Summary of Original Proposal

Multi-scale Simulation Including Chemical Reactivity in Materials Behavior through Integrated Computational Hierarchies

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BACKGROUND - NSF PROGRAM OBJECTIVES

The Program Announcement emphasized "knowledge and distributed intelligence" as a specific research synthesis. KDI research is to achieve major new capability for generation, modelling, representation, and presentation of information and underlying data on highly complex systems that involve enormous ranges of scales in their critical parameters. Cross-disciplinarity is essential. So are conscious, deliberate efforts to convert huge bodies of data into useful information.

This project is in the "New Computational Challenges" (NCC) focal area. [The other two areas are "Knowledge Networking" (KN), and "Learning and Intelligent Systems" (LIS).] NCC projects are to investigate the tools for discovery, modeling, simulation, prediction, and understanding of behavior of complex systems. Presumed in these aims is the need for substantive advances in hardware and software to do three things: handle complexity and scale, facilitate geographically dispersed collaboration, and support real-time interaction and control with the target systems.

THE OPPORTUNITY

The science of advanced materials stands at a crossroads in the journey toward true computational prediction of materials behavior. Progress in simulations, quantum chemistry, and surface science as well as in computer power, parallel processing architecture and programming, and software object

management is obvious. Accurate quantum theoretical treatments of chemical effects are possible for many molecules, slabs, and surfaces. Realistic simulations of mechanical properties of materials systems are growing in effectiveness.

Participants in this project are among the leaders in many of these developments. Even though several have a remarkable amount of linkage via Quantum Theory Project, a key link was missing. The advances remain largely unconnected. Predictions of complex macroscopic processes in technologically relevant realistic systems "from the atoms up" are stil rare. More specifically, essentially *nothing* has been done to link chemistry and mechanical simulations at the level essential for predicting and controlling chemical-mechanical phenomena.

An example of the opportunity is in the 10 May 1999 issue of Physical Review Letters [1]: those authors state that conventional interatomic potentials cannot reconcile their experiments and computer simulations of crack propagation in Silicon. The reason is clear. Cracks and similar mechanical phenomena rarely occur in vacuuo. In realistic situations reactants are present. As fresh material is opened by the crack, chemical reactions occur, modifying the energetics, rates, and morphologies.

TARGET PROBLEM

The UF program aims to develop computational methodology to predict and describe chemical-mechanical behavior of real materials. Such behavior depends upon the simultaneous presence of both strain and chemical reactivity. These processes are the basis for [2]

- slow or sub-critical crack growth in solids,
- stress corrosion,
- static and cyclic fatigue,
- chemical-mechanical polishing, and
- selective etching or nano-machining.

Today the construction, electronics, optics, and transportation industries are not only plagued by but also exploit the acceleration of chemical activity via the imposition of stress. The troublesome aspect is exemplified by premature component failure. The beneficial aspect is found in processing techniques to produce critical surfaces.

These effects result from the synergistic action of high strain and chemical reactivity on material surfaces. Simulation of such processes demands the development of a methodology for reliable treatment of both chemical reactivity (including solvents and contaminants) and mechanical strain to fracture. The studies must use a large ensemble of particles while accounting for large departures of individual atoms from both mechanical and chemical equilibrium. Quantum chemistry, surface electronic structure, and ensemble simulations of mechanics must be integrated simultaneously.

RESEARCH STRATEGY

Achieving realistic, useful combinations of quantum chemistry and surface physics with mechanics therefore is the program objective. Simulations involving many length scales ("multi-scale simulation") will result naturally from the research. Such simulations in and of themselves are not new [3, 4, 5, 6, 7, 8, 9] and there is already a KDI group at Cornell University with this task [10].

It is not obvious how to do such multi-scale simulations including atomic-scale chemical effects. Standard quantum-chemical calculations are too slow to be incorporated unaltered. Most efforts

to date have been limited to such electronic structure methods to calculate potential functions for atomic-level ensemble methods. The novel feature in the UF program is the reach downward to the length scales of chemical reactivity and quantum mechanics. This will involve meshing ab-initio quantum chemistry and surface science methods with ensemble simulations and micro-mechanics via so-called Transfer Hamiltonians. Unlike schemes that use quantum mechanics for improved potentials in the simulations, the objective is to use the full potency of the quantum mechanical methods to extract chemical reactivity, reaction energies and paths, and chemical reaction rates for highly strained systems with a solvent. It is both a more difficult goal and an inescapable one.

Three major components characterize the strategy.

1. Construct computational methods that integrate:
   (a) first-principles, quantum mechanical calculations of electronic states of molecules and extended systems;
   (b) large scale ensemble calculations for the dynamical behavior of molecules and clusters;
   (c) dynamical calculations of highly strained macroscopic structures.
2. Combine these multi-scale simulations of chemically sensitive materials with critical experimental data that verify:
   (a) performance;
   (b) validity;
   (c) robustness and scope.
3. Develop and implement software technologies that manage information flow among assemblies of large, disparate computer programs without significant hands-on manipulation.

The theoretical and computational tools required to initiate simulations of materials that incorporate the essential effects of chemistry will be applied to three prototypical systems. One will be brittle fracture of SiO_2, exacerbated by the influence of solvents. Another will be chemical polishing of surfaces, in which chemical reactions and solvent effects both need to be described. A third will consider dislocations emitted in Silicon. Unlike the two other applications, this one requires the introduction of excited state potential energy surfaces.

EXPECTED OUTCOMES

Successful completion will result in computational methodology and software that can uniquely describe chemically mediated and strain-enhanced processes in materials. The ability to model such complicated phenomena reliably has enormous economic implications. These pertain to the aging of materials, the effects of air on sensitive electronic components, the breakdown of semiconductors, and a wealth of other applications. What is standing in the way is the inability to couple chemistry, as described by theoretical/computational chemistry methods, to the more macroscopic scales of brittle fracture and related events. This program promises to alleviate that severe limitation of simulation methods.

Explicit education and outreach goals are included. The post-doctoral associates trained in the program will be disseminators of the methodology and program directions to other institutions. Graduate students will be trained in the fully integrated program. Workshops and short courses will be used to form the nucleus of a distributed computational center in which many investigators share resources, methodologies and results, through open access to programs, computers and the exchange of post-doctoral fellows and students. New courses and content will be designed that treat both the individual methods and the integrated approach developed.

RESEARCH TEAM

The team spans four universities, six departments, and two companies, centered at the Quantum Theory Project of the University of Florida. The team includes experts in all computational scales, from the submicroscopic quantum mechanical scale at the core of the analysis, to continuum descriptions. We also include an experimental component to provide the kind of unambiguous, incisive experiments that challenge and verify theory.

Project direction is by Rod Bartlett as PI, assisted by co-PI's Joe Simmons, H-P. Cheng, Sam Trickey, and Mike Zerner. The other senior personnel are Jim Dufty, Frank Harris, T.J. Dickinson, K.A. Jackson, and S. Yip (MIT). ACES-QC staff Marshall Cory and Keith Runge also will assist as will Neil Ostlund of HYPERCUBE. In addition, a long-standing relationship between the Quantum Theory Project and IBM has led to a partnership that will provide a significant upgrade of the computer facilities needed for this project through the IBM Shared University Research (SUR) program.

SUMMARY

Many tools are in place. The challenge has been issued: synthesize them into a comprehensive new tool. The future of predictive materials development depends upon combining the vastly different scales in simulations to respond to the details of the quantum mechanical description of the chemistry. Success will yield dramatic advances in the science of materials.

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