaborators, in addition to Simmons and Yip, include Jim Rustad and Rene Corales at PNNL.