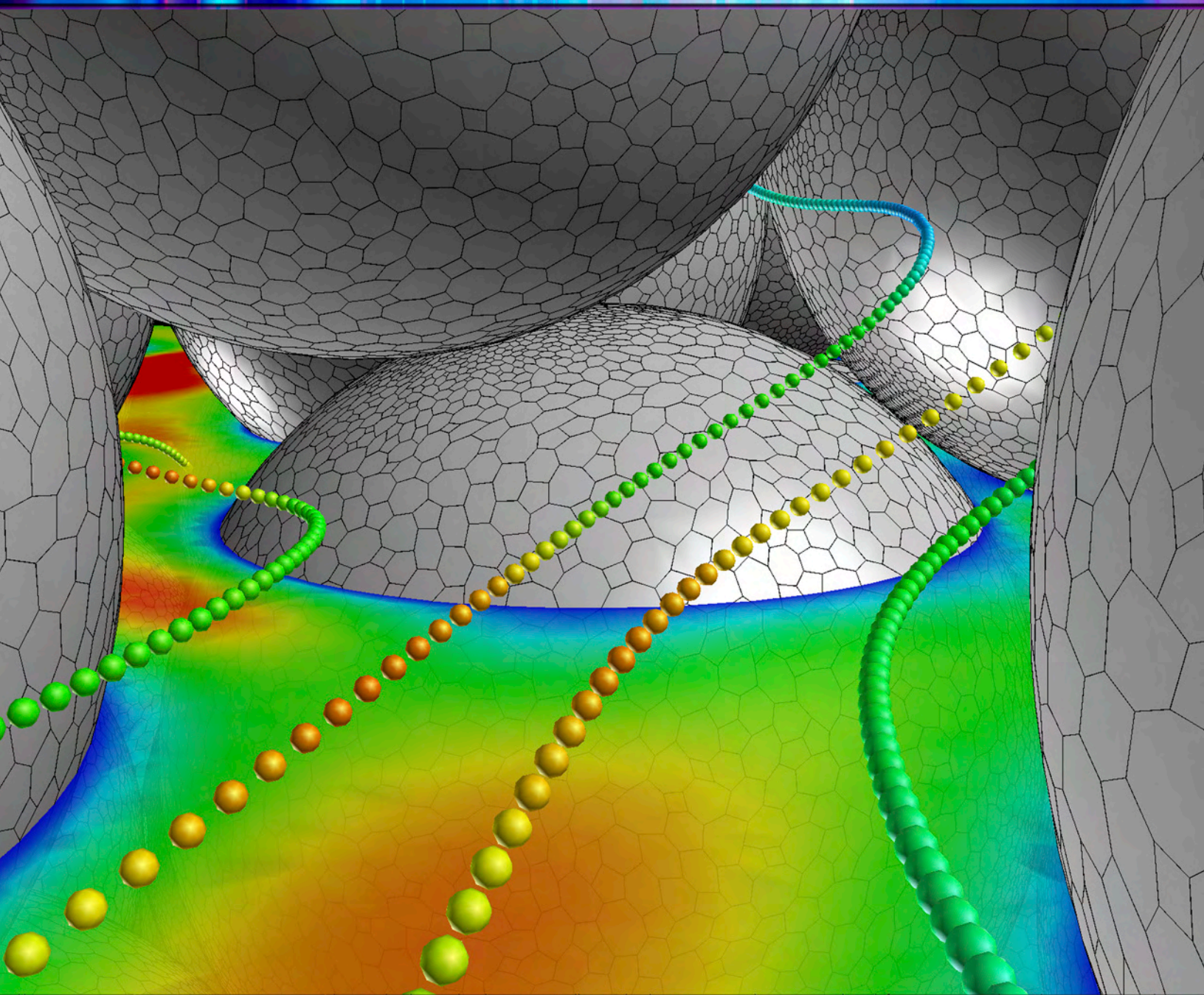


# SCIENTIFIC IMPACTS AND OPPORTUNITIES FOR COMPUTING

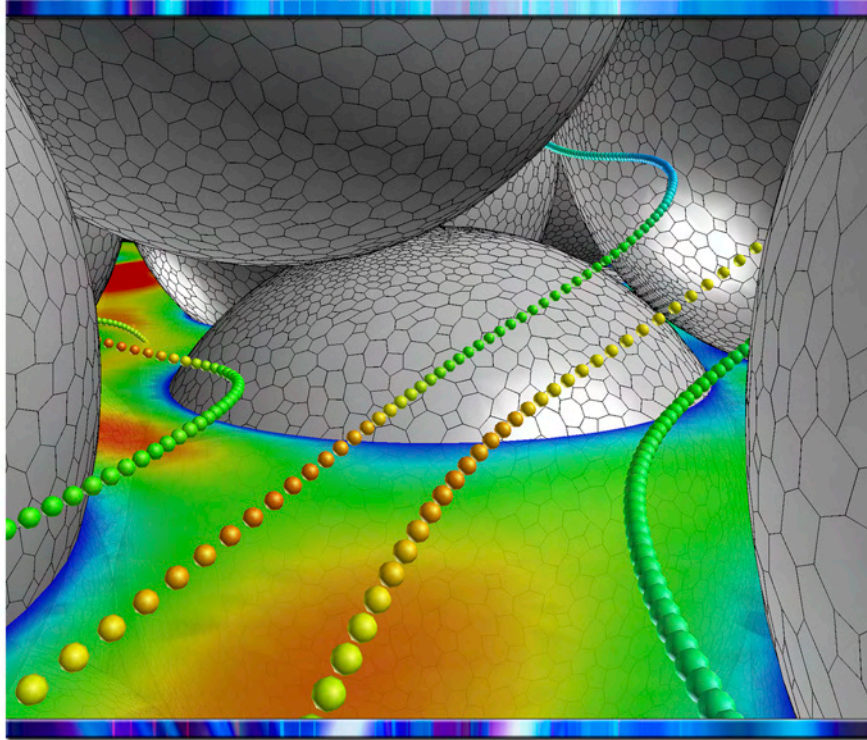


  
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On the cover:



*Modeling Subsurface fluid flow: Simulated velocities (colors on 2D plane) and pathlines (colored small spheres) within a computed velocity field, based on finite volume simulation of fluid flow partial differential equations at the pore scale. The colors of the small spheres and coloration of the 2D velocity plane indicate the local velocity magnitude (red = high). The pore geometry is generated by randomly packing spheres (representing solid soil grains) of uniform size. The computational mesh on the solid grain surfaces is indicated by polygons on the surfaces. Courtesy of Tim Scheibe, PNNL Simulations, Cindy Rakowski; visualizations John Serkowski, PNNL. Research funded by U. S. Department of Energy, Office of Science, Environmental Remediation Sciences Program.*

Report of the workshop

# SCIENTIFIC IMPACTS AND OPPORTUNITIES FOR COMPUTING

January 9 -12, 2008

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# CONTENTS

Acknowledgements .....	ix
List of Figures .....	vii
Section 1: Introduction.....	1
Section 2: Theoretical and Computational Opportunities in Nanoscience .....	5
Section 3: Three Grand Challenge Studies in Superconductivity .....	11
Section 4: Combustion Modeling for Fuels and Engines .....	19
Section 5: Basic Research Needs for Electrical Energy Storage .....	29
Section 6: Five Research Needs in the Geosciences.....	37
Appendix A: Workshop Program and Agenda.....	43
Appendix B: Acronyms and Terminology .....	49
Appendix C: Workshop Attendees .....	57



# LIST OF FIGURES

## Nanoscience

- 2.1 Scaling of density functional calculations for ferromagnetic FePt nanoparticles.....5
- 2.2 Image illustrating a nanocatalysis problem.....7
- 2.3 Snapshot of a 10 ps molecular dynamics simulation of water molecules at a titanium dioxide surface. ....7
- 2.4 Comparison of experimental neutron scattering data for water on titania against data from molecular dynamics simulations.....7
- 2.5 Artist rendition of CBH I. ....9

## Superconductivity

- 3.1 Basic electronic structure of the cuprates mapped onto the Hubbard model.....12

## Combustion

- 4.1 Energy consumption by end use and relative use by end use from 1950 to 2005. ....19
- 4.2 Gasoline engines, diesel engines, and HCCI engines. ....20
- 4.3 Multiscale combustion simulation methods in practical combustors. ....21
- 4.4 Nanoparticle agglomeration in high temperature regimes.....23
- 4.5 Schematic of the chemical looping combustion process. ....23
- 4.6 Terascale DNS of a turbulent autoignitive hydrogen/air jet flame.....24
- 4.7 LES grid surface topology and injector dynamics in hydrogen-fueled IC engine.....25

## Energy Storage

- 5.1 A 3D self-assembled electrochemical cell structure. ....31
- 5.2 Solvated ion size in electrolytes from computer simulation. ....33
- 5.3 A single solvated ion in a slit pore between two graphene sheets. ....33

5.4 Snapshot of 1.6 M CaCl<sub>2</sub> solution in a slit pore between two graphene sheets.....33

5.5 An *ab initio* study of the growth of carbon nanotubes on iron. ....34

**Geosciences**

6.1 CSEM imaging offshore Brazil, to map subsurface hydrocarbons.....37

6.2 Modeling the Hanford 300 area .....40

6.3 A 3D computer simulation of lipopolysaccharides membranes .....41



# ACKNOWLEDGEMENTS

In October 2002, a DOE Basic Energy Sciences Advisory Committee workshop produced a foundational report, “Basic Research Needs to Assure a Secure Energy Future,” which outlined basic research needs for a reliable, economic, and environmentally sound energy supply for the future. Since then, a series of workshops have brought together the country’s leading research scientists to discuss and to define the fundamental Grand Challenges, Priority Research Directions and Cross-Cutting Issues in their respective fields, which must be pursued to advance disciplinary science, technology development, energy self sufficiency, and other societal needs.

In selecting the research science agenda for this workshop, “Scientific Impacts and Opportunities for Computing,” the organizers acknowledge the importance of these BES workshop reports, and their formative role in directing recent science research in areas of critical importance to the United States’ energy and environmental future.

The BES Workshop Reports formed the basis for discussions at the “Scientific Impacts and Opportunities for Computing” workshop, where participants described the computational efforts that would be needed to solve their science problems. The workshop focused on five areas of science, and on the representation of the problem sets in those areas where computing must play an important role.

The relevant BES Workshop Reports were: “Basic Energy Needs: Catalysis for Energy Applications,” held August 6-8, 2007; “Basic Research Needs for Clean and Efficient Combustion of 21st Century Transportation Fuels,” held October 29-November 1, 2006; “Basic Research Needs for Electrical Energy Storage,” held April 2-4, 2007; “Basic Research Needs for Geosciences: Facilitating 21st Century Energy Systems,” held February 21-23, 2007; “Basic Research Needs for Materials under Extreme Environments,” held June 11-13, 2007; and “Basic Research Needs for Superconductivity,” held May 8-10, 2006.

The reports are at <http://www.sc.doe.gov/bes/reports/list.html>.

This workshop was conducted for the Office of Advanced Scientific Computing Research to identify high impact opportunities in computing for investment in research to maintain the nation’s preeminence in scientific discovery and competitiveness. Acknowledgement is given to session chairs, invited speakers and participants for scientific foresight, lively discussion, and content. Workshop and proceedings coordinated by Debbie McCoy, website by Cindy Latham, editorial by Agatha Bardeel, and graphics design by Allison Gray, Oak Ridge National Laboratory.



# INTRODUCTION

As the world nears the end of the first decade of the 21st century, people have become increasingly conscious of challenges they face in energy self-sufficiency and in containing the environmental impact of our existing modes of life. Every country faces the same daunting task: how to meet energy needs for home, business and transportation, while at the same time reducing emissions of greenhouse gases to the atmosphere. Here in the U.S., research in the basic energy sciences is addressing these critical problems with new initiatives and new investments. The computing community is encouraged by a revolution in high-powered computing that is now nearing the petascale. A capability that until recently was beyond imagination is now poised to address the complexity of these critical energy problems. The Office of Science Advanced Scientific Computing Research (ASCR) facilities at Oak Ridge National Laboratory (ORNL), Argonne National Laboratory (ANL) and at the National Energy Research Science Center (NERSC) are now at advanced terascale capacity (trillions of computations per second), and anticipating petascale capability (quadrillions of computations) in the 2010-12 time frame.

To explore the potential that high-performance computing (HPC) will have to revolutionize key basic energy scientific research, the “Scientific Impacts and Opportunities for Computing” workshop met January 10-12, 2008. The workshop participants in five areas of basic energy research – nanoscience, superconductivity, combustion science, energy storage science and the geosciences – explored how the computing systems currently deployed can be used to advance the science in their key research domains. Looking to the future, participants explored how current systems with expected upgrades, and the two petaflops systems to be deployed by Department of Energy and National Science Foundation before the end of this decade, can most productively be used to create new scientific discoveries in these key energy research areas.

This report of the “Scientific Impacts and Opportunities for Computing” workshop describes some fundamental scientific and computational challenges associated with research programs in the five basic energy fields. The panelists and workshop participants were asked to identify and define a set of high-value, near-term (12-18 months) and 5-year-term R&D studies for each scientific domain, in which the supercomputing facilities now becoming available could solve problems of importance to secure the energy future, and to contribute to the long term interests of the U.S.

Five sessions were held, each with a presentation of the state of the science, followed by panel discussions in which individual researchers described how computationally intensive methods would help to elucidate their basic science problems, and assist them in working to solution. What emerged were specific, targeted proposals in fundamental research areas, which will further the energy research to meet present and future needs. These proposals are presented in this report.

## *1.1 NANOSCIENCE AND COMPUTING*

Nanoscience involves understanding and manipulating matter at length scales of the order of nanometers (1 billionth of a meter); nanotechnology involves controlling and exploiting the properties of materials that derive their properties and function from features at the nanoscale. Nanoscience is poised to make significant contributions to securing U.S. energy security, with the assistance of HPC to facilitate the simulation of fundamental processes. Many of the elementary steps of energy conversion (charge transfer, molecular rearrangement and chemical reactions) take place at the nanoscale. Thus, the development of new materials, as well as the methods to characterize, manipulate, and assemble them, creates an entirely new paradigm for developing new energy technologies. “The overlap of experimentally and computationally accessible length scales is a tremendous opportunity for science and technology,” said ORNL’s Paul Kent. “It would provide many opportunities to gain detailed knowledge of the dynamic processes at the nanoscale, moving in the direction of the designer materials.” To address the research potential, the DOE sponsored a Basic Energy Sciences (BES) workshop, “Basic Research Needs for Materials under Extreme Environments,” June 11-13, 2007. The BES workshop, “Basic Research Needs in Catalysis for Energy,” August 6-8, 2007, identified research opportunities for catalysis. Materials are central to every energy technology, and future energy technologies will place increasing demands on materials performance with respect to extremes in stress, strain, temperature, pressure, chemical reactivity, photon or radiation flux, and electric or magnetic fields. Operating conditions require new materials that can reliably withstand extreme thermal and pressure environments. To lower fuel consumption in transportation, future vehicles will demand lighter weight components with high strength. Next-generation nuclear fission reactors require materials capable of withstanding higher temperatures and higher radiation flux in highly corrosive environments, for long

periods of time without failure. In addition to assisting in the development of new materials, computer-assisted exploration of temperature-dependent free energy barriers in nanomagnets has immediate relevance to data storage applications. Computational simulations offer nanoscience research the *in-situ* environments which permit the observation of processes under conditions that replicate real-world/real-time conditions.

### 1.2 SUPERCONDUCTIVITY AND COMPUTING

Superconductivity offers powerful new opportunities for restoring the reliability of the power grid and increasing its capacity and efficiency. Superconductors are capable of carrying current without loss, making the parts of the grid they replace dramatically more efficient. In a world of global warming and energy shortages, coming to understand why superconducting materials transmit electricity without resistance and without loss, would open the door to new superconducting materials operating someday at room temperature. To address the research opportunities in this field, the DOE sponsored a BES workshop, “Basic Research Needs in Superconductivity,” May 8-10, 2006. The research being conducted today at the Oak Ridge Leadership Computing Facility seeks to understand how existing superconductors work at the atomic scale: why and at what temperatures they lose their resistance to electricity and become superconducting. Atomic level computer simulations have enabled researchers to study the Hubbard Model, a mathematical lattice of electrons on copper atoms, to determine how the electrons interact with each other as the metal becomes superconducting. It was found that the electrons pair, a phenomenon known as “Cooper pairing.” Further, progressively greater computational simulations now possible with increased computing capability have shown that the electron pair interaction is due to a magnetic interaction, or “spin fluctuations” on the copper oxide planes. Increasing the current-carrying capability of superconductors requires blocking the motion of “Abrikosov vortices,” tubes of magnetic flux, which form spontaneously inside superconductors upon exposure to magnetic fields. Ultimately, superconductivity is a nanoscale phenomenon. Its two composite building blocks — Cooper pairs characterizing the superconducting state and Abrikosov vortices controlling its current-carrying ability — have dimensions ranging from a tenth of a nanometer to a hundred nanometers. Their nanoscale interactions among themselves and with structures of comparable size determine all of their superconducting properties. Researchers can now use direct numerical simulation (DNS) to simulate superconducting phenomena in confined geometries, using computer clusters of a hundred or more nodes, to isolate the interaction of Cooper pairs and Abrikosov vortices with nanoscale boundaries and architectures. In this way they can come to understand these nanoscale interactions and eventually design

functional superconductors. The promise of nanoscale fabrication, characterization, and simulation for advancing the fundamental science of superconductivity and rational design of functional superconducting materials for next-generation grid technology has never been higher.

### 1.3 COMBUSTION AND COMPUTING

Transportation fuels for automobile, truck, and aircraft engines are currently produced by refining petroleum-based crude oil, but as the supply of this commodity continues to decline, new fuels, and new engines in which they can be efficiently combusted, must be found and developed. Both fuel and engine technologies must be advanced. As the BES Workshop “Basic Research Needs for Clean and Efficient Combustion of 21st Century Transportation Fuels” reported, research scientists in combustion-related studies face the challenge ultimately of developing “a validated, predictive, multiscale, combustion modeling capability to optimize the design and operation of evolving fuels in advanced engines for transportation applications.” High performance computing will play a central role in the development of multiscale combustion modeling, by considering the full range of scales from quantum up to continuum macroscale. In this new paradigm, direct simulations over several decades of scales will be performed on petascale computers, to provide detailed scientific understanding; and models that encapsulate the understanding will be developed to bridge the different ranges of scales. The objective is to provide quantitative physical understanding of the underlying issues of aromatic chemistry and soot nanoparticle growth and oxidation, heterogenous reactive multiphase flow, and turbulence-chemistry interactions under low temperature, high-pressure environments for diverse fuels. Existing fuels are major pollutants when they burn in an engine, and the underlying mechanism for inception, growth and oxidation of soot emissions is poorly understood. Qualitative understanding of underlying nanoparticle soot processes will allow better strategies for control. At the molecular and quantum scale, novel Monte Carlo/Molecular Dynamics calculations are being used to bridge the time scales in soot formation. This approach traces out trajectories of soot particle growth that with appropriate sampling can lead to representations of soot particle shapes and distributions. At the fine-continuum level, DNS is used to perform numerical experiments that enable our understanding of the microphysics of reacting flows. DNS provides full access to time-resolved 3D fields, simulating fundamental chemistry-turbulence interactions that underly many of the phenomena observed in engines including autoignition, soot formation and transport, stratified premixed flame propagation, and flame stabilization. The goal of high-fidelity combustion simulations is to provide a better understanding of the micro-physics of these interac-

tions and to develop and validate reduced model descriptions used in engineering simulations. The temporal and spatial numerical resolution requirements are enormous in DNS, requiring petascale computing resources. In partnership with computer scientists, combustion science researchers have developed an optimized scalable, extensible DNS code that scales on multicore architectures. Hundreds of terabytes of data are produced from a DNS simulation. Automated data mining and visualization approaches are required to extract salient information from the simulation. Collaborations with computer scientists on parallel topological feature segmentation and tracking are enabling the morphology of key scalar structures to be correlated with one another.

For new engine research, large eddy simulation (LES) technique is a third area where computing power and scale assists new research. Here, researchers combine the LES technique with Advanced Engine Combustion R&D activities, supported under the DOE Office of Vehicle Technologies. Resource allocations awarded under the INCITE program will enable a series of benchmark simulations that identically match the geometry and operating conditions of select optical engine experiments. The combination of detailed experiments and complementary simulations performed at the identical conditions, and the joint analysis of data that follows, will provide the basic science foundation required to systematically address the targeted research areas identified in the DOE's Basic Energy Sciences Report.

#### ***1.4 ADVANCED ELECTRICAL ENERGY STORAGE AND COMPUTING***

Meeting world energy demand will require efficient electrical energy storage. Revolutionary improvements are needed to level the cyclical nature of intermittent renewable resources, and to progress from today's hybrid electrical vehicles to plug-in hybrids or all-electric vehicles. This will require transformational advances in the materials and chemical sciences that underpin the energy storage research field, as the BES Workshop on "Basic Research Needs for Electrical Energy Storage" reported when it met April 2-4, 2007. Computational support for the research in terms of predictive modeling of complex, multicomponent systems over multiple length and timescales means significant advances can be made in the fundamental understanding of nanoscale phenomena in storage batteries. In the drive to advance the science, theory, modeling, and simulation complement experimental efforts. Researchers need insight into novel charge storage mechanisms, the ability to predict trends, to establish design criteria for new materials, guidance from simulations to direct experiment and the ability to address a broader range of materials systems and compositions. Here are the key research questions: Can electrical energy stor-

age research develop a fundamental understanding of electronic and ionic transport in solutions and electrodes? How can nanostructures in multicomponent, electrode/electrolyte systems be controlled? How can battery and capacitive systems be modeled, across length and time scales? With supercomputer-assisted research, on a scale of one to five years, energy storage research can expect to yield the following: In one year, prototype models of simple capacitive and battery systems; experiments with model systems, demonstrating understanding and techniques to address diffusion, EDLC (electrochemical double-layer capacitors), interface and salivoin phenomena. In three years, competent models that yield results that guide experimental directions, and experiments demonstrating promising approaches to achieve significant improvements. In five years, with adequate funding, the predictive capability for new systems and credible approaches to transformational improvements.

#### ***1.5 GEOSCIENCES AND COMPUTING***

Long-term geologic sequestration represents a critical limitation to advancing the security of the U.S.'s energy future. As the BES Workshop "Basic Research Needs for Geosciences: Facilitating 21st Century Energy Systems" reported February 21-23, 2007, HPC facilities are very important in the search for long-term strategies for nuclear waste disposal and for subsurface imaging of flow and transport issues, transport properties and in situ characterization of fluid trapping, isolation and immobilization, mineral water interface complexity, and biogeochemistry in extreme subsurface environments. This sequestration includes both geologic sequestrations of greenhouse gases and of nuclear waste. Supercomputing is indispensable for research in the Geosciences, for simulation of multiscale systems for ultra-long times, hundreds of years to as long as a million years; and for integrated characterization, modeling, and monitoring of geologic systems. Researchers also hope to compute the thermodynamics of complex fluids and solids, to predict long-term reaction rates, the influence of mixed, multicomponent solvents, and better theories of interfacial reactivity and dynamics. Some premier computer-assisted research directions that HPC will make possible in the Geosciences, includes mineral water interface complexity and dynamics, nanoparticle and colloid chemistry and physics, biogeochemistry in extreme subsurface environments, and dynamic imaging of flow and transport. Each year, faster computing resources are coming on line and being made available to the scientific community. This will directly affect the size, scale, and complexity of geophysical imaging problems which researchers will be able to address.



# THEORETICAL AND COMPUTATIONAL OPPORTUNITIES IN NANOSCIENCE

## 2.1 INTRODUCTION

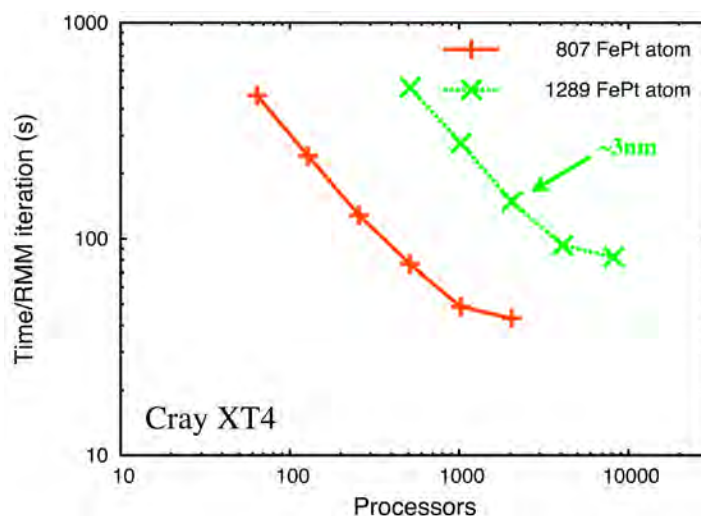
Nanoscience involves understanding and manipulating matter at length scales of the order of nanometers (1 billionth of a meter); nanotechnology involves controlling and exploiting the properties of materials that derive their properties and function from features at the nanoscale. Nanostructured materials behave differently than their macroscopic counterparts. For example, gold is an inert metal in macroscopic form and, indeed, its inertness is part of its attraction as a precious metal in jewelry and biomedical applications, such as dentistry. However, nanoparticles made from gold are highly reactive and are being explored as catalytic materials. This diversity of behavior exhibited at the nanoscale, combined with the strong dependence of properties on size and surface area, opens the possibility of creating new nanostructured materials with exotic and unprecedented properties and function. The idea of assembling nanostructured materials into devices, or incorporating them into existing devices, drives much of the excitement about nanoscience and nanotechnology, and lies at the heart of its potential to revolutionize many fields, from materials, chemistry and physics to biology and medicine. In view of this potential, and to ensure that the U.S. stays at or near the forefront of the fields of nanoscience and nanotechnology, the U.S. government currently invests over \$1.4 billion annually through a coordinated, multi-agency effort that includes 13 federal agencies which conduct and/or fund research.

Nanoscience represents a particularly promising opportunity for petascale and exascale computational science. From the very beginning of the planning for the National Nanotechnology Initiative, it was foreseen that theory, modeling and simulation would play a significant role in advancing nanoscience and nanotechnology [Dixon, Cummings, Hess 2000]. The reasons are clear – the complexity of experiments at the nanoscale and the nature of the measurements (e.g., scanning probes [Park, Pan, Meunier *et al.* 2006]) imply that a theoretical/computational model will invariably be needed to interpret experiments. Furthermore, it is frequently the case that theoretical/computational methods are the only direct way to investigate phenomena in a way that isolates critical components (e.g., understanding nanocatalysis means quantifying the relative effect of nanoconfinement on reaction rates and the presence of catalytic sites [Santiso, Kostov, George *et al.* 2007]); typically, simulations

can do this much more cleanly than experiment). As another example, computational simulations led to the discovery of deep insights into the second law of thermodynamics, and fluctuations out of equilibrium that are particularly relevant to nanoscale systems [for a review, see Evans, Searles 2002]. Once discovered, these theoretical predictions were subsequently verified experimentally [Carberry, Baker, Wang *et al.* 2007; Carberry, Reid, Wang *et al.* 2004.].

Finally, computational nanoscience problems can demand for their solution the largest computing platforms available at any given time, whether the problems be first principles calculations on nanostructures, or molecular-level simulations of self assembly of organic, inorganic or biological systems (or hybrids of these), or multiscale methods. Computational nanoscience, as in many other areas, involves a trade-off between size of the system, the accuracy of its representation, and, for dynamics, the length of time to be simulated; petascale and exascale computing resources open the possibility to extend nanoscience computations along each of these axes, individually or in concert. Thus, theoretical and computational nanoscience is a fertile area for investment of petascale and exascale resources.

As a case in point, consider the recent developments in quantum mechanics-based simulation methods that, combined with continued improvements in supercomputers, have resulted in qualitatively new and exciting tools for theoretical and for computational nanoscience. Methods such as density



**Fig. 2.1.** Scaling of density functional calculations for ferromagnetic FePt nanoparticles. Courtesy of P. Kent, ORNL.

functional theory (DFT) are now able to treat quantum mechanical problems with sufficient accuracy in a wide variety of nanoscale science. Crucially, in many systems there is now an overlap of the experimentally and technologically relevant length and time scales with those achievable in high-quality, well-converged simulations. While computationally expensive, requiring the largest supercomputers, these simulations are poised to greatly aid in the understanding and development of nanoscale science and technology.

Density functional calculations for about 1000 heavy atoms have recently been shown to run well on thousands of processors, with larger simulations of lighter atoms also being routinely possible. This new capability is the result of over a decade of continuous improvement to the algorithms and parallel implementations. Due to the high computational cost, the relatively straightforward nature of these calculations is still largely unknown in the nanoscale research community. Fig. 2.1 illustrates the scaling achieved for a nanomagnetic problem, in which the aim is to understand the role of structure on the magnetic properties of FePt nanoparticles. These are candidate materials for future high-density magnetic recording media. The largest 1289 atom nanoparticles are almost 3nm in diameter, which is close to the experimentally and technologically relevant size regime of 3-5nm.

Thus, it is clear that the combination of new science, new algorithms and new hardware open extraordinary opportunities in theoretical and computational nanoscience.

### 2.2 COMPUTATIONAL MATERIALS SCREENING

#### 2.2.1 Case Study

Computational fluid dynamics has evolved to the extent that one can design an airplane on a computer and one can trust it will fly. Why can't we design the material of which the wings are made? As with computational fluid dynamics, the underlying fundamental equations to compute material properties have been known for many years. The key difference is the enormous gap between the length scale of the Schrödinger equation and the macroscopic length scale material properties require before the success of a material in a particular practical application can be determined. To bridge this gap is an important research theme in many computational groups. The approach is to connect the different computational methods at different length scales and to use multiscale modeling techniques to bridge this gap.

Interestingly, in the field of chemical engineering and catalysis there are some recent successes to be reported and new catalytic materials discovered [Smit, Maesen 2008; Honkala, Hellman, Remediakis *et al.* 2005; Maesen, Beerdsen, Smit

2007]. The key to the success of these studies is a very good understanding of the underlying reaction mechanisms, such that the catalytic activity can be related to a relatively simple material property, for which computer simulations are a screening tool.

Systematic screening of materials requires significant computer resources. For example, the screening for new catalysts for hydride waxing involved only the 180 known zeolite structures [Smit, Maesen 2008] and could easily be extended to include the 3.5 million hypothetical zeolite structures [Thomas, Klinowski 2007; Earl, Deem 2006]. However, algorithms must be developed to screen such a large number of materials efficiently and the computer resources must be orders of magnitude larger than those used for screening limited data sets.

### 2.3. AB INITIO STRUCTURE AND DYNAMICS OF NANOSCALE SYSTEMS

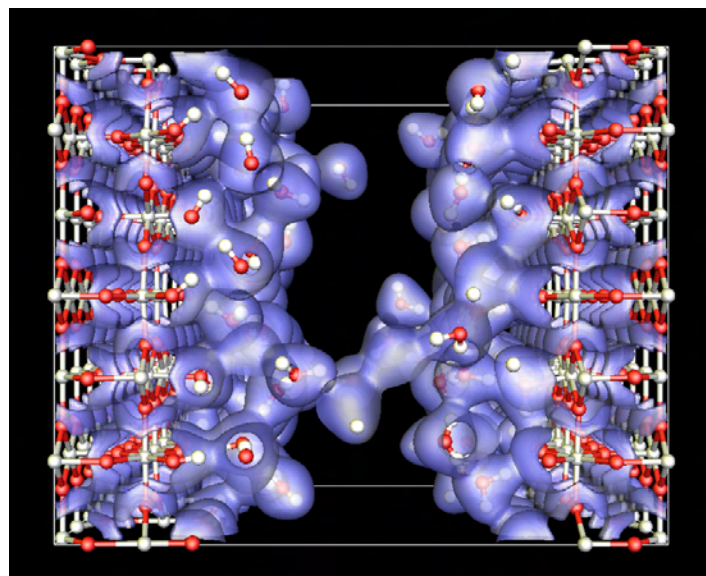
#### 2.3.1 Case Study

The common computational challenge of first principles calculations is both to extend the length scales and increase the speed of calculation at fixed size. Because the interactions at the nanoscale are complex, it is typically necessary to perform many large calculations with high throughput, rather than a single "champion" calculation. The accessibility of nanometer length scales in quantum mechanics-based simulations is opening a new area of simulation that traditionally has been reserved for classical molecular dynamics (CMD) simulations. Study of the finite temperature evolution of small nanoscale systems has recently become possible, enabling the investigation of chemistry in solution, such as the catalytic properties for fuel cells (see Fig. 2.2). Density functional theory accounts for the bond breaking and making processes necessary to understand and optimize catalysis at the atomic level.

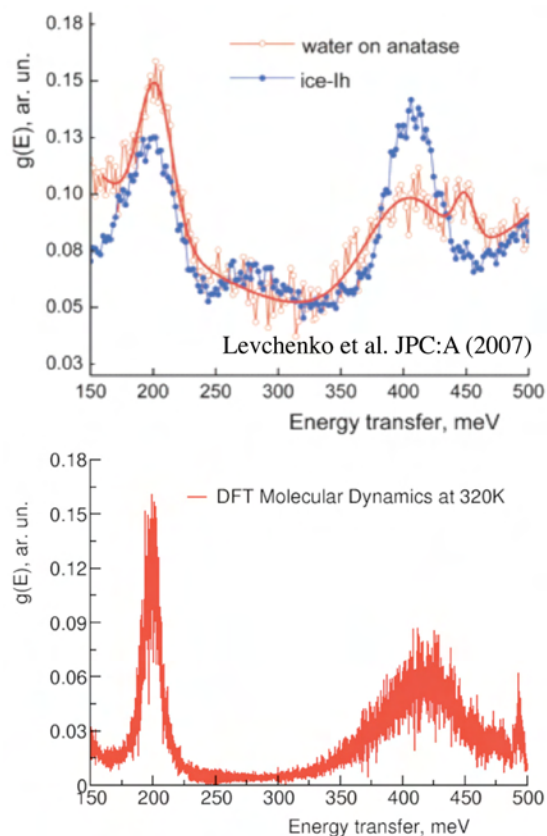
A prototype *ab initio* molecular dynamics (AIMD) simulation of water on titania surfaces, consisting of almost 700 atoms and over 10 picoseconds of dynamics, was recently achieved (Fig. 2.3). In this system, the titania surface catalyses proton transport in water. The bond breaking essential to this process rules out the use of non-reactive CMD simulations, which lack the necessary chemistry. This simulation is noteworthy because not only was it the first large-scale AIMD simulation on this system, but also the large-scale calculations required only one week of continuous computation, per trajectory. This rapid turnaround is necessary so that a set of calculations can be completed in an acceptable human timescale.



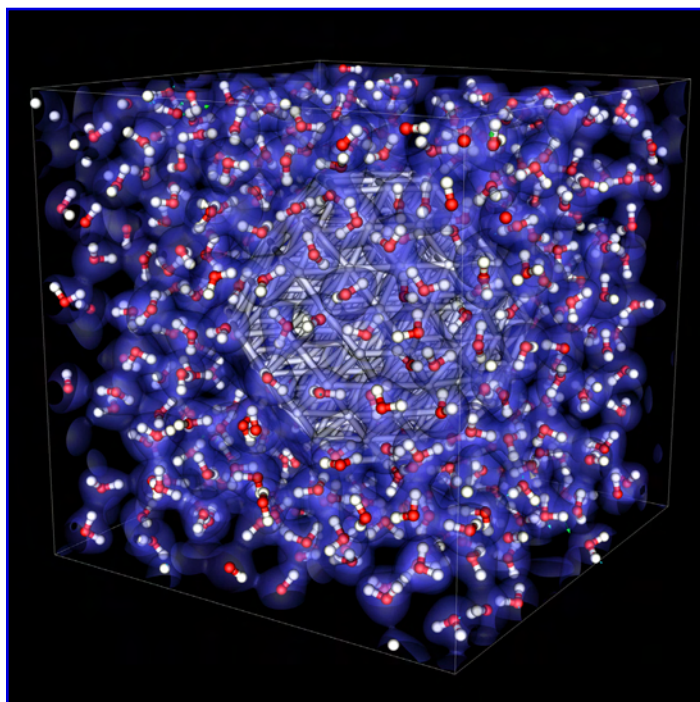
In large-scale AIMD simulations of dynamic processes, the computational and scientific challenge is to obtain sufficient statistics. For the case of water on titania, proton exchange occurs rapidly (in of the order of picoseconds), but much longer simulations may be required for other systems. When enough statistics have been obtained however, there is the new and powerful possibility to compare the calculated dynamics with experimental techniques, such as quasi-elastic neutron scattering (QENS) studies, which also yield dynamical information. Fig. 2.4 compares the measured quasi-elastic neutron scattering data with the simulated data, over the range of energy transfer that corresponds to ps time scales. Remarkable agreement is obtained without any fitting parameters: the data are truly independent. The comparison illustrates a new opportunity for nanoscale AIMD simulation with cross-validation of simulation data with experimental information on the dynamics. In the illustrated calculations, the authors have demonstrated how the individual atomic contributions to the experimentally measured vibrational density of states (Fig. 2.4) can be understood. The titania simulations serve as a simple prototype: They can be extended to other chemical or even soft matter systems, provided sufficient statistics can be obtained. These AIMD simulations complement CMD simulations that interpret QENS data relevant to ns timescales and beyond [Mamontov, Vlcek, Wesolowski *et al.* 2007].



**Fig. 2.3.** Snapshot of a 10ps molecular dynamics simulation of water molecules at a titanium dioxide surface. The isosurface denotes the electronic charge density. Courtesy of J. Sofo, University of Pennsylvania.



**Fig. 2.4.** Comparison of experimental neutron scattering data for water on titania (top, red curve) against calculated data from 10ps molecular dynamics simulations (bottom). Features are well reproduced without any fitting to experiment. Courtesy of J. Sofo, University of Pennsylvania.



**Fig. 2.2.** Image illustrating a nanocatalysis problem with a 201 atom platinum nanoparticle surrounded by 427 water monomers (1482 atoms). Courtesy of M. Neurock, University of Virginia.

## 2.4 FREE ENERGY CALCULATIONS IN PHYSICAL, CHEMICAL, AND BIOLOGICAL SYSTEMS

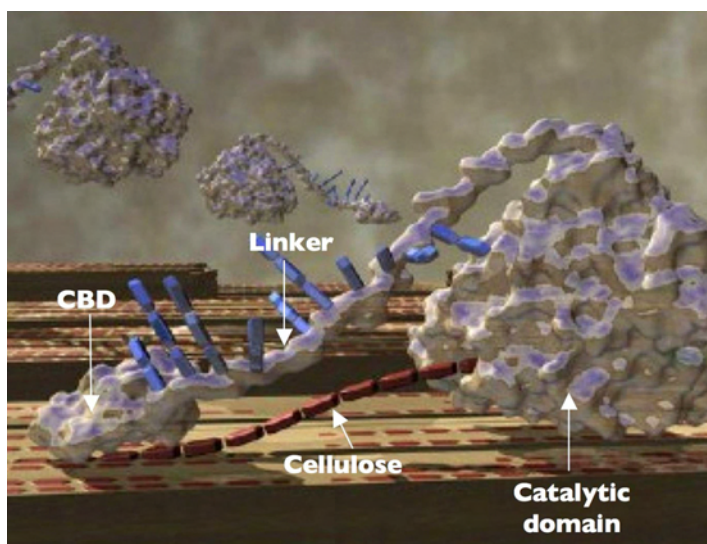
### 2.4.1 Case Study

This is a particularly opportune time for a sustained investment in the development of new algorithms (and new implementations of existing algorithms) for electronic, atomic and molecular-based (EAMB), many-body simulations on petascale and exascale computing architectures. Many-body EAMB simulations are crucial to understanding fundamental processes and interactions in the physical, biological, and nanosciences, as well as interpreting many experiments on such systems, and providing the tools to design and optimize (i.e., engineer) functional systems composed of multiple physical, biological, and nano building blocks.

Of particular interest are complex macro- and biomolecular systems that undergo conformational and/or structural change in response to their environment or as part of their function, since these lie at the heart of many natural and synthetic processes. The conformational states in which macro- and biomolecular systems exist, and between which they transition, correspond to minima in free energy of the systems. Free energy is a measure of the energy of the system that takes into account entropic and thermal effects, and so differs from the potential or kinetic energies that the atoms in a system possess by virtue of their positions and velocities respectively. Thus, while potential and kinetic energies are trivial to calculate in an atomistic classical molecular dynamics or mechanics (CMD or CMM) simulation, in which the positions and velocities of atoms are computed as a function of time, free energies remain a challenge since they require higher-order information [Kofke 2005; Kofke, Frenkel 2004]. For example, the conformation into which a protein folds corresponds to the minimum free energy conformation, thus determining its function [Anfinsen 1973]. Many biological molecules (including proteins such as transmembrane signaling proteins) undergo conformation changes as part of their function; such conformation changes may be between two or more similar low free-energy conformations, or may represent switching from one minimum free energy conformation to another, reflecting a shift in the minimum, due to changed local conditions. Understanding the relative free energies of various conformations of nanoscale systems, including macromolecular and biological molecules such as proteins, is thus an extremely important area of nanoscience, yet one in which little progress has been made, because of the high computational cost.

Another ubiquitously important area in biosystems is self-assembly, resulting in the creation of such integral structures as membranes, and at larger scales, virus capsids, microtubules, and flagella. Self assembly is also a crucial future capability for large-scale manufacture of nanotechnology-based systems, yet its principles are not understood enough to be able to design and control self assembly in a highly predictive fashion. Hence, understanding the way nature controls self assembly will provide important insight into its application within nanotechnology. Self assembly is driven by weak forces (van der Waals, electrostatic, hydrogen-bonding and hydrophobic forces, as opposed to covalent bonds), resulting in long timescales to reach equilibrium configurations. From a computational point of view, a structure obtained from even a heroically long MD simulation may not represent the minimum-free-energy structure of a self-assembled system; hence, methods are required for determining the minimum free energy structure in self-assembling systems. A recent breakthrough in free energy calculations is the Wang-Landau (WL) method [Wang, Landau (*PhysRevE*) 2001, Wang, Landau (*PhysRevL*) 2001], and its continuum analog [Zhou, Schulthess, Torbrügge *et al.* 2006; Yan, Faller, de Pablo 2002; Shell, Debenedetti, Panagiotopoulos 2002], applicable to atomistic CMD simulations. The WL algorithm is particularly well suited to petascale platforms, because it is based on random walks in energy space that can be implemented in parallel, and relies on the collection of statistics from thousands of such random walks; hence, in principle it can be readily implemented in a perfectly parallel fashion on petascale and exascale platforms.

As one illustration of the utility of free energy methods, the work of Zhao *et al.*, who performed free energy calculations for the linker peptide from a cellulase enzyme, cellobiohydrolase I (CBH I) is cited. CBH I is one of the most active cellulases known. This enzyme hydrolyzes cellulose in a “processive” manner, moving along a cellulose chain to liberate cellobiose residues. For this reason, it has been cited as an example of nature’s nanomachines [Cook, Brown, Sandor *et al.*]. CBH I is a multidomain enzyme, consisting of a large catalytic domain containing an active site tunnel and a small cellulose binding module. The two are joined to one another by a 26 amino acid linker peptide (Fig. 2.5). The linker domain plays a significant role in enzyme function; mutation studies show reduced or full negation of enzymatic activity, when the linker is removed. However, although the amino acid sequence in the polypeptide chain of the linker is known, the nature of the linker structure and its relation to the catalytic and binding domains is unknown. Through extensive (0.32 micro-second) CMD simulations using the technique of Ciccotti and coworkers [Carter, Ciccotti, Hynes *et al.* 1989; Ciccotti, Ferrario, Hynes *et al.* 1990],



**Fig. 2.5.** Artist rendition of CBH I. The cellulose binding domain (CBD) interacts with the cellulose surface to detach cellulose molecules from the biomass, which are then shepherded to the catalytic domain for hydrolysis. Courtesy of M. Himmel, NREL.

Zhao *et al.* have computed the potential of mean force (essentially, a free energy profile) as a function of end-end distance for the system of linker + aqueous solvent [Zhao, Rignall, McCabe, *et al.* 2008] and found evidence for two stable states. The simulation results support an energy storage mechanism (spring-like motion) of the linker under stretching and compression, that is consistent with processive depolymerization of cellulose by Cel7A. Since this spring-like motion is a key element in the processive depolymerization of cellulose by Cel7A, the efforts to understand this mechanism, and thus to engineer more capable cellobiohydrolases in the future, are important factors in making the conversion of biomass to biofuels more efficient. The calculations described would be extended dramatically in scope and accuracy, by an efficient implementation of the WL algorithm on petascale and exascale platforms.

## 2.5 CONCLUSION

Nanoscience represents a particularly promising opportunity for petascale and exascale computational science. It has long been apparent that theory, modeling and simulation will play a significant role in advancing science at the nanoscale, and in developing nanotechnology. That is because the complexity of experiments and the nature of the measurements demand a theoretical/computational model to interpret experiments. The increasing overlap of experimentally and computationally accessible length scales represents a tremendous opportunity for science and technology, and for computational and theoretical approaches in particular. It will provide the capability to gain detailed knowledge of the dynamic processes

and properties of nanostructures, moving in the direction of designer materials.

In recent years, many DOE Basic Energy Sciences workshops have emphasized the growing importance of fundamental research in the nanosciences, including the crucial importance of theory and computation. For example, the BES workshop on “Basic Research Needs for Materials under Extreme Environments” [[http://www.sc.doe.gov/bes/reports/files/MUEE\\_rpt.pdf](http://www.sc.doe.gov/bes/reports/files/MUEE_rpt.pdf)] evaluated the potential for developing new materials that will meet demanding future requirements. The Basic Energy Sciences workshop on “Basic Research Needs in Catalysis for Energy” [[http://www.sc.doe.gov/bes/reports/files/CAT\\_rpt.pdf](http://www.sc.doe.gov/bes/reports/files/CAT_rpt.pdf)] identified opportunities for catalysis. Because all the elementary steps of energy conversion (charge transfer, molecular rearrangement, chemical reactions, etc.) take place at the nanoscale, the development of new nanoscale materials, as well as the methods to characterize, manipulate, and assemble them, creates an entirely new paradigm for developing new energy technologies. “Nanoscience Research for Energy Needs” [[http://www.sc.doe.gov/bes/reports/files/NREN\\_rpt.pdf](http://www.sc.doe.gov/bes/reports/files/NREN_rpt.pdf)] highlighted the role of nanoscience in solving the coming energy challenge, and includes specific description of the contribution theory and computation will make to meeting the challenge. Two reports, “Theory and Modeling in Nanoscience” [[http://www.sc.doe.gov/bes/reports/files/TMN\\_rpt.pdf](http://www.sc.doe.gov/bes/reports/files/TMN_rpt.pdf)] in 2002 and “Opportunities for Discovery: Theory and Computation in Basic Energy Sciences” [[http://www.sc.doe.gov/bes/reports/files/OD\\_rpt.pdf](http://www.sc.doe.gov/bes/reports/files/OD_rpt.pdf)] in 2004, describe more specifically the potential for theoretical and computational research to impact nanoscience.

Computational simulations offer nanoscience research the *in-situ* environments to observe processes under conditions that replicate real-world/real-time conditions (temperature, pressure, atmosphere, EM fields, fluids), with minimal loss of image and/or spectral resolution. New algorithms and molecular dynamics calculations adapted to large scale computing capacity offer great potential to solve complex problems. The essential computational challenge, whether the method is AIMD, DFT or CMD, or a combination of these, is to accelerate the time evolution of the simulations, using improved parallel methods and new integration algorithms, in order to obtain sufficient statistics in an acceptable time-scale for the phenomena under study. Petascale and exascale computing will accelerate the development of the next generation of these tools, as well as permit their application to increasingly complex nanoscale systems.

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# THREE GRAND CHALLENGE STUDIES IN HIGH TRANSITION TEMPERATURE SUPERCONDUCTIVITY

## 3.1 INTRODUCTION

In a world of global warming and energy shortages, coming to understand why some superconducting materials transmit electricity without resistance at elevated temperatures above the boiling point of nitrogen would open the door to new superconducting materials operating someday at room temperature. To find such materials, which quest is sometimes called the ‘Holy Grail’ of superconductivity research, would pave the way for enormous energy savings: power cables and grids that would transmit electricity without losses, practical electrical vehicles, super-efficient, high-speed trains, and a new generation of electronics, which make use of the unique properties of strongly correlated superconducting materials.

The goal is still elusive. Despite intense experimental and theoretical efforts, the high temperature superconducting cuprates have not found widespread application to technology, as was anticipated at the time of their discovery 22 years ago [Bednorz, Müller 1986]. This is because the maximum critical temperature ( $T_c$ ) of  $\sim 150\text{K}$  is still of limited benefit, and because of the technical problems associated with lack of ductility, naturally occurring grain boundaries which limit the critical current in superconducting wires, and large thermal fluctuations at higher operating temperatures. In addition, there is currently no generally accepted theory of the anomalous normal state properties or of the origin of the pairing interaction in these materials. Although enormous progress has been made towards understanding the properties of the Hubbard and related models thought to describe the  $\text{CuO}_2$  planes common to all cuprates, it is still not absolutely clear whether this model even possesses a superconducting ground state at  $T=0$  in two dimensions. Solving the problem of high temperature superconductivity will involve not only solving such effective models, but also understanding how materials-specific properties influence their parameters, and in which cases they lead to a higher  $T_c$ . Only then will theory be in a position to predict or at least to guide the search for new, higher critical temperature superconductors.

Several recent developments in computational science suggest that the time is ripe to make significant progress towards this goal. First, recent advances in quantum cluster

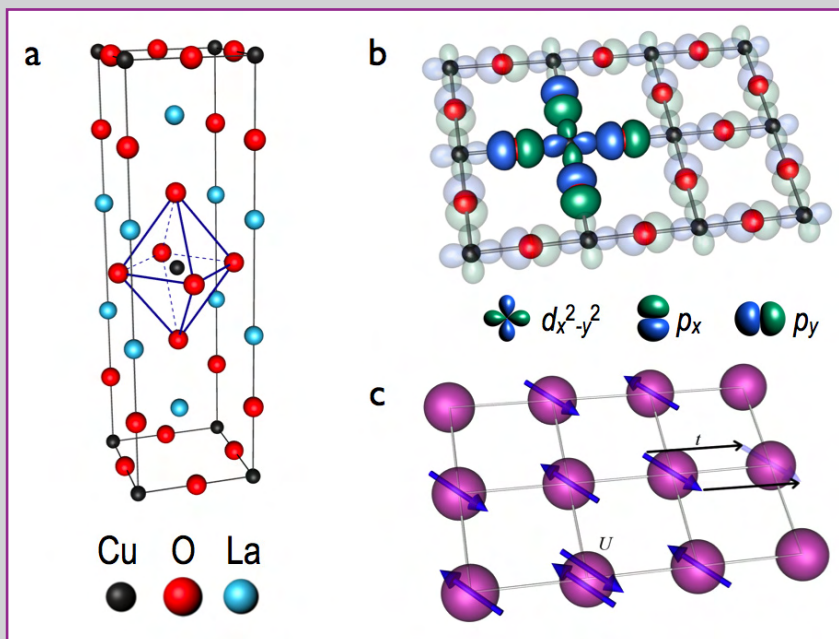
theories [Maier *et al.* (*RMP*.) 2005] now strongly suggest that the Hubbard model develops strong  $d_{x^2-y^2}$  order due to spin fluctuations [Maier *et al.* (*Phys. Rev. Lett.*) 2005, (*Phys. Re. Lett.*) 2006, (*Phys. Rev. B.*) 2006, (*Phys. Rev. B.* 75) 2007, (*Phys. Rev. B.* 76) 2007]. This was controversial as little as three years ago. Similar calculations are now able to describe, within the superconducting state, the spectral properties of quasiparticle excitations [Haule, Kotliar 2007]. Secondly, new methods have been developed to include strong electronic correlations in *ab initio* calculations of band structure. Since a few months after the discovery of the La-Ba-Cu-O material, it has been known that the ‘parent’ compound  $\text{LaCuO}_4$  is a charge transfer insulator, although band calculations predict that it should be a good metal. This is due to strong local Coulomb interactions, primarily affecting the Cu  $d$  states.

The previous five years have seen impressive and exciting developments in supercomputer studies of highly correlated electron materials. Examples of these developments include the incorporation of strong electron correlation effects in *ab initio* calculations based on Density Functional Theory (DFT), which improve on the usual Local Density Approximation (LDA). These new methods include the LDA+U approach [Anisimov, Aryasetiawan, Lichtenstein 1997], the Self-Interaction Corrected Local Spin Density (SIC-LSD) method [Perdew, Zunger 1981], and LDA combined with Dynamical Mean Field Theory (LDA+DMFT) [Lichtenstein, Katsnelson 1998]. New developments in quantum Monte Carlo (QMC) techniques include diffusion and variational QMC simulations [Kolorenc, Mitas 2007]; these QMC methods are mainly applied to simpler transition metal oxides. Remarkable results for conventional superconductors have been achieved with a new, *ab initio* version of the Eliashberg theory of strong coupling superconductivity [Floris, Profeta, Lothiotakis *et al.* 2005].

Thirdly, considerable progress has been made in learning how to ‘downfold’ the band structure information, in order to understand how atomic scale details of specific materials influence the parameters entering effective models of the Cu-O plane [Pavarini, Dasgupta, Saha-Dasgupta *et al.* 2001]. Only in such a way can one hope to describe the quantitative and sometimes qualitative differences among different cuprate

### THE CUPRATES, THE HUBBARD MODEL AND SUPERCONDUCTIVITY

Here we discuss how the basic electronic structure of the cuprates can be mapped onto the single-band Hubbard model, using the prototypical superconductor  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  as an example. In the undoped parent compound  $\text{La}_2\text{CuO}_4$  (depicted in **Fig. a**) one can imagine an octahedron with O atoms at its corners and a Cu atom at the center. The essential unit for superconductivity, which is common to all cuprates, is the  $\text{CuO}_2$  plane that is formed in the crystal by the Cu atoms and the horizontal O atoms of the octahedron (see **Fig. b**). In the parent compound, all but one of the Cu  $3d$  orbitals are occupied, which can be viewed as one spin- $1/2$  hole being located on each Cu atom. The role of Sr, which substitutes for La and lies outside the planes, is to remove electrons from the  $\text{CuO}_2$  planes. The remaining “hole” is localized mainly on the O  $2p$  orbital, and due to hybridization with the neighboring Cu  $d_{x^2-y^2}$  orbitals is somewhat delocalized onto the neighboring Cu atoms (see **Fig. b**). By taking the Coulomb repulsion of electrons into consideration, Zhang and Rice [Zhang, Rice 1988] have shown in a seminal calculation that the hole on the O  $p$  orbital forms a spin-zero singlet state, with the hole on the central Cu atom. This singlet state is similar in nature to the state one obtains by removing the spin- $1/2$  hole on the Cu. One can thus justify the use of the simplified single-band Hubbard model depicted in **Fig. c** to describe the superconducting planes. Here the holes are represented by spin- $1/2$  particles (blue arrows) that hop between sites on a square lattice with a hopping amplitude  $t$ , and an on-site Coulomb repulsion  $U$ . Due to the Pauli exclusion principle, only holes with anti-aligned spins can occupy the same site; this results in a tendency for spins to align in opposite directions, “antiferromagnetically”, on neighboring sites. This single-band Hubbard model has been studied extensively over the past two decades, but only with the remarkable advances in computing (both methods and computer power) in recent years has it been possible to systematically investigate the predictions of this model. One remarkable success of the model is the prediction of a very unusual d-wave superconducting state, which is actually observed in the cuprates. A realistic, materials-specific description of the cuprates will however likely require extensions of the model; one should at least explicitly incorporate the separate Cu  $d_{x^2-y^2}$  and the O  $p$  orbitals in the  $\text{CuO}_2$  plane. Some experiments suggest that the apical O (the oxygen atoms situated at the tops and bottoms of the octahedra) plays an important role, and should be incorporated in the model as well.



**Fig. 3.1.** The basic electronic structure of the cuprates mapped onto the single-band Hubbard model, using the superconductor  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ . The Hubbard model has been studied extensively over the past two decades, but only with the remarkable advances in computing in recent years has it been possible to systematically investigate the predictions of this model.

Courtesy of F.C. Zhang and T.M. Rice, *Phys. Rev. B* 37, 3759 (1988).

materials, the most striking of which is the vast difference in critical temperatures among 1-layer cuprate materials (e.g.,  $\text{HgBa}_2\text{CuO}_4$  [ $T_{c,\text{max}} \sim 90\text{K}$ ],  $\text{Bi}_2\text{Sr}_2\text{CuO}_6$  [ $T_{c,\text{max}} \sim 10\text{K}$ ]), although the doping mechanism and placement of the dopant relative to the  $\text{CuO}_2$  plane may also play a role. While most of this work has been accomplished in the framework of DFT, very recent attempts have been made to include correlations as well [Lechermann, Georges, Poteryaev *et al.* 2006]. Fourthly, *ab initio* methods have recently been applied to defect states and other inhomogeneities, stimulated by new, high-resolution data from scanning tunneling spectroscopy (STS) [McElroy, Lee, Slezak *et al.* 2005; Slezak, Lee, Wang *et al.* 2008]. These works represent a new approach to determining the pairing in high- $T_c$  materials and possibly to engineering higher temperature materials, by exploiting the local correlations between these inhomogeneities and the superconducting gap function measured by STS.

Finally, it should be noted that a number of problems in applied superconductivity are amenable to large-scale computational approaches, and heretofore they have not even been attempted because they were beyond the reach of current computational capability. This includes the problem of the reconstruction of a cuprate grain boundary and the calculation of the critical current through such an interface. Preliminary calculations suggest that the exponential dependence of the critical current on misorientation angle observed in such systems, believed responsible for the suppression of critical current in high temperature superconducting wires, can be explained but that this requires *ab initio* calculations of the structural and electronic reconstruction of grain boundaries for commensurate angles [Gurevich, Pashitskii 1998].

Based upon these developments and the importance of understanding high temperature superconductivity, three grand challenge (GC) studies have been proposed: (1) testing the Hubbard model pairing interaction, (2) inhomogeneity and pairing, and (3) materials-specific simulations of the cuprates.

In thinking about these, it is useful to remember how the framework for calculating the properties of the traditional low  $T_c$  superconductors was established. Following BCS [Bardeen, Cooper, Schriffer 1957], Eliashberg proposed a set of coupled non-linear integral equations, which described the dynamics of the phonon-mediated pairing interaction [Eliashberg 1960]. The kernel  $2F(\omega)$  of the Eliashberg equations was related to the phonon density of states, which was measured by neutron scattering. Numerical solutions of the Eliashberg equations gave a frequency dependent superconducting gap, which led to well defined structure in  $dI/dV$  tunneling experiments. The linking of the structure in the phonon density of states, determined from neutron scattering

with the  $dI/dV$  tunneling spectrum, provided direct evidence that the electron phonon coupling was responsible for superconductivity (although this was not questioned), and that the Eliashberg equations provided the appropriate description (this was questioned by some). Following this, LDA frozen phonon calculations were developed, which provided material-specific results for  $2F(\omega)$  and gave a remarkably complete framework for understanding the low  $T_c$  superconductors [Kortus *et al.* 2001].

The first project, as outlined below, is to determine whether the Hubbard pairing interaction provides an appropriate description of the cuprate pairing mechanism. Here, the development of dynamic cluster Quantum Monte Carlo (QMC) simulation techniques replaces the numerical solution of the Eliashberg equations, and neutron scattering data from spin fluctuations replaces the phonon scattering. The second project on inhomogeneity reflects an important aspect of the cuprate superconductors, which is believed to open a new way to explore the pairing mechanism. Because of the strong correlations and relatively short coherence length (size of the pairs), the local spin, charge and pairing correlations can be strongly affected by impurities or local structural deviations. Here the goal of the project is to provide further insight into the structure of the pairing interaction and to address the important question of optimal inhomogeneity. That is, could  $T_c$  or other properties be enhanced in a system with nanoscale inhomogeneities or nanoscale ordered structures.

The last project focuses on the important problem of materials-specific calculations. As with the second project, this also will address questions regarding the pairing mechanism. Does the Hubbard model and its extensions provide a framework for describing the cuprates? How are the parameters that enter the model related to the atomic arrangement, constituents, and the basic electron structure? Just as the input to the Eliashberg equations is now determined by LDA frozen phonon calculations, we seek to determine the effective model parameters for a strongly correlated system. This will require melding the many-body and electronic structure approaches.

### 3.2 FIRST GC: SUPERCONDUCTIVITY AND PAIRING INTERACTION IN THE HUBBARD MODEL

The half-filled Hubbard model exhibits antiferromagnetism and when doped a pseudogap phase, stripes, and d-wave pairing correlations are found. These properties are remarkably similar to those observed in the cuprate materials and arise from a model in which  $U/t$ ,  $t'/t$  and the doping  $x$  are the only parameters.

Theoretical and computational predictions must be verifiable to gain scientific value and general acceptance in the community. Hence it is crucial to test the scientific hypotheses that the 2D Hubbard model provides the appropriate framework for a description of the cuprates. Recent dynamic cluster QMC simulations of the 2D Hubbard that have analyzed the pairing interaction responsible for superconductivity in this model help relate the predictions for the Hubbard model to experiments on cuprates, particularly neutron scattering and angle-resolved photoemission scattering [Maier *et al.* (*Phys. Rev. B.* 75) 2007; (*Phys. Rev. B.* 76) 2007]. The computational studies have shown that the dominant contribution to the pairing interaction in the Hubbard model originates from spin fluctuations and hence can be described by a simple spin susceptibility representation  $\chi(q)$  with a temperature-dependent coupling strength  $J(q)$  and the spin susceptibility  $\chi(q)$ .

### 3.2.1 Joint Computational and Experimental Study of Spin Fluctuations in Pairing Interactions

Experiments cannot measure the pairing interaction directly in the cuprates, but the recent computational advances for the Hubbard model imply a link between the pairing interaction and the spin susceptibility of specific materials, and thus can be used to obtain experimental results. By using the same spin susceptibility representation as for the Hubbard model, and combining neutron scattering measurements of the spin susceptibility with ARPES results to fit the effective coupling strength, an effective pairing interaction can be determined for actual materials, and the predictions of the Hubbard model can be tested.

To perform this experimental validation of computational predictions requires measurements of the absolute intensity of the wave vector and energy dependence of the dynamic magnetic susceptibility  $\chi''(q, \omega)$ . Electron-doped materials offer a unique opportunity because the transition temperatures and upper critical fields in these materials are relatively low [Wilson *et al.* 2006]. Therefore, one can probe  $\chi''(q, \omega)$  over the wide energy range below and above the critical temperature  $T_c$ , without the need to worry about phonon contaminations, and determine the normal state  $\chi''(q, \omega)$  at zero temperature. Together with angular-resolved photoemission spectra and scanning tunneling microscopy data on the same samples [Matsui *et al.* 2005; Pan *et al.* 2006; Niestemski *et al. in review*], these results can be used as inputs to predict  $T_c$  and the superconducting condensation energy, based on the numerical Hubbard model calculations. If necessary, the model can be refined until an accurate fit of the experimental data is obtained.

## 3.3 SECOND GC: UNRAVELING THE ROLE OF INHOMOGENEITIES IN THE PAIRING AND THE SUPERCONDUCTING TRANSITION TEMPERATURE

While an experimental validation of spin fluctuation-mediated d-wave superconductivity would be a remarkable step forward, some of the complexity found in actual cuprate materials is missing in this picture. Recent experiments have shown that nanoscale charge and spin inhomogeneities emerge in a number of cuprates [Dagotto 2005]. Phase separation into hole-rich and hole-poor regions in Hubbard-like models was predicted by theory two decades ago [Gor'kov, Sokol 1987; Zaanen, Gunnarson 1989; Emery, Kivelson, Lin 1990; Emery, Kivelson 1993], and was first discovered in the cuprates when neutron scattering experiments reported evidence for spatial stripe modulation of spin and charge densities [Tranquada *et al.* 1995]. In this state, periodically spaced lines of hole-rich regions separate antiferromagnetic stripes of copper spins. While the existence of stripes in some of the cuprate materials remains a matter of debate, other inhomogeneous states have been revealed recently in scanning tunneling microscopy (STM) measurements. Random superconducting gap modulations were discovered in underdoped BSCCO [Lang *et al.* 2002], and a 'checkerboard' electronic crystal state was observed in the pseudogap regime of a Na-doped cuprate material [Hanaguri *et al.* 2004]. Very recently, similar modulations of a pseudogap in the electronic spectrum were also found above the superconducting transition temperature [Gomes *et al.* 2007], indicating the possibility that local pairs form in nanometer-sized pairing regions before they become coherent and form the superconducting condensate. This view is also supported by recent  $\mu$ SR experiments [Sonier *et al.* 2008].

The discovery of inhomogeneous states raises several interesting questions about their role in the cuprates. Do they cause high-temperature superconductivity or do they merely play a peripheral role? Do they enhance or suppress the pairing mechanism? Another important question is whether there is an optimum inhomogeneity that maximizes the transition temperature [Kivelson, Fradkin 2005]. For example, can one have a higher value of  $T_c$  for the cuprates in a striped array in which there is strong pairing in the spin-correlated low-hole regions, and good hole mobility in the higher density hole regions? Or is it possible to increase  $T_c$  in a multilayer system composed of layers with different doping?

### 3.3.1 Solving Spin Inhomogeneities with HPC

Despite strong theoretical [Kivelson, Fradkin 2005; Carlson *et al.* 2002; Arrighoni *et al.* 2004; Martin *et al.* 2005;



Aryanpour *et al.* 2006; Loh *et al.* 2007; Tsai, Kivelson 2006; Doluweera *et al.* 2007] and experimental interest, these questions remain largely unanswered. Theoretical studies are difficult, because of the complexity of the problem. One has to deal simultaneously with strong electronic correlations and inhomogeneous states, and therefore studies have been based largely on phenomenological descriptions or on models that have little overlap with reality. The need to solve appropriate microscopic models, such as an inhomogeneous Hubbard model, opens up an exciting opportunity for HPC. The complexity and scale of the problem becomes clear when one considers a Hubbard model with random disorder, which is a minimal problem simulation to describe the random spatial modulations observed in the STM studies. Current simulations of the homogeneous Hubbard model without disorder use about 5 teraflops and run on the order of 103 processors. Disorder averaging adds another level of complexity, increasing the computational requirements by a factor of 103 – 104. This turns quantum cluster simulations of a disordered Hubbard model into a petascale computing problem. Similarly demanding for computational simulation is a “striped” model with periodically modulated inhomogeneities. Here one must look at a system that is large enough to contain a stripe array, without frustrating it. This can change the cluster size one must study by a factor of 4, or even 8. To include additional disorder in a perfectly periodic striped system will again require petascale computation.

Inhomogeneities can be incorporated in the Hubbard model by spatially varying the local Coulomb repulsion between electrons. In a striped system, for example, a large Coulomb repulsion will keep the holes out of the spin-correlated low-hole regions, and a small Coulomb repulsion will allow the holes to aggregate to the regions in between. Multilayer systems with varied doping perpendicular to the layers may be modeled in a similar way, or with a layer-dependent chemical potential. In addition, the inclusion of longer range Coulomb interactions, which factor in the stripe problem as well as the multilayer problems, will require another level of self consistency. Self consistent DMRG calculations, which include the long range Coulomb interaction treated in Hartree approximation, have been carried out successfully. The necessary iterations make this a computationally demanding problem. Questions that these simulations can address in the near term include the effect of inhomogeneities on  $T_c$ , the pairing interaction, and the electronic spectrum. In the long term, one could explore whether an optimum inhomogeneity exists that maximizes  $T_c$ .

To understand the role of inhomogeneities in the cuprates poses a great challenge and is undoubtedly an important step towards solving the high- $T_c$  puzzle. The computations for inhomogeneous Hubbard models will have a significant im-

act on our scientific understanding of high temperature superconductivity. But these studies also have the potential to make predictions of importance to technology. If the simulations predict an optimal inhomogeneity that maximizes  $T_c$ , for example, then one could use this knowledge to structure new, cuprate-based materials with even higher transition temperatures.

### 3.4 THIRD GC: MATERIALS-SPECIFIC SIMULATIONS BY “BRIDGING” AB INITIO SIMULATIONS AND SIMULATIONS OF SIMPLER CUPRATE MODELS

One of the key questions the theory of the high temperature superconducting cuprates must address is the large difference observed in the superconducting transition temperature in different cuprate materials. From the perspective of the Hubbard model, this must mean that its parameters (such as  $U/t$  and  $t'/t$ ) [Pavarini, Dasgupta, Saha-Dasgupta *et al.* 2001], or extensions to the model [Annett, Martin, McMahan *et al.* 1989], which might include the hybridization between the strongly interacting Cu d-bands and the O p-bands, or the degrees of freedom of coupling to the lattice, must in some way strongly depend on the chemical composition of the particular materials.

A commonly used approach to materials-specific simulations in strongly correlated electron systems derives the parameters of the effective model Hamiltonian from *ab initio* electronic structure calculations that are based on the LDA to DFT. Unlike applications to semiconductors and transition metals, for which the LDA-based DFT has been very successful, applying the LDA itself to strongly correlated transition metal oxides usually does not give a correct description of the ground state electronic structure. In the parent compounds of the cuprate high temperature superconductors, for example, LDA calculations predict a metallic ground state instead of the experimentally observed insulator with antiferromagnetic order [Pickett 1989]. The shortcomings of the LDA, which are attributable to its inability to describe localized electrons that exhibit strong Coulomb interactions, can be overcome with orbital dependent extensions, such as the LDA+U [Czyzyk, Sawatzky 1994] or the SIC-LSD method [Svane, Temmerman, Szotek *et al.* 2000].

#### 3.4.1 Simulating Excited State Properties of Metal Oxides

Following the spirit of the Hubbard model, the LDA+U method [Anisimov, Aryasetiawan, Lichtenstein 1997] augments the LDA functional with a local on-site Coulomb interaction term. With a simple Hartree-Fock-like treatment of

the additional correlations, the LDA+U calculations rectify the shortcomings of the LDA method and accurately predict the electronic ground state of insulating transition metal oxides. With a more sophisticated treatment of correlations in the LDA+DMFT method, excited state properties of simple transition metal oxides have been predicted with great success. In Vanadates, with typically one correlated d-band, the simulations predict spectral functions that are in excellent agreement with photoemission experiments [Pavarini, Yamasaki, Nuss *et al.* 2005]. Recently, the LDA+DMFT simulations [Kunes, Anisimov, Lukoyanov *et al.* 2007; Kunes, Lukoyanov, Anisimov *et al.* 2007] have been applied successfully to transition metal monoxides such as NiO and MnO materials, in which the p-d hybridization plays an important role.

Effective Hamiltonians for the cuprates that include p-d hybridization terms and are derived from LDA calculations have been proposed in the literature, and indeed it is found that the p-d and p-p hopping parameters are quite sensitive to the chemical composition of materials. DCA/QMC simulations with these materials-dependent Hamiltonians however, (in analogy to the LDA+DMFT method, this approach will be called LDA+DCA), have not been successful [Kent, Saha-Dasgupta, Jepsen *et al.* *submitted*] in predicting the experimentally observed superconducting transition temperatures. A parametric study of the three-band model with the DCA/QMC method shows that the superconducting transition temperature is very sensitive indeed to the strength of the p-d hybridization [Kent, Saha-Dasgupta, Jepsen *et al.* *submitted*]. These simulations indicate that a more appropriate treatment of the material-specific electronic structure might indeed allow us to make the connection between effective Hamiltonian-based model simulations and the first principles electronic structure calculations of specific materials. Two routes are currently being explored: (1) use the SIC-LSD method instead of the LDA, as the former properly describes the parent compounds of the cuprates as a starting point for the DCA/QMC simulations; (2) include dynamic correlations on all Cu-d orbitals in the LDA+DCA treatment, analogous to the successful LDA+DCA simulations of NiO and MnO. Both of these approaches require effective models that are significantly more complex than those studied so far, and will require considerably larger computational resources.

### 3.5 SUMMARY AND FUTURE GRAND CHALLENGES

The stated goal of the three grand challenge studies we propose is to develop a calculation framework for understanding and predicting the properties of the high- $T_c$  cuprates.

Beyond this, the implicit goal is to develop a framework for understanding and predicting the properties of strongly correlated electron materials. Just as the Eliashberg-LDA-phonon theory provided a framework for calculating the properties of a variety of materials, we believe that the DCA/QMC material-specific effective Hamiltonian framework that is being developed will be applicable to a range of electronic problems in strongly correlated materials. We envision future grand challenge studies in which the Eliashberg-LDA-phonon approach is used to “screen” possible materials in the search for higher- $T_c$  superconductors, as well as to search for more isotropic materials with higher  $j_c$  values. Similarly we see future grand challenge programs based on the DCA/QMC/effective Hamiltonian approach, which will range from searching for higher  $T_c$  materials, to the study of grain boundaries and critical current problems. Beyond this, the design of a new generation of electronics, which makes use of the unique properties of strongly correlated materials, will lead to a range of future grand challenge projects.

*Thomas Schulthess, Peter Hirschfeld, Thomas Maier, Pengcheng Dai, and Doug Scalapino*

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# COMBUSTION MODELING FOR FUELS AND ENGINES

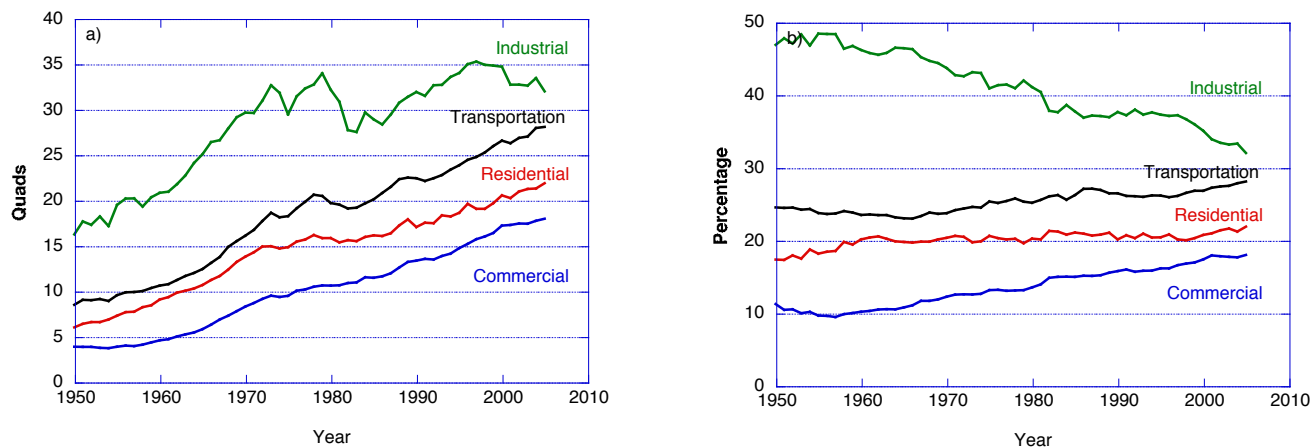
## 4.1 INTRODUCTION

Combustion provides over 90% of the energy for the United States, primarily for transportation and the production of electricity. Transportation has become the second largest consumer of energy in the U.S. (see Fig. 4.1), and utilizes the largest fraction of petroleum fuel, nearly 60% of the nation's total [Annual Energy Review 2005]. Unlike other sectors of energy usage, transportation technologies are concentrated in only three main areas: gasoline engines, 67%, diesel engines, 21%, and jet turbines, 12%. The monolithic nature of the transportation technologies offers the opportunity for large impacts from targeted improvements in a few key systems.

The United States and indeed the world face several major energy challenges in the 21st century. The cheap, light, sweet crude oil that has driven economic development in the 20th century is becoming less abundant, at the same time that demand is increasing. At the same time, CO<sub>2</sub>, a primary product from combustion, has been identified as a primary culprit in global climate change. The nation has also become concerned with assuring a secure and economically viable energy supply.

To inform the scientific foundation that will enable technology breakthroughs in transportation fuel utilization, the Office of Basic Energy Sciences in the U.S. Depart-

ment of Energy (DOE) convened the Workshop on “Basic Research Needs for Clean and Efficient Combustion of 21st Century Transportation Fuels,” from October 30 to November 1, 2006 [DOE Office of Basic Energy Science 2006]. Priority research directions were identified by three panels. The first two panels focused on engines or fuels and worked backward from technology drivers to scientific research needs. The first panel focused on *novel combustion*, as embodied in promising new engine technologies. The second panel focused on *fuel utilization*, inspired by the unique (and largely unknown) challenges of the emerging fuel streams entering the market. The third panel explored crosscutting science themes and identified general gaps in our scientific understanding of 21st-century fuel combustion. After the workshop, co-chairs and panel leaders distilled the collective output to produce eight distinct, targeted research areas that advance one overarching grand challenge: *to develop a validated, predictive, multiscale, combustion modeling capability to optimize the design and operation of evolving fuels in advanced engines for transportation applications*. High performance computing will play a central role in the development of multiscale combustion modeling, by considering the full range of scales from quantum up to continuum macroscale. In this new paradigm, direct simulations over several decades of scales will be performed on petascale computers, to provide detailed scientific understanding; and models that encapsulate the understanding will be developed to bridge the different ranges of scales.



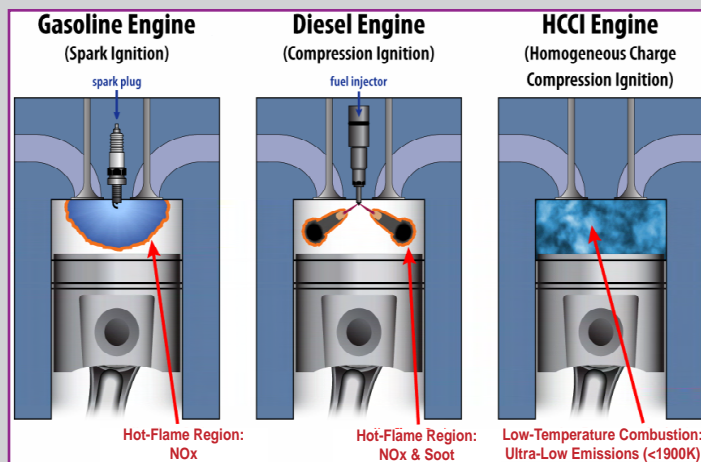
**Fig. 4.1.** Energy consumption, at left, by end use in the United States from 1950 to 2005 in quadrillion BTUs (Quads). Relative energy use, at right, by end use in the U. S. from 1950 to 2005. (Source: Energy Information Administration, Annual Energy Review 2005, Report No. DOE/EIA-0384[2005].)

### NEW FUELS FOR NEW ENGINES

Fuels for automobile, truck and aircraft engines are produced by refining petroleum-based sweet crude oil. Gasoline, diesel fuel and jet fuel are each made with specific physical and chemical characteristics dictated by the engine type in which they are to be burned. As new fuels refined from oil sands, oil shale, coal, and biofeedstocks emerge, both uncertainties and strategic opportunities arise. Rather than energy-intensive refining of these qualitatively different emerging fuels to produce gasoline and diesel equivalents, we can achieve a “dual revolution,” coordinating advances in both fuel and engine systems.

Spark-ignited gasoline engines utilizing catalytic after-treatment operate cleanly but well below optimal efficiency. Diesel engines operate more efficiently at higher compression ratios, but produce soot and  $\text{NO}_x$ . Burnout and/or removal can prove problematic. Novel engine concepts endeavor to surmount these challenges. Direct injection gasoline engines operate without throttle plates, increasing efficiency, while retaining a catalytic converter. Ultra-lean, high-pressure, low-temperature diesel combustion seeks to avoid the pollutants, while maintaining high efficiency.

A novel combustion concept, homogeneous charge compression ignition (HCCI), seeks to join the best of diesel and gasoline engines. HCCI employs a premixed fuel-air charge ignited by compression, with the ignition timing controlled by in-cylinder fuel chemistry (see Fig.4.2). Each of these strategies must permit and even exploit fuel flexibility, as the 21st-century fuel stream matures. The new fuel sources and advanced engine concepts present such a vast design and operation parameter space that only technologies built upon a predictive science capability will mature.



*Fig. 4.2. Gasoline engines use spark timing to control ignition. Diesel engines rely on timed injection of fuel. In contrast, ignition timing in HCCI engines is controlled purely by the ignition chemistry of the fuel, which requires a thorough understanding of the complex ignition processes. Predictive modeling is required to optimize this nonlinear, multidimensional parameter space.*

The “Basic Research Needs for Clean and Efficient Combustion of 21st century Transportation Fuels” workshop identified one overarching grand challenge: “The development of a validated, predictive, multiscale, combustion modeling capability to optimize the design and operation of evolving fuels in advanced engines for transportation applications.” Realizing this challenge requires a broad array of discovery and use-inspired research, integrating experiment, theory, modeling and simulation.

Predictive capability will fundamentally change fuels research and engine development. Establishing an understanding of sufficient depth and flexibility will facilitate realistic simulation of fuel combustion in existing and proposed engines. An experimentally validated, predictive capability for combustion is a daunting challenge. Spatial and temporal scales of importance span 9 orders of magnitude, ranging from atomic scales up to those of an engine combustion chamber. The combustion chemistry of 21st-century fuels includes hundreds of different fuel molecules and many thousands of possible reactions and reactive intermediates contributing to the oxidative release of energy stored in chemical bonds. This complex chemistry also dictates pollutant emissions, engine knock conditions and, for HCCI, ignition timing.

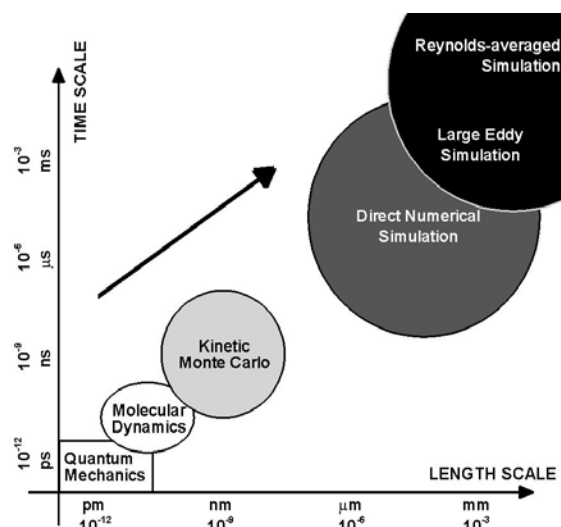
Turbulence, transport, and radiative phenomena have a profound impact on local chemistry in combustion devices, but are poorly understood. Even with a rapid growth in computing power, combustion phenomena are and will remain too complex to simulate in the detail, and methods that condense information and accurately propagate uncertainties across length and time scales will be required to optimize fuel/engine design and operation. High performance computing combined with advanced algorithms will play a central role in unraveling the complex interplay of chemistry and turbulence in the combustion devices of the future.

## 4.2 MULTISCALE SIMULATION METHODS

The length scales that are relevant in IC (in-cylinder combustion) engines range from Angstroms (atomic/molecular processes), to several nanometers (nm) (soot particles), to several micrometers (fuel droplets), to a fraction of a millimeter (smallest aerodynamic scales), to several centimeters (bore diameter), possibly up to meters (the size of the entire device); the range of time scales is commensurately broad. A dynamic range of  $\sim 1,000$  in length scales is a practical upper limit for current terascale computing; petascale computing and algorithmic advances may push this to  $\sim 10,000$ . Even with enormous increases in computing power, it is unlikely that a single simulation approach would fully resolve all scales in the foreseeable future. Rather, multiscale approaches are required to model the effects of unresolved scales on larger resolved scales, and to incorporate the relevant feedback mechanisms, which govern the different dynamic regimes of the turbulent combustion. The challenge of the study of systems with multiple scales is to translate a rigorous description of processes occurring at small length scales or short time scales, into a model that can be used in calculations that do not resolve these scales.

As shown in Fig. 4.3, the wide range of simulation approaches that are applied to combustion systems includes: quantum mechanics approaches that describe intra-atomic processes for a small number of atoms; Molecular Dynamics and Kinetic Monte Carlo methods that describe inter-atomic processes for a population of atoms; and continuum mechanics approaches that describe chemical and physical processes at macroscales. Continuum mechanics approaches may be further categorized by the range of spatial and temporal scales that are resolved. In direct numerical simulation (DNS), the continuum mechanics governing equations are solved directly; all relevant fluid and chemical scales are resolved. In large eddy simulation (LES), spatially filtered forms of the governing equations are solved; the dynamics of the large scales are captured explicitly, while the effects of small scales must be modeled.

In the following, a set of case studies for the near term (18-month to 3-year time period) is presented. These studies require petascale computing to provide quantitative physical understanding of the underlying scientific issues related to aromatic chemistry and soot nanoparticle growth and oxidation, heterogeneous reactive multiphase flow, and turbulence-chemistry interactions under low-temperature, high-pressure environments for diverse fuels.



**Fig. 4.3.** Multiscale combustion simulation methods for bridging decades in length and time scales in practical combustors.

## 4.3 TWO CASE STUDIES

### 4.3.1 Soot Simulation Case Study

**Automated Combustion Kinetics – Aromatic Chemistry for Soot Growth and Oxidation.** Hydrocarbon combustion is the mainstay of energy production throughout the world, but new demands are being placed on this technology to curb pollution and to adjust to alternative fuels. Meeting these demands requires a detailed and adaptive understanding of combustion kinetics. This in turn means understanding reactive radical chemistry over the full range of temperatures, pressures, and fuel/air mixtures found in current and emerging combustion devices. Theoretical kinetics will be an essential tool in acquiring this understanding.

There are three key challenges in improving our theoretical capability to handle this task.

- **Kinetic complexity:** At combustion energies, the number of intermediates, products, and reaction paths grows to a high power with the number of carbon atoms in the radical reactants. For any one reaction path, the most computationally demanding step in characterizing the kinetics is the electronic structure calculations that describe the potential energy surface (PES) in the vicinity of the path. The sheer number of radical species and associated reaction paths will require a qualitative increase in the capacity of computer resources.
- **Beyond steepest descent:** Many statistical theories of reaction kinetics describe the reaction in terms of steepest descent paths with harmonic-like excursions of the reactants off the path. In many reactions, highly anharmonic hindered rotor type excursions off the path are known to

be important. Trajectory determinations of inelastic kinetics are also important, as they control the pressure dependence of reactions. Such inelastic processes, as well as anharmonic reactive processes, increase the range of the PES electronic structure which calculations must explore.

- **Chemical intuition:** At present, the study of any one set of reactants with multiple reaction pathways generally requires considerable human chemical intuition, to search for and find appropriate reaction paths and reaction intermediates. As the complexity of the reactants grows, the human/computer interaction is the rate-limiting step in the time to solution.

There has been some progress in dealing with the above challenges. In recent years researchers, the Truhlar group or Klippenstein and Harding for example, have married electronic structure methods to kinetics methods so that the selection of where to calculate the PES can be in principle driven by convergence of the kinetic rates. In related research, new ways of interpolating computed potential energies have been developed, by the Collins or Thompson groups for example, that can estimate locally the interpolation error. This means that electronic structure calculations may be launched only if required by both the kinetics calculations and the size of the interpolation error. Finally, several research groups, Klippenstein and Harding for example, are beginning to teach computers human chemical intuition about where in configuration space reaction intermediates and their reaction paths may be found.

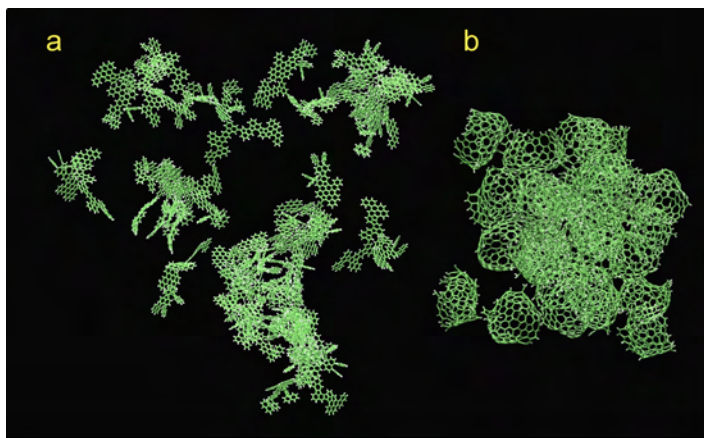
With these recent advances and with a few man-years of software development, we should be able to develop and apply a program of automated combustion kinetics that would do the following with little human assistance. Given the identities of the reactants, the identity of any buffer gas that controls the pressure dependence, and any thermodynamics knowledge of possible products, the program would direct in-parallel appropriate electronic structure methods. These would map out reaction paths and reaction intermediates to a degree of accuracy necessary to converge the reaction kinetics, to grow an interpolation of the computed potential energies that would reduce the number of electronic structure calculations needed, and do the same for any relevant inelastic processes with the buffer gas. These would then compute the converged reactive kinetics (generally via statistical theories) and inelastic kinetics (generally via trajectories), as a function of temperature and pressure, over whatever range the user requires. On a petaflops computer, whole families of hundreds of reactions could be studied in parallel at a consistent level of theoretical treatment. A problem area of combustion chemistry where this approach could be applied is the aromatic chemistry of soot growth and oxidation.

**Multiscale Soot Simulation.** In combustion environments, soot formation is a fascinating multiscale problem of nanoparticles growth, both in length scale and in time scale. Soot formation is initiated by reactions of carbon-based fuel molecules produced by partial fuel combustion. These initial reactions produce large organic molecules containing carbon rings, which are referred to as polycyclic aromatic hydrocarbons (PAH). Large PAH associate and condense to form small nascent particles in the size range of 5nm. These incipient particles grow in size to form carbon spheres in the size range of 15 to 50nm, and aggregate to form larger branched-chain particles of widely varying size. A typical size for a soot particle produced by a modern conventional diesel engine is ~200nm. At higher temperatures, soot particles react rapidly with oxygen and under some conditions can be completely oxidized before making it into the exhaust stream [Homann, Wagner 1967]. The fundamental challenge in predicting soot formation lies in the fact that soot formation is a heterogeneous process at even atomic length scales (~O(10<sup>-10</sup> m) which has an enormous impact on the soot morphology and overall yield.

Recent work reported in the literature [Violi 2004, Izvekov, Violi 2005] has revealed how chemical changes and transformation can propagate upward in scale to help define the function of the particle structures. In particular, the morphology of the nanoparticles is critical in determining the overall growth and agglomeration behavior of higher molecular structures compounds. Fig. 4.4 shows snapshots obtained using Molecular Dynamics simulations of nanoparticle agglomeration in high temperature regimes [Izvekov, Violi 2006]. The sheet-like particles (a) do cluster in small agglomerates, while the round particles (b) tend to cluster with a preferred back-to-back orientation. Current models report a simplified notion of the coagulation process, in which two particles coagulate after collision if the kinetic energy of the particles is lower than their interaction potential, which depends on van der Waals attraction and Born repulsion forces. Particle morphology plays an important role in the clustering process and this information is necessary to build a realistic model for particle formation.

Soot modeling approaches present in the literature are not suitable frameworks for including morphology dependent nucleation, surface growth, and agglomeration processes. Novel Monte Carlo/Molecular Dynamics calculations [Violi, Voth, Sarofim 2005; Violi, Venkatnathan 2006] have been developed to bridge the time scales in soot formation. This approach traces out trajectories of soot particle growth that with appropriate sampling can lead to representations of soot particle shapes and distributions.





**Fig. 4.4.** Nanoparticle agglomeration in high temperature regimes from molecular dynamics simulations.

In order to extract realistic information on the formation of particles, multiple independent simulations of the AMPI code must be carried out to obtain statistically significant averages. Preliminary studies have shown the need of 108 calculations per point, to obtain convergence on particle formation with an average diameter of 4 to 5nm. In addition, for realistic predictions of soot formation, soot clusters of size approaching  $1\mu\text{m}$  are needed, resulting in a huge increase in the number of realizations. Simulating such a large system of nanoparticles is already well beyond the range of current multiteraflops computing systems. However, with petascale computing, we can begin to approach these requirements.

### 4.3.2 Heterogeneous Reacting Flow Case Study

Coupled processes involving various multicomponent interactions are not only common to reacting systems described earlier, but also are relevant to many processes which play a significant role in the entire energy cycle, as listed below:

- **Fuel production and processing:** catalytic crackers,  $\text{H}_2$  production, S removal, Coal gasification, clean-up ( $\text{SO}_x$ ,  $\text{NO}_x$ , Hg,  $\text{CO}_2$ ), biomass (cellulosic) pyrolysis and gasification, nuclear fuel production
- **Energy production:** fuel cells, coal and biomass combustion, nuclear reactors and separation, silicon production and coating for photovoltaic applications, novel combustion technologies such as oxycombustion and chemical looping combustion
- **Energy utilization and efficiency:** polymerization reactors, catalytic reactors, multiphase flow reactors used in most energy-intensive industrial processes

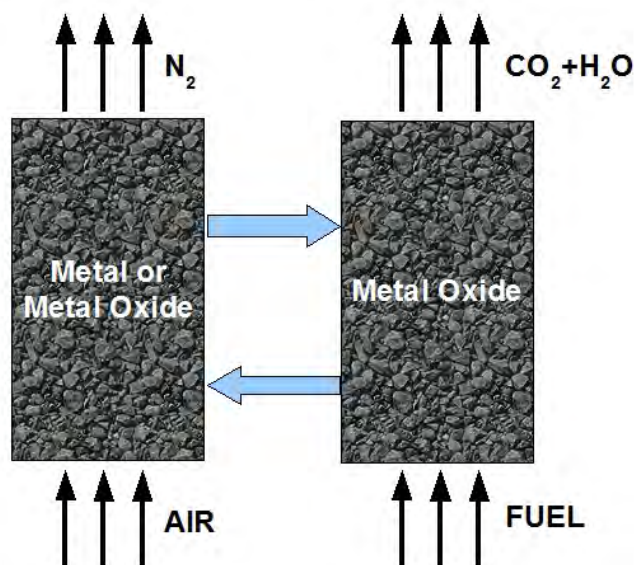
Most of these applications are generally categorized as heterogeneous reacting flows, where it is important to model the interaction between the various phases accurately to build predictive simulation capability. In this case study, one particular problem which has potential to yield a carbon-

negative combustion technology will be simulated. The process is referred to as chemical looping combustion (CLC). The adaptation of this process for bio-ethanol would be studied. This process (as shown in Fig. 4.5) mimics the hemoglobin in humans where an oxygen carrying metal like Ni is oxidized in the first reactor, in the presence of air, and transported to a second reactor, where the fuel reduces the metal oxide to produce  $\text{CO}_2$  and water. The advantages of this process are:

- Higher efficiency with lower entropy losses
- No thermal  $\text{NO}_x$
- Separated  $\text{CO}_2$  stream for sequestration

Thus, in combination with biofuels, this process leads to an efficient, low-emissions and potential carbon-negative technology, as the  $\text{CO}_2$  is easily amenable to sequestration.

Through a DOE Office of Science ASCR initiative on Multiscale Mathematics and Research program, there is an ongoing effort to develop a multiscale and multiphysics mathematical framework to address the needs of simulations in heterogeneous chemical reacting flows. As part of this effort, a scalable framework is being developed to couple the microscopic chemical reactions on the catalyst surface (in this case the metal particles) using Kinetic Monte Carlo, and the flow around the particles using Lattice Boltzmann method [Frantziskonis, Mishra, Pannala *et al.* 2006]. The above parallel multiscale framework will be adapted for the bio-ethanol CLC process and the parametric simulations of this process will give us the requirements for the catalyst to make this process viable. These properties will then be used to guide the experimental catalyst formulators, as well as to guide chemists designing catalysts using first principle techniques to narrow the search for potential materials. The



**Fig. 4.5.** Schematic of the chemical looping combustion process. Courtesy of S. Pannala, ORNL.

ultimate goal is to extend such a multiscale framework to simulate the entire range of scales needed for energy devices. And to harness the power of petascale and exascale computers for rapid design and prototyping of breakthrough energy technologies.

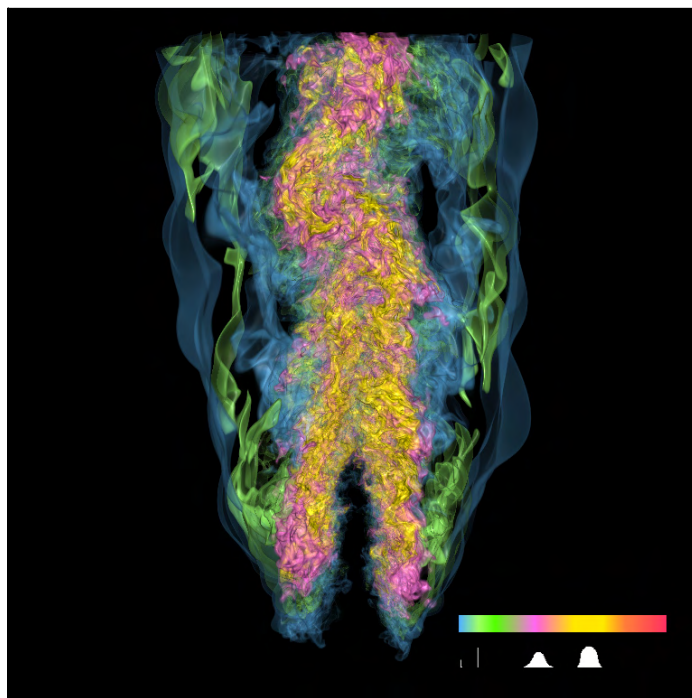
#### 4.4 CONTINUUM SIMULATIONS

High fidelity continuum simulations are needed that capture complex aero-thermo-chemical interactions, and in particular, that capture and discriminate the effects of fuel variability. Through a 2008 DOE INCITE award, DNS and LES approaches will be used to investigate ‘turbulence-chemistry’ interactions in combustion of alternative fuels, for well-defined laboratory configurations. In the near term, DNS will be used to understand how a lifted autoignitive flame is stabilized on ignition intermediates, and how thermal and composition stratification in kinetically-controlled compression ignition combustion can be used to control the rate of combustion. Fundamental understanding of these issues is needed to develop robust and reliable ignition and combustion models for the combustion regimes observed under low-temperature combustion engine environments. The application of LES provides the formal ability to treat the full range of multidimensional time and length scales that exist in turbulent reacting flows, in a computationally feasible manner, and thus provides a direct link to key experimental studies of relevant combustion devices.

#### 4.5 TWO CASE STUDIES

##### 4.5.1 DNS Case Study

**Flame Stabilization in Turbulent Lifted Autoignitive Jet Flames.** In many modern combustion systems such as diesel engines and gas turbines, fuel is injected into an environment of hot gases, and a flame may be stabilized through the recirculation of hot air and combustion products. Under such conditions, a turbulent lifted flame is formed and the hot environment admits the possibility of autoignition, as a mechanism contributing to the stabilization of the flame base. In fact, recently autoignition was found to be the principal stabilization mechanism, revealed by the presence of hydroperoxy radical, an important ignition marker species. Unattainable from measurements, it was revealed by DNS on a terascale computer, the CrayXT3 at ORNL (see Fig. 4.6) [Yoo, Chen, Sankaran 2007]. A diverse fuel source, ranging from hydrogen to biofuels to traditional large hydrocarbons, will exhibit a wide range of ignition and flame characteristics, and thereby likely will affect the position downstream of the nozzle where the flame is stabilized, and sooting processes downstream of this position.



**Fig. 4.6.** Terascale DNS of a turbulent autoignitive hydrogen/air jet flame with 1 billion grid cells, 3.5 million cpu hours on CrayXT3 at ORNL. Volume rendering of hydroperoxy radical, a key ignition marker.

A lifted autoignitive turbulent slot jet flame configuration will be used to study flame stabilization mechanisms. The roles of autoignition, flame propagation, and organized fluid motion at the lifted flame base will be identified. Diverse fuels exhibiting a wide range of ignition characteristics representative of oxygenated and multistage ignition fuels will be considered. A parametric study with co-flow temperature and ambient pressure will be conducted. Comparisons with experimental data will be made, both at ambient pressure and at high-pressure from a lifted jet flame in a spherical bomb [Pickett 2005-07]. Of particular interest is the influence of turbulent transport on the slower, rate-limiting chemical reactions that occur in the negative temperature coefficient regime of multistage ignition fuels, such as n-heptane at high pressure [Liu, Hewson, Chen 2006]. This chemical kinetic-turbulent transport coupling may have a significant effect on the ignition timing, and hence, lift-off height. Particle tracking will be used to aggregate Lagrangian statistics associated with the highly unsteady autoignition processes. These and other statistics will be used to test closure hypotheses of advanced turbulent combustion models.

**Thermal and Concentration Stratification Effects on HCCI Combustion.** Homogeneous charge compression ignition (HCCI) engines are considered a viable concept as an alternative to diesel engines. In contrast to conventional compression-ignition (CI) engines, HCCI engines exploit a

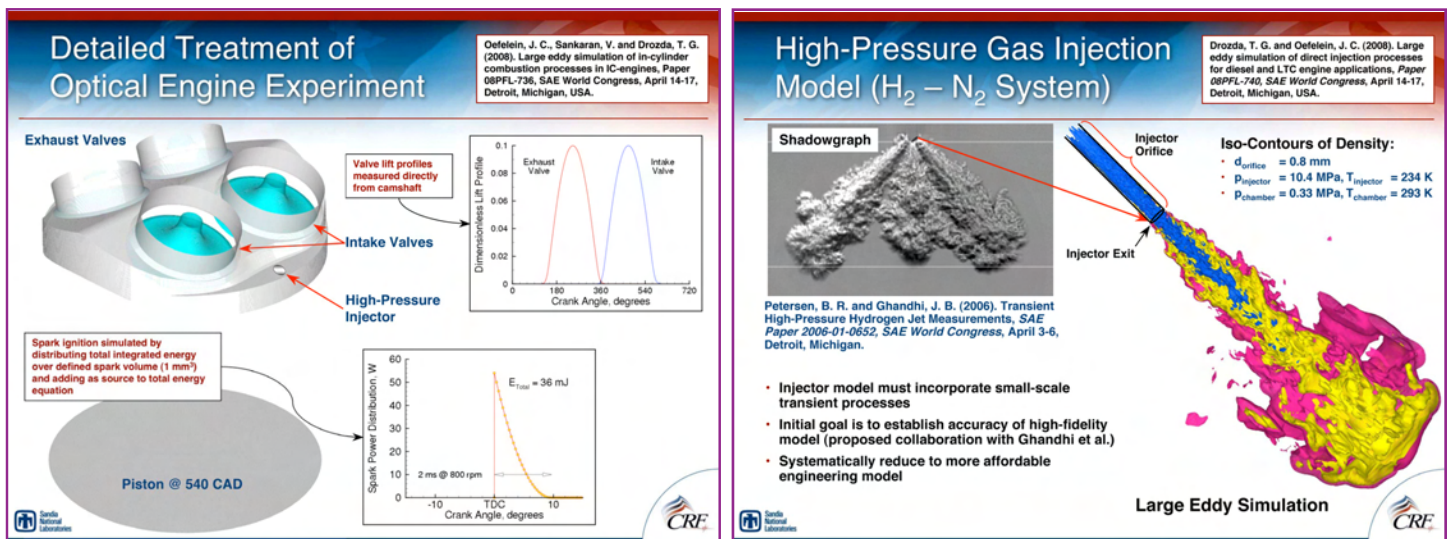
lean intake charge that is well mixed prior to combustion. HCCI engines may thus provide efficiency gains over spark-ignition engines, and lower emissions compared with CI engines. At present, the combustion mode in HCCI engines is not well understood, as both volumetric and front-like combustion modes can occur. A major challenge posed by this method of combustion is to control the heat release rate, and in particular, to provide a means to spread it out over several crank angle degrees, suppressing the occurrence of a rapid rate of pressure rise. One possible control strategy is to introduce inhomogeneities in the temperature or mixture composition, in order to produce the desired heat release.

We propose to study the influence of temperature and concentration stratification on characteristics of ignition and subsequent combustion in an HCCI environment. Algorithmic improvements will be pursued to accelerate the time to solution in this high-pressure regime. These involve implicit temporal filtering of the short acoustic wavelength, together with high-order methods for efficient utilization of the computational grid. The computational configuration corresponds to a three-dimensional, constant volume chamber with the initial turbulence and scalar fields prescribed by an energy spectrum. The temporal and spatial evolution of autoignition from an initial scalar spectrum at representative HCCI engine pressures will be obtained from 3D DNS, with detailed hydrocarbon mechanisms for ethanol, n-heptane, and a surrogate biofuel. The influence of turbulent mixing on ignition delay will be studied, particularly in the negative temperature coefficient regime, where the cool flame kinetics is slow by comparison to mixing. The DNS will also address the effects of stratification (i.e., thermal, concentration, dilution) on the ignition front structure, emissions and

heat release characteristics associated with mixed modes of combustion [Chen, Hawkes, Sankaran *et al.* 2006]. The resulting DNS data will be used not only to gain fundamental understanding and key parametric dependencies, but also to advance models for combustion in HCCI engines [Cook, Pitsch, Chen *et al.* 2007]. We will perform DNS benchmark comparisons with LES in the same canonical configuration.

#### 4.5.2 LES Case Study

The objective of this research is to combine a unique high-fidelity simulation capability, based on the Large Eddy Simulation (LES) technique, with the Advanced Engine Combustion R&D activities supported under the DOE Office of Vehicle Technologies. Resource allocations awarded under the INCITE program will enable a series of benchmark simulations that identically match the geometry and operating conditions of select optical engine experiments. The investment in time and resources will provide two significant benefits. After systematic validation of key processes using available experimental data, quantitative information can be extracted from the simulations that is not otherwise available. This information will provide (1) a detailed and complementary description of intricately coupled processes not measurable by experimental diagnostics, and (2) the information required for understanding and developing improved predictive models. The combination of detailed experiments and complementary simulations performed at the identical conditions, and the joint analysis of data that follows, will provide the basic science foundation required to systematically address the targeted research areas identified for Clean and Efficient Combustion of 21st Century Transportation Fuels.



**Fig 4.7.** Images on left show the LES grid surface topology and related details for calculations of the CRF optically accessible hydrogen-fueled IC-engine. Images on right show the corresponding high-pressure injector dynamics simulated in this engine, with results compared to the shadowgraph data of Peterson and Gandhi. Ports have been removed to illuminate valves but included in the calculations. Courtesy of J.C. Oefelein and T.G. Drozda, Combustion Research Facility, SNL.

As part of our long-term operating plan under the Advanced Engine Combustion program, needs and milestones in three critical areas have been established: (1) to continue a progression of LES studies focused on the CRF optically accessible hydrogen-fueled IC-engine ( $H_2$ -ICE), (2) to establish a parallel task focused on homogeneous-charged compression-ignition (HCCI) engines, and (3) to begin a series of supporting studies focused on the development and validation of multiphase combustion models with emphasis placed on direct-injection processes. The integrated set of research tasks includes an optimal combination of in-cylinder and out-of-engine studies to validate and understand key phenomenological processes typically present in IC-engine flow environments at the actual operating conditions.

***LES of the CRF Hydrogen-Fueled IC-Engine.*** This work is focused on benchmark simulations of the CRF (Combustion Research Facility) optically accessible hydrogen-fueled IC-engine, shown in Fig. 4.7, with emphasis placed on in-cylinder mixing and combustion processes, and comparisons with the available experimental data. Our primary goal is to provide a detailed understanding of injection strategies and the three-dimensional characteristics of in-cylinder combustion processes. The benchmark simulations will provide the most resolved high-fidelity results of in-cylinder combustion processes to date. Our analysis will focus on multidimensional turbulence-chemistry interactions and related cycle-to-cycle variations. Results will provide a clear understanding of the power density limitations associated with hydrogen-fueled engine cycles, maximum fuel efficiency,  $NO_x$  emissions, turbulent mixing characteristics, turbulence-chemistry interactions, and the effects of mixture stratification as a function of local processes over full engine cycles.

***LES of Direct Injection Processes for Hydrogen and Combustion Applications.*** This research is being conducted as a subset of the task outlined above. The goal is to establish benchmark simulations aimed at understanding high Reynolds number, high pressure, direct-injection processes for hydrogen and low-temperature engine applications (see Fig. 4.7, right side). Direct injection of hydrogen has emerged as a promising option for improving fuel economy and emissions in  $H_2$ -ICEs. Similarly, direct-injection of liquid fuels for low-temperature engine applications such as HCCI has many advantages. To understand these processes, we have initiated a series of benchmark calculations that identically match key experimental efforts. Fig. 4.7 shows an example result from LES, compared to shadowgraph data of Petersen and Ghandhi [Petersen, Ghandhi 2006; Petersen 2006]. This represents the initial starting point to study a series of high-pressure gas injectors designed for use in hydrogen-fueled

IC-engines [Drozda, Oefelein 2008]. We will also focus on issues related to liquid jet breakup, using the case studies provided by Pickett.

#### 4.6 CONCLUSION

The Workshop on “Basic Research Needs for Clean and Efficient Combustion of 21st Century Transportation Fuels” (2006) advanced one overarching grand challenge: to develop a validated, predictive, multiscale, combustion modeling capability to optimize the design and operation of evolving fuels in advanced engines for transportation applications. High-performance computing will play a central role in the development of multiscale combustion modeling, by considering the full range of scales from quantum up to continuum macroscale. In this new paradigm, direct simulations over several decades of scales will be performed on petascale computers, to provide detailed scientific understanding; and models that encapsulate the understanding will be developed to bridge the different ranges of scales.

Using multiscale simulation methods and continuum mechanics approaches, we have explored here the research potential of a set of case studies for the near term (18-month to 3-years) which require petascale computing. We aim to provide quantitative physical understanding of the underlying issues of aromatic chemistry and soot nanoparticle growth and oxidation, heterogenous reactive multiphase flow, and turbulence-chemistry interactions under low temperature, high pressure environments for diverse fuels.

These are systems with multiple scales and the challenge is to translate a rigorous description of processes occurring at small length scales or short time scales, into a model that can be used in calculations that do not resolve these scales. The length scales that are relevant in IC (in-cylinder combustion) engines range from Angstroms (atomic/molecular processes), to several nanometers (nm) (soot particles), to several micrometers (fuel droplets), to a fraction of a millimeter (smallest aerodynamic scales), to several centimeters (bore diameter), possibly up to meters (the size of the entire device); the range of time scales is commensurately broad. A dynamic range of  $\sim 1,000$  in length scales is a practical upper limit for current terascale computing; petascale computing and algorithmic advances may push this to  $\sim 10,000$ . Even with enormous increases in computing power it is unlikely that a single simulation approach would fully resolve all scales in the foreseeable future. Rather, a ‘divide and conquer’ approach will be taken, where a given approach can directly simulate  $\sim 3$ -4 decades in scales, and models are used to bridge between the scales and bootstrap to larger scales. Multiscale approaches will model the effects of unresolved

scales on larger resolved scales, and incorporate the relevant feedback mechanisms, which govern the different dynamic regimes of turbulent combustion.

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Sreekanth Pannala, Carlos Pantano,  
Angela Violi, and Al Wagner**

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# BASIC RESEARCH NEEDS FOR ELECTRICAL ENERGY STORAGE

## 5.1 INTRODUCTION

The United States continues to rely on imported, ever more costly fossil fuels for its primary energy source. In the past few months of 2008, the cost of imported oil has risen to more than \$120 a barrel. The impact hits hard in several ways. The rapidly rising cost of fossil fuels affects economic security, as there is a direct link between energy use and GDP. It affects the American and the world's environmental security, as continuing burning of fossil fuels increases carbon emissions and greenhouse gases. Reliance on foreign energy resources impacts U.S. energy security, when an insecure supply results in brownouts and blackouts in large urban centers, during peak demand times. Finally, our national security is affected during reliance on resources controlled by sometimes unfriendly foreign regimes.

Competition for dwindling resources is also creating a potential for conflict. The increasing demand for energy in the rapidly growing economies of China and India is raising concern that the U.S. can continue to obtain the energy supplies needed to support its economy and lifestyle. The demand for energy is expected to outpace the supply for the foreseeable future, creating steadily increasing competition. All of this contributes to an urgency to achieve reorientation in the way the U.S. acquires, distributes, and uses energy. The DOE's Basic Energy Sciences Workshop, "Basic Research Needs for Electrical Energy Storage," held April 2-4, 2007, explored many of the fundamental issues which must be addressed if the U.S. is to achieve a reorientation of acquisition, storage, distribution and energy use.

Fundamentally, the problems are:

- a rapid, global growth in demand
- new, complex challenges of production, distribution and consumption sectors in the 21st century
- vulnerability of energy supplies and distribution, in a time of terrorism and warfare in oil-rich areas of the world
- an aging electric grid and pipeline infrastructure
- concentration of energy assets in the hands of governments who use energy as a geopolitical weapon
- and, finally, evidence of dependence on fossil fuels has a negative impact on climate and that adverse climate change is accelerating

In the past two years, public awareness of energy issues has increased. "Energy and the environment have emerged as

among the most potent forces reshaping the global economy in the 21st century," the Council on Competitiveness reported in September 2007. Investment in research and development is the best way to achieve energy assurance. And yet current federal spending on R&D is well below the potential market value. Current federal energy R&D funding is 0.15-0.4% of the U.S. energy expenditures (depending on how energy R&D is defined). That is ~5 times smaller than it was in 1980, so that 1% of U.S. energy expenditures in 2007 would correspond to \$10 billion a year energy R&D funding.

Technological innovation offers the best opportunity to balance energy with national economic and environmental security. Current electrical energy storage technologies, based on chemical energy storage (batteries) and electrochemical capacitive (EC) energy storage, fall short of meeting future needs. Rechargeable batteries have limited energy storage capacity and slow recharge cycles that restrict their use. Batteries also have limited lifetimes because of degradation of their electrode materials during charge/recharge cycles. Electrochemical capacitors (ECs) are related to batteries, but they store energy directly as charge, whereas batteries store energy in chemical reactants capable of generating charge. ECs have higher discharge rates, and thus higher power performance, than batteries because their charge is not limited by kinetics and mass transport, as is the case with batteries. Because ECs store charge physically rather than chemically, these devices have longer lifetimes than batteries. Among notable innovations for future energy storage are electric double layer capacitors (EDLC), also known as supercapacitors or ultracapacitors. These have received much attention recently because of their power delivery performance, which can fill the gap between dielectric capacitors and traditional batteries. These systems are thought to play an important role in complementing or replacing batteries in the energy storage field.

## 5.2 ROLE OF PETASCALE COMPUTING IN ELECTRICAL ENERGY STORAGE

Maximizing the utilization of solar and wind energy and the use of electric vehicles will require efficient electrical energy storage (EES), far exceeding the capabilities of available energy storage technologies. Revolutionary improvements are needed to level the cyclic nature of intermittent renewable sources and to enable the progression from electric vehicles to plug-in hybrids or all-electric vehicles.

Meeting this challenge will require transformational advances in electrical energy storage technologies and in the underpinning materials and chemical sciences. It will require significant advances in the fundamental understanding of nanoscale phenomena; and in the predictive modeling of complex, multicomponent systems, over multiple length and timescales. To advance the electrical storage science agenda, the DOE's Basic Energy Sciences workshop, "Basic Research needs for Electrical Energy Storage," was held April 2-4, 2007. The focus was to identify new, emerging, and scientifically challenging areas in materials and chemical sciences with the potential for significant impact on electrical energy storage technologies.

Progress in the electrical energy storage science field can benefit significantly from an integrated approach involving experimental efforts and complementary theory, modeling, and simulation. Such an approach will provide the necessary insight into novel charge storage mechanisms that will lead to new battery and capacitor systems. Computer modeling and simulation can help predict trends, provide guidance for experiments, and provide the ability to address a broader range of materials systems and compositions. Large multiscale computations can provide fundamental understanding of processes such as phase transitions in electrode materials, ion transport in electrolytes, charge transfer at interfaces, electronic transport in materials, and the evaluation of complex systems

Chemical energy storage science seeks materials and mechanisms that store more energy per unit volume, tolerate thousands of charge/discharge cycles, have ultra-long lifetimes, are safe, and come at low cost. Researchers seek a factor of >3 in energy density, and 100 in recharge time. Batteries are dynamic systems that change with every charge/discharge cycle. The apparently simple interface between electrode and electrolyte is in fact a complex set of phases which change with time.

### 5.2.1 Understanding the Mechanisms and Kinetics in Chemical Storage

The fundamental challenge of chemical energy storage science is that there is a knowledge gap in the basic understanding of the mechanisms and kinetics involved in chemical storage. We need improved understanding of the correlation of interface structure with reactivity, and of the molecular-level ion intercalation or reaction at the solid-liquid or gas-solid interface. We do not now know how structural defects, such as dislocations, change during cycling, nor their relationship to fracture formation/prevention, although work is proceeding [Gabrisch, Yazami, Fultz 2002]. In the case of  $\text{LiCoO}_2$ , researchers seek to find out to what extent thermodynamics and kinetics of ion reactions differ between nano and bulk.

Novel ideas are needed to handle the nanoscale processes (10-150 nm) relevant to technology.

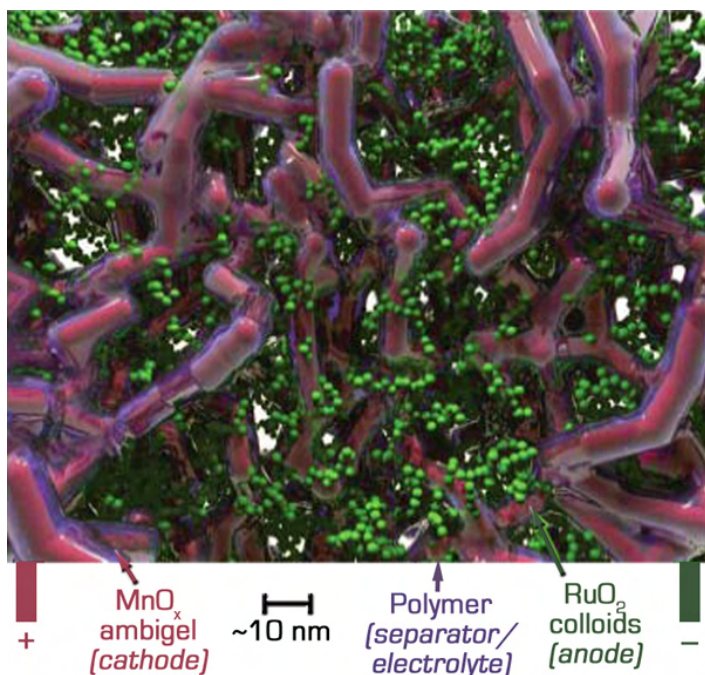
Electrochemical capacitive storage includes supercapacitors (also known as electric double-layer capacitors) and pseudocapacitors (that exhibit characteristics of both electric double-layer capacitors and batteries). These capacitive storage systems offer high power density, fast charge/discharge cycles, and high reliability for thousands of cycles. Capacitive systems have lower energy densities than batteries, and significant advances are needed to meet the requirements for efficient electrical energy storage.

The electrochemical double-layer capacitor stores charge physically using two electrodes immersed in an electrolyte. Pseudocapacitors bridge the gap between capacitors and batteries, incorporating attributes of both. Electrochemical capacitors (ECs) offer versatile solutions for harvesting and regenerating energy. However, the fundamental understanding of ECs is still rudimentary. An understanding of charge storage mechanisms, of tailored multifunctional materials, and new electrolytes is required. Beyond this, at a more fundamental level, researchers seek to understand the key issues that underlie capacitive storage science itself, issues involving interfaces, dynamics and charging. Computing approaching petascale is important in furthering such understanding of fundamental energy storage issues. Specifically needed:

- *Reverse Monte Carlo simulations to understand the relationship between pore size and interacting species.* What is the equilibrium structure of ions and solvent in confined geometry? How would pore size, surface area and surface chemistry or functional group affect capacitive storage?
- *Multifunctional nano architectures to enable* ionic and electronic conductivity; facile permeation of electrolyte; effective charge storage functionality
- *In situ tools to characterize electrode-electrolyte interface during charging/discharging,* to develop and implement techniques to monitor spatial resolution from atomic to mesoscopic, temporal resolution down to femtoseconds, and changes in structure and composition

**Chemical Energy Storage:** Present day electrochemical cell structure consists of a positive electrode, an electrolyte separator, and a negative electrode. The future promises a 3-D device, consisting of self-assembled nanoscale-electrochemical cell structures containing multifunctional components. In Fig. 5.1, the cathode is a  $\text{MnO}$  ambipol, the





**Fig. 5.1** For energy storage, electrochemical batteries offer novel designs and strategies. A 3-D self assembled electrochemical cell structure containing multifunctional components. Battery has a MnO ambigel cathode, RuO<sub>2</sub> colloids anode, and a polymer as separator/electrolyte. Courtesy of H. Feil, Philips Research Laboratories, Eindhoven, The Netherlands.

separator electrolyte is a polymer, and the anode is composed of RuO<sub>2</sub> colloids. Such complex chemical energy storage requires research into solid electrolyte interfaces (SEI) and interphases. We need new strategies for design of novel electrodes with tailored architectures and self-repairing mechanisms. We need new electrolytes with stability at > 4 V, and a tailored solid-electrolyte interphase (SEI), where electrodes and electrolytes can be designed as a system. All of this requires multidimensional, *in situ* characterization tools and the kind of computational modeling that only HPC can provide.

**Capacitive energy storage** research is focused both on materials for storage and on the electrolyte interactions. In conventional storage materials, particle size, pore size, and the pore structure of the electrode all are heterogeneous and this limits performance. New multifunctional materials are needed for electrical charge storage, using multiple mechanisms. Researchers hope to design materials with tailored pore sizes and architectures, functionalized pores specifically designed for higher charge density. To achieve their goals, they hope to use computational tools optimized for capacitive storage. They also seek an improved understanding of bulk phase electrolytes, electrolyte/electrode interactions,

electrodes designed to enhance pseudocapacitance, and *in situ* characterization.

**Rational materials design through theory and modeling.**

Researchers need the computational capacity to do combined mechanical, electrical, chemical, and transport simulation so that they can achieve a fully predictive modeling of performance and stability of the battery and capacitive systems. Computational simulation will further the understanding of the kinetics of phase changes, electrochemistry at the nanoscale, charge transport in mixed conductors, computational materials design, transport and evolution in electrode microstructures, and structure and role of reaction interfaces.

Work now underway supports new and expanded studies in:

- Nanoscale materials and chemical sciences
- Diffusion and transport in fluids and ionic media
- Liquid / solid / gas interfaces
- Multiple electron redox systems
- Intercalation in electrode materials

The key questions in energy storage research are:

- Can we develop a fundamental understanding of electronic and ionic transport in solutions and electrodes?
- Can we understand the physical and chemical processes at the electric double layer and at the electrolyte/electrode surface?
- How do we control nanostructures in multicomponent, electrode/electrolyte systems?
- How can we model battery and capacitive systems across length and time scales?

**With proper funding, in one year** researchers can produce prototype models of simple capacitive and battery systems. Experiments with model systems will demonstrate both the understanding and the techniques to address issues such as diffusion, EDL, interface, and salvation phenomena. **In three years**, researchers can produce competent models that will yield results to guide experimental directions. Experiments will demonstrate promising approaches to achieve significant improvements. **In five years**, researchers would have the predictive capability for new systems, and credible approaches to transformational improvements.

### 5.3 CARBIDE-DERIVED CARBON AND NOVEL OPPORTUNITIES FOR ENERGY STORAGE

Supercapacitors are devices that store electrical energy electrostatically and are used in applications where batteries cannot provide sufficient power or charge-discharge rates. Until now their higher cost compared to batteries with similar performance has limited the use of supercapacitors in many household, automotive and other cost-sensitive applications. Porous carbon materials are widely used as supercapacitor electrodes. Extraction of metals from carbides can generate a broad range of potentially important carbon nanostructures. They are known as Carbide-Derived Carbons (CDC). The CDC structure depends on the crystal structure of the carbide precursor as well as on process parameters, including temperature, time, and environment. Extraction of silicon, boron, aluminum, zirconium or titanium from their respective carbides by chlorine at 200-1200C results in the formation of micro- and mesoporous carbons, with a specific surface area up to 2000 m<sup>2</sup>/g. CDC technology allows the control of carbon growth on the atomic level, monolayer by monolayer, with high accuracy. The pore size to ion size ratio determines the efficiency of electrochemical energy storage devices.

Today, batteries are ubiquitous, but supercapacitors are becoming more advanced. The latter have higher power density than existing technologies, the ability to complement batteries in hybrid power systems and enable other high power applications. In supercapacitors, the fact of increasing energy density is paramount, and the key is to be able to understand and predict electrode and electrolyte properties. Electrochemical double layer capacitors (EDLC) are based on activated carbon. Electrical energy storage research wants to design novel storage materials for these, which have controlled structure and porosity and controlled surface functionality and charge. The challenge is to design material architectures that have high capacity, and to do so, we must understand pore structure at the nanoscale, and ion size influences on charge storage [Choi, Blomgren, Kumta 2006]. Traditional electrolytes, aqueous or organic, are corrosive and cause concerns about toxicity and safety. Ionic liquid electrolytes are safer, but conductivity is low. What is needed for new energy storage solutions is aqueous and non-aqueous electrolytes with immobilized matrix, produced from sustainable sources, featuring high ionic conductivity, chemical and thermal stability, and a large electrochemical stability window (>5V). Such materials must be non-toxic, biodegradable, and/or recyclable. What is sought is exceptional performance with long device lifetime.

There are currently four modeling and theory methods in use in computational electrical storage science: equivalent

circuit models, continuum models (Poisson-Nernst-Planck equations), atomistic models (Monte Carlo, molecular dynamics), and quantum models (*ab initio* quantum chemistry and DFT). Very few of these methods have been applied to supercapacitors. The theoretical work on transmission line models is useful for an understanding of what impedes energy transmission through the material, but offers no predictive capacity. Recent efforts have been made to better model materials at the microstructure. Fractal models are being used to describe microstructure and transmission line equations to describe blocking electrodes [Eikerling, Kornyshev, Lust 2005]. There are a large number of variables that must be included, and first principles calculations are needed to resolve the model parameters. At the same time researchers have made advances in understanding EDLC, with molecular dynamics (MD) simulations which show a picosecond response to a sudden change in surface charge in a carbon nanotube.

#### 5.3.1 Carbide-Derived Carbon (CDC) Case Study

Experimentalists have achieved precise control over the structure and pore size distribution in CDC. This material is of particular importance for novel energy storage applications, as CDC has a carbon porosity of 50%. CDC also has a network of open pores, it can take various forms, numerous carbides can be used, and the linear kinetics can be grown to a large thickness. Researchers have succeeded in modeling the interface between carbon and silicon carbide (SiC), an important wide band gap material for novel energy storage [Cambaz, Yushin, Gogotsi *et al.* 2006], to better understand what occurs at the atomic level. In studying the carbide lattice, the template for CDC, it was found that positions and spatial distribution of carbon atoms in the carbide affect the structure and the pore size of CDC. The pore size distributions were calculated using a NL DFT model [Yushin, Nikitin, Gogotsi 2006]. Carbide-derived carbon is an attractive material for energy storage, as the choice of starting material and synthesis conditions gives an almost unlimited range of porosity distributions. In CDC the pore volume is tunable, capable of being controlled between 55 and 85%. Carbon remains amorphous until at least 1000C. The question now is, can the carbon pore structure be predicted [Yushin, Nikitin, Gogotsi 2006].

With the recent development of porous carbons with controllable pore size, the basic question arises: What are the stable pore sizes and shapes in porous carbons at the nanoscale? The size and shape of pores have a profound effect on the energetics of adsorptive storage, a problem of great potential technological importance. Because of the nanosize of the pores, the chemical details of the environments matter, and therefore quantum mechanical treatment is important

and necessary at the atomic level. The challenge for computing is the multiple scales, the statistical distributions of the pores and their contents and the fact that multiple components (electrode, ions and solvents) are all essential for the functioning electrode [Gogotsi *et al.* 2005; Laszlo, Kertesz, Gogotsi 2007].

In this area there are important new findings. Conventional wisdom says that increasing the porous carbon surface area is good only insofar as the pores are large enough to accommodate the ion and its solvation shell. But recent research shows an anomalous increase in carbon capacitance at the pore size below 1 nm (Chmiola, Yushin, Gogotsi, Portet, Simon, Taberna 2006). Further research into the state of the ions in the subnanometer pores confirms this. In studying capacitance arising from the anion and cation separately, it was found that in all cases, greater than 85% of pores were less than the diameter of the electrolyte ion and the shell of the associated solvent molecules, though the average pore size was still greater than or equal to the size of the bare electrolyte ion. The results show that the smaller anion has larger capacitance, but researchers must discover why the capacitance increases with decreasing pore size. They must discover if the energy required to remove solvent molecules from an ion (supplied by the external circuit) can be recovered during discharge (Chmiola, Largeot, Taberna, Simon, Gogotsi 2008 *in press*).

Furthermore, researchers working with the small pore model still are not able to predict behaviors at the nanoscale. Model systems for graphite and nanotubes are needed, with several variables, as carbon structure is affected by temperature, oxygen pressure, the rough state of the surface, surface chemistry and the heating rate. There also are research questions

about the hydration structure of ions in bulk ionic solution, and whether there is an electrical double layer in the carbon pore wall at the nanoscale (Figs. 5.2-5.4). Further questions arise about capacitance in ionic liquids. Research has confirmed that ionic liquids have larger capacitance in carbons with smaller pore size and the question then arises, how to match a porous electrode with an ionic liquid (Largeot, Portet, Chmiola, Taberna, Gogotsi, Simon 2008 *in press*).

*The role for HPC in energy storage research is to model filled porous carbon structures, focusing on the energetics of a series of filled pores. Carbon nanotubes would serve as ideal models. We would study the variation of ions and solvent molecules, the relative stabilities with respect to*

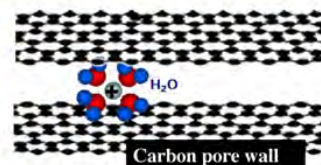
## Restricted Hydration Structure

### Hydration structure of ions in bulk ionic solution

Y. Marcus, *Chem. Rev.* 88, 1475 (1988)

H. Ohtaki, T. Radnai, *Chem. Rev.* 93, 1157 (1993)

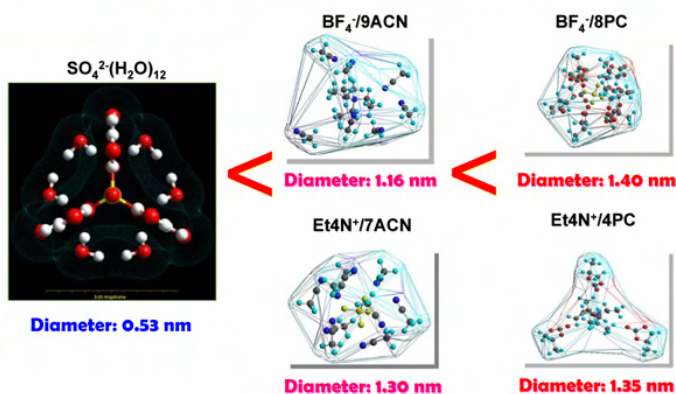
### Ionic Structure of "NANOSOLUTION"



### Electrical double layer in nanoscale

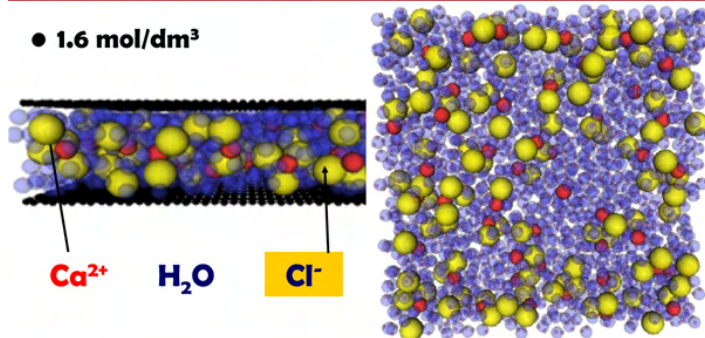
*Fig. 5.3 Schematic showing a single solvated ion placed in a slit pore between two graphene sheets. The coordination number of an ion (the number of solvent molecules) in a narrow pore is smaller than that in solution.*

## Solvated Ion Size in Electrolytes from Computer Simulation



*Fig. 5.2 Solvated ion size in electrolytes from computer simulation, showing a sulfate ion in water and tetraethylammonium and tetrafluoroborate ions in acetonitrile and propylene carbonate solvents.*

## Snapshots of Molecules and Ions



*Fig. 5.4 Snapshot of 1.6 M  $\text{CaCl}_2$  solution in water placed in a slit pore between two graphene panes. All graphics this page courtesy of Katsumi Kaneko, Hirofumi Kanoh, Tomonori Ohba, Natsuko Kojima, Department of Chemistry, Graduate School of Science, Chiba University.*

empty pores, and pores filled with solvent only, and the effect on the work function of the pore walls (Figs. 5.2-5.4). We would study the affinities of various pore shapes for solvents vs. for solutes. These would require primarily quantum mechanical calculations. The difficulty is that competing demands would be put on the modeling by the electrochemical potential and by redox processes at the surface, by the role of specific solute ions, and the role of the solvent. These must be treated together and for different pores.

**There are several theory and modeling challenges.** These include the structure and behavior/properties of solvent and ions inside pores; the problem of ion transport near electrified surfaces and inside mesopores and micropores, to predict capacitance energy and charging dynamics; wetting phenomena and desolvation of ions at high voltages and high rates; developing modeling tools that include both chemistry and dynamics (e.g., *ab initio* MD and electronic structure of carbon); the modeling of new capacitor electrolytes (e.g., ionic liquids and new solid electrolytes); identifying model experimental systems for validation of simulations (e.g., ion transport in a carbon nanotube); and multiscale modeling of electrochemical capacitors (electronic interfacial structure → pore-scale dynamics → charging profiles).

In mathematical theory (beyond equivalent circuits), we must derive nonlinear transmission line models for large voltages, use modified Poisson-Nernst-Planck equations (steric effects, correlations), and continuum models coupling charging to mechanics. For the physics and chemistry of solvent and ions in nanopores, we must develop accurate models for MD and MC simulations, explore the entrance of ions into nanopores—desolvation energy and kinetics—and study ion transport, wetting, surface activation, and chemical modification. For the physics and chemistry of electrode materials, we must study electron and ion transport in capacitor electrodes; and develop the theory of capacitance of metal ox-

ides and conducting polymers. Finally, to achieve validation against simple model experiments, we must study ordered arrays of monodisperse pores, single carbon nanotubes and use vibrational spectroscopy, neutron and X-ray analysis of ions and solvent in confined spaces.

## 5.4 OPPORTUNITIES IN ENERGY STORAGE

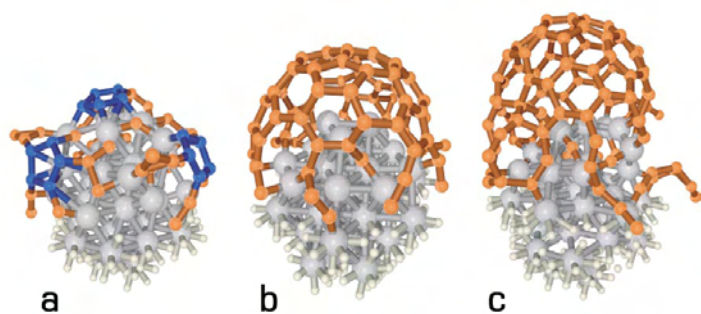
Batteries are complex, multiphase systems composed of chemically reacting ionic species, organic, inorganic, and metal oxide materials, with length and timescales extending from the atomic to the macroscopic. From a computational perspective their study requires state of the art methods including the ability to calculate entropy, free energy, and hydrophobicity. These are active research topics which share many of the features and challenges of biological cells.

The DOE's BES Workshop on "Basic Research Needs for Electrical Energy Storage," held April 2-4, 2007, outlined the basic research agenda for novel energy storage solutions for the 21st century. To find new storage solutions, researchers must work to understand the thermodynamic properties of storage batteries at the nanoscale, liquid-solid interfaces, complex chemical reactions, intercalation, ionic conductivity and ion channels, the mechanics of adsorption and every facet of surface structure. These are all problems for which high-performance computing (HPC) is ideally positioned to give researchers the guidance they need.

### 5.4.1 Multiscale Modeling

In materials and chemical science, there is by now a hierarchy of standard tools, all of which will benefit from HPC. These are quantum chemistry using *ab initio* techniques and/or density functional theory, Car-Parrinello or First Principles molecular dynamics (MD), force field MD using codes such as AMBER and CHARMM, Heisenberg models of magnetic materials, and continuum methods using elasticity theory or micromagnetics. All are promising approaches for understanding the atomistic processes in energy storage, and with computational advances moving quickly to petascale, the methods promise success in the quest for novel storage solutions.

Much of the work in energy storage is at the nanoscale and there is a remarkable confluence of the sizes of nanoscale systems whether inorganic, such as the recently fabricated 7x7x7 nm<sup>3</sup> iron nanocubes [Dumestre *et al.* 2004], or proteins such as Cel6A, an enzyme which breaks down cellulose [T. A. Jones *et al.* 1999].



**Fig. 5.5** An *ab initio* molecular dynamics simulation of the growth of carbon nanotubes on a 1 nm Fe catalyst. Early stage (a), snapshots of the growth process (b), (c). Reprinted with permission from Raty, Gygi, and Galli (2005) *Phys. Rev. Lett.* 95, 096103. Copyright 2005, The American Physical Society.

Studying such systems at the quantum level is a daunting problem. A single electron system requires solution of a partial differential equation in 3 variables. For  $N$  particles it is  $3N$  variables. For  $N$  interacting electrons the computational effort scales exponentially with  $N$ . The best we can do currently is  $\sim 20$  sites by exact diagonalization or 1000 sites by quantum Monte Carlo techniques (with limited basis sets). The most likely advances in this area are to further develop density functional theory (DFT) approaches, which at worst scale as  $N^3$  and in some cases linearly with  $N$ .

Molecular Dynamics (MD) is another important research tool for understanding the energy storage activity at the nanoscale. Ions are described by classical mechanics (Newton's laws,  $F=Ma$ ) using empirical or semi-empirical force fields which describe long range (Coulomb, Lennard-Jones), and short range (Bond stretching, bending) forces. Codes such as CHARMM and AMBER are available for biological as well as inorganic systems. A recent simulation of 106,189 atoms of Aquaporin [Tajkhorshid *et al.* 2002], which required several weeks of computer time for 10 nanoseconds of simulated time, could be run for microseconds of simulated time in a few weeks on a modern system such as the Blue Gene/L [Deng *et al.* 2004].

In first principles molecular dynamics the forces are not empirical but calculated 'on the fly' using DFT. An example of this technique is a recent simulation of the growth of carbon nanotubes on iron [Raty, Gygi, Galli 2005]. See Fig. 5.5.

In summary, the research needs for successful simulations include:

- ability to span length and timescales
- adequate planning to take advantage of petaflop systems
- standards for data sharing
- interoperative codes which can share data
- genuine community effort
- data repositories, data mining

If we receive what is needed, the opportunities for success in developing new materials are there. It is a golden opportunity, as the problems to be resolved are at the very edge of where these research fields are now approaching. Ideally, computational advances would be coupled to the data repositories and the computational arm of the research world would combine with experimental probes such as cryo-em, which are now underway.

*Gil Weigand, J.W. Davenport, Yury Gogotsi, and James Roberto*

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# FIVE RESEARCH NEEDS IN THE GEOSCIENCES

## 6.1 INTRODUCTION

Serious challenges must be faced in this century as the world seeks to meet global energy needs, reduce emissions of greenhouse gases to the atmosphere, and maintain a safe and sustainable environment. To meet these challenges, it will be necessary to capture and sequester a substantial fraction of the anthropogenic-produced CO<sub>2</sub>, develop safe and effective storage of nuclear wastes, and effective remediation strategies for contaminants that may affect groundwater and other resources. In fact, the challenge to store the byproducts of our energy production technologies safely and securely, especially CO<sub>2</sub> and nuclear waste, remains one of the key obstacles to developing a new energy agenda for the nation. As a result, the ability to predict the transport of wastes and associated contaminants in subsurface geologic environments is one of the most important and daunting challenges facing the DOE.

Geologic formations are composed of complex natural materials and to address these requires a coupling of experimental and theoretical approaches across a broad range of spatial scales (from molecular to field), and across temporal scales ranging upward to geologic time. To meet these challenges the Office of Basic Energy Sciences, Geosciences Research Program sponsored a workshop, “Basic Research Needs in Geosciences: Facilitating 21st Century Energy Systems,” from February 21-23, 2007 [DOE Office of Basic Energy Sciences 2007]. The purpose of the workshop was to define the scientific challenges which must be addressed in the area of geologic sequestration of both CO<sub>2</sub> and nuclear wastes. Although this workshop focused on grand challenges and priority research directions for the disposal of CO<sub>2</sub> and nuclear waste, many of the scientific challenges are implicit in other areas of importance to the Office of Science, such as subsurface environmental remediation [“Environmental Remediation Sciences Program Strategic Plan: Providing the scientific basis to solve the DOE’s intractable problems in environmental remediation and longterm stewardship,” September 2007].

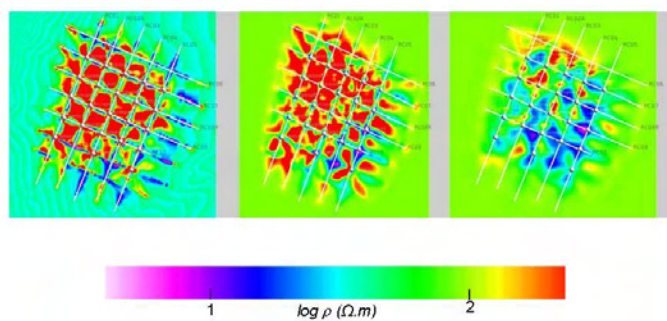
We present five priority research directions (PRDs) or scientific grand challenges (GCs) outlined in the Basic Research Needs (BRNs) for Geosciences, followed by specific examples of how high performance computing (HPC) leading to petascale can help address them.

## 6.2 GC: INTEGRATED CHARACTERIZATION, MODELING AND GEOLOGIC SYSTEMS

Advances in knowledge of geological processes will help to build better models and such knowledge, when high resolution geochemical and geophysical measurements are integrated into the models, will lead to progress in subsurface computational simulation.

### 6.2.1 Geophysical Imaging Case Study

Over the last 17 years, researchers have been developing techniques to construct and appraise solutions to the 3D geophysical inverse problems for electrical conductivity imaging. Great progress has been made to develop large-scale solutions to such problems, including waste site and vadose zone characterization, and geothermal and oil and gas reservoir exploration and monitoring. The philosophy has been to develop 3D inverse or imaging solutions with as much rigor as possible and to avoid approximations in which speed sacrifices accuracy of solution. To achieve this goal, the exploitation of massively parallel computing is of critical importance, employing conjugate gradient-type, quasi Newton, Gauss-Newton and Krylov subspace solution techniques, including a variety of constraints to stabilize the inversion/imaging process.



**Fig. 6.1.** CSEM (Compact Source Electromagnetic Imaging) offshore the Brazil Coast, to map subsurface hydrocarbons. The images show integrated resistivity depth sections. Average resistivity was computed over three depth ranges. At left, water bottom to 500M below mud line (BML); at center, interval 500 to 1500M BML; at right, interval 1500 to 2500M BML. Resistivity is rendered on a base 10 log scale. Courtesy G. Newman.

To cope with the typically large computational requirements of the 3D imaging problem, new strategies exploit computational parallelism and optimized finite-difference meshing. A recent imaging experiment utilized 32,768 tasks/processors on the IBM Watson Research Blue Gene/L (BG/L) supercomputer. Imaging of a large-scale geophysical field data set was successfully completed over a 24-hour period, which previously required more than four months of computing time on distributed clusters, utilizing 1024 tasks on an Infiniband fabric. While delivering a satisfactory gross-scale image for the depths of interest, the experiment provides important evidence for the necessity of discriminating between horizontal and vertical conductivities for maximally consistent 3D conductivity imaging experiments. More importantly, the time to solution speed at which this result was delivered is critical to the success of the research process.

It is now believed that the point will soon be reached at which any further improvement in subsurface 3D image reconstruction will require multiple types of geophysical data measurements running together, in particular seismic and electromagnetic (EM) data (Fig. 6.1). Joint imaging of EM and seismic data has much appeal, especially when a model of a property of the rock can be incorporated into the inversion process to describe flow and transport properties of the subsurface (porosity, saturation and permeability). These properties are often of much greater interest than the geophysical parameters. However for such joint geophysical imaging experiments, the computational requirements are enormous. It is here that further exploitation of HPC for joint geophysical imaging will be critical, if the technology is to help solve some of the major problems facing society today, including waste legacy issues and energy and environmental security. Specific applications include environmental site characterization and monitoring, safe and verifiable sequestration of CO<sub>2</sub> to mitigate effects of global warming, and a new technology for locating bypassed hydrocarbon and geothermal resources (Fig. 6.1), which are difficult to detect with existing 3D geophysical imaging technologies. Each year, faster computing resources are being made available to the scientific community through government agencies and industry. The petaflops computing barrier will be breached in the next year or two, and the exaflops will soon follow. This will directly affect the size, scale and complexity of geophysical imaging problems that can be addressed.

### **6.3 PRD: MINERAL-WATER INTERFACE COMPLEXITY AND DYNAMICS**

The fundamental objective of this PRD is to translate a molecular-scale description of complex mineral surfaces into thermodynamic quantities, for the purpose of linking that with macroscopic models. Researchers would follow in-

terfacial reactions in real time, in order to understand how minerals grow and dissolve and how the mechanisms couple dynamically to changes occurring at the interface.

#### **6.3.1 Molecular Scale Simulation Case Study**

Molecular scale computation is an essential component of geochemistry, both for rate problems and for reaction thermodynamics. Because geochemical environments involving interfaces and water are so complex, it is almost always impossible to unambiguously determine key chemical species, the strengths of their interactions, and the rates of elementary reactions that form the foundations of any modern understanding of the relationship between structure and reactivity. Early methodologies tended towards a division of labor between first-principles quantum-chemical specialists who computed potential surfaces, and molecular dynamics specialists who parameterized those surfaces and used them to run molecular dynamics (MD) calculations.

Geochemical communities have responded to increasing computational power, which has allowed electronic structure-based computations to be performed on problems that a decade ago were only accessible using parameterized force fields. Essential aspects of this change were driven not only by faster processors, but also by algorithmic investments (such as NWChem) that converted computational geoscientists from single to multiple processors (typically 50-100). Another key aspect of this progress has been the development of density functional methods (DFT), which allow the community to do reasonably accurate calculations on transition metal systems and also to do first-principles MD. This has opened up much of the periodic table to reaction dynamics approaches, whereas previously researchers were restricted to small subsystems where reactive force fields had been parameterized.

At the same time, increasing availability and expertise in parallel processing resources, (including DOE user facilities such as NERSC and the Molecular Science Computing Facility [MSCF]), have greatly expanded simulation timescales for classical molecular dynamics. Whereas five years ago it was routine to accurately resolve the potential of mean force for a surface complexation reaction, it is now possible to routinely evaluate barrier-crossing efficiencies, allowing determination of quantitatively precise reaction rates. Moreover, it is possible to run a sufficiently high number of repetitions to evaluate the pressure- and temperature-dependence of the reaction rates. This allows determination of activation parameters that can be compared directly with experimental measurements. In the coming peta- and exa-scale era, when geochemists routinely will be using 1,000s to 10,000s of cores, it is easy to see the same swap occurring between computation using parameterized force fields



and first-principles methods, as has happened in the previous decade. Whereas now we calculate water exchange rates and activation parameters on Al-oxide nanoparticles using parameterized methods, it seems clear that in the peta- and exascale years, DFT methods will be used to calculate water exchange rates and activation parameters on other nanoparticles with a more complex electronic structure. These calculations will be far easier and more accurate than those performed with parameterized force fields now, because there will be no awkward parameterization procedure.

The community will soon face some of the limitations of density functional theory. Particularly as the focus is more on quantitative prediction of reaction rates, the DFT-based barriers will not have real predictive capability. One area of particular importance to geochemistry is the chemistry and physics of water, where Car-Parrinello DFT approaches have been used. Going beyond these methods in large aqueous systems requires immense computing resources, but this seems to be necessary for investigators who require a truly accurate understanding of solvation.

Other priority research directions, grand challenges or cross-cutting themes in which molecular scale simulation provides important insight are: Microscopic basis of macroscopic complexity (PRD), computational thermodynamics of complex fluids and solids (GC), nanoparticulate and colloid chemistry and physics (PRD), the microscopic basis of macroscopic complexity (CC), and thermodynamics of the solute-to-solid continuum (CC).

#### **6.4 GC: SIMULATIONS OF MULTISCALE GEOLOGIC SYSTEMS FOR ULTRA-LONG TIMES**

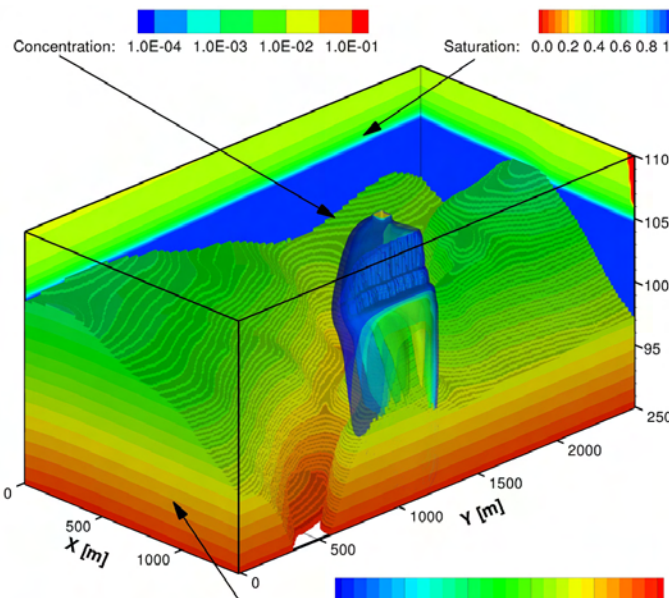
Anthropogenic perturbations of subsurface storage systems will occur over decades, but predictions of storage performance will be needed that span hundreds to many thousands of years, timescales that reach far beyond standard engineering practice. “The latter is an unprecedented requirement dictated by the need to sequester materials in the subsurface for hundreds to thousands of years,” notes the BES workshop report, “Basic Research Needs for Geosciences: Facilitating 21st century Energy Systems” of February, 2007. “Mathematical and numerical frameworks must capture the stochastic nature of geologic media and the non-linear dynamic physical and chemical processes that occur in geologic formations and must recognize that subsurface systems may or may not be in equilibrium. Conceptual model development from the pore scale upward as guided by observations and data from laboratory and field experiments will be used to define a mathematical framework

amenable to computation.” Achieving the ability to simulate the performance of subsurface storage systems requires a major advance in modeling capability that will accurately couple information across scales, i.e., account for the effects of small-scale processes on larger scales, and the effects of fast processes as well as ultra-slow evolution on long time-scales. The ultimate objective is reliable, long-term predictions of subsurface processes that span multiple spatial and temporal scales, with significant improvement in the quantification of uncertainty.

##### **6.4.1 Multiscale Reactive Transport Modeling Case Study**

Current understanding of reactive processes in the subsurface is that a strong dichotomy exists between scales in field and laboratory. An example is mineral reaction rates which differ by many orders of magnitude between the two scales. Reasons for this discrepancy may be attributed to multiscale processes, close to equilibrium reaction rates, and modifications in the reacting mineral surface caused by natural processes over long timespans, which lead to a reduction in the field rate, compared to the lab. As long as this dichotomy persists, it will be difficult to impossible to carry out predictive simulations with sufficient confidence. For example, predictions of changes in minerals in the subsurface caused by CO<sub>2</sub> injection and increased acidity will necessarily have a high degree of uncertainty, because of poor knowledge of mineral reaction rates. Unfortunately the physical and chemical complexity of these sites overwhelms the capabilities of even the most state-of-the-art groundwater models. Of particular concern is the representation of highly heterogeneous stratified rock/soil layers in the subsurface and the biological and geochemical interactions of chemical species within multiple fluid phases. Other challenges facing subsurface groundwater modeling are the difficulty in characterizing the system being modeled, upscaling from pore to continuum and from laboratory to field, and developing new, computationally efficient algorithms for representing multiscale processes.

Recent advances in pore scale modeling suggest that a multiple interacting continuum approach is needed to adequately represent reactive transport at laboratory and field scales. To help meet these needs, the next-generation pore reactive flow and transport code (PFLOTTRAN) is currently being developed under a SciDAC-2 project entitled: “Modeling Multiscale-Multiphase-Multicomponent Subsurface Reactive Flows using Advanced Computing.” PFLOTTRAN is a parallel multiphase flow and multicomponent reactive transport model written from the ground up employing PETSc data structures and solvers for its parallel framework



**Figure 6.2.** Modeling the Hanford 300 area: Hanford 300 Area tracer plume at 7500 hours simulation time calculated using the Richards equation mode in PFLOTRAN. The plume originates from an infinite, rate-limited source which straddles the water table below the South Process Pond and is the result of transport due to hourly fluctuations in the Columbia River stage apposed by a more steady and higher inland pressure head. The model domain is viewed from the southeast with the Hanford unit hidden (topographic surface depicts the contact between the Hanford and Ringold units). Courtesy G. Hammond, and P.C. Lichtner (2008) DOE ERSP Annual PI Meeting, Lansdowne, VA.

[Hammond, Lichtner, Lu 2007; Mills, Lu, Lichtner *et al.* 2007]. The code employs domain decomposition for parallelization and implements an efficient parallel I/O through hierarchical data format (HDF5).

Recently, PFLOTRAN has been run on a one billion node real-world problem (Hanford 300 Area) as proof-of-concept for petascale computing (Fig. 6.2). The code ran successfully, albeit slowly, taking approximately 3.6 hours to run 15 timesteps on 1024 cores on ORNL's Jaguar Cray XT3 computer. During this time 55 GB checkpoint/restart files were written every other timestep. The code has also demonstrated a relative parallel efficiency of 79% at 12000 cores, based on a strong-scaling study performed with a similar 500 million node problem executed on 3000-12000 cores. Performance at this level is likely beyond the state of the art of the mainstream parallel groundwater modeling community.

The state of the art for the mainstream groundwater community (including multiphase flow and multicomponent reactive transport) is problem sizes on the order of 1 million to 10 million nodes, with 1 million to 30 million degrees of freedom overall (spatial nodes+phases+chemical constitu-

ents). Although many applications have been executed on up to 1024 cores, it is likely that most scale efficiently to only 100-200 cores.

To further realize the unprecedented simulation resolutions possible at the petascale, multilevel preconditioners/solvers must be developed that are asymptotically optimal (i.e., that converge at rates independent of the mesh size) and efficiently parallelizable. Straightforward adaptations of existing multilevel methods are not effective because subsurface reactive flow problems present additional difficulties in the form of heterogeneous material properties and complicated reaction fronts involving phase changes.

### 6.5 PRD: TRANSPORT PROPERTIES AND IN SITU CHARACTERIZATION OF FLUID TRAPPING, ISOLATION AND IMMOBILIZATION

Injected CO<sub>2</sub> is immobilized by buoyancy trapping of fluids by geologic seals, capillary trapping of fluid phases as isolated bubbles within rock pores, and sorption of CO<sub>2</sub> or radionuclides on solid surfaces. Specific advances will be needed so that the interplay of interfacial tension, surface properties, buoyancy, the state of stress, and rock heterogeneity in the subsurface is understood and represented.

Multiphase fluid flow depends on the dynamic and hysteretic contact angle behavior as contact lines move over complex surfaces. The contact angle dynamics depend on subpore-scale physical and chemical heterogeneities, and are sensitive to impurities in the liquid phases and on mineral surfaces. In lattice Boltzmann and particle methods, realistic contact angle dynamics controlled by fluid-fluid and fluid-solid interactions occur in a natural manner. However, this realistic behavior is not necessarily the correct behavior for specific systems. In pore network and traditional computational fluid dynamics (CFD) models, a contact angle dynamics model must be explicitly coupled to the fluid dynamics model. The development of better ways of including contact line dynamics in simulation of multiphase fluid flow in fractured and porous media is an outstanding challenge.

#### 6.5.1 Modeling Multiphase Fluid Flow Case Study

With 1 million computing core hours, it would be possible to carry out pore network simulations with O(10<sup>9</sup>) pore volumes. For a variety of subsurface materials, the corresponding physical size would be on the order of the size of a core sample (on the order of one decimeter). To simulate multiphase fluid flow, 10<sup>6</sup> core hours could be used on lattice Boltzmann models, with complex pore spaces on 2048 × 2048 × 2048 grids. Voxel maps of complex pore spaces from

X-ray tomography of this size may also be available during the next few years. Lattice Boltzmann models with better stability that can handle larger viscosity and density ratios are under development. The increased performance comes at the expense of an increase in complexity, but these advanced lattice Boltzmann models will be more computationally efficient than particle models. With 106 core hours, it should be possible to carry out three-dimensional smoothed particle hydrodynamics simulations (SPH) on the scale of present day pore network model simulations ( $\approx 10,000$  pores). (*See cover illustration.*) In the case of traditional CFD methods, it would be possible to simulate multiphase fluid flow in fracture networks with 100 to 1,000 individual fractures, with 106 core hours. This is important because it is not possible adequately to characterize natural fracture networks of this size, or accurately to determine the time dependent distribution of fluids within them.

Another important advantage of computer simulations is that it is possible systematically to vary parameters that cannot be varied in a well controlled manner in experiments. To perform experiments of this type, in which fluid viscosities and densities, surface tension, wetting characteristics and flow conditions are varied, would require on the order of 100 simulations. Consequently 100 million core hours would be required to advance from a very significant feasibility demonstration, to a worthwhile and groundbreaking scientific investigation.

## 6.6 PRD: BIOGEOCHEMISTRY IN EXTREME SUBSURFACE ENVIRONMENTS

Microorganisms strongly influence the mineralogy and chemistry of geologic systems.  $\text{CO}_2$  and nuclear material isolation will significantly perturb the environments for these microorganisms. Major advances are needed to describe how populations of microbes will respond to the extreme environments of temperature, pH, radiation, and chemistry that will be created, so that a much clearer picture of biogenic products, potential for corrosion, and transport or immobilization of contaminants can be assembled.

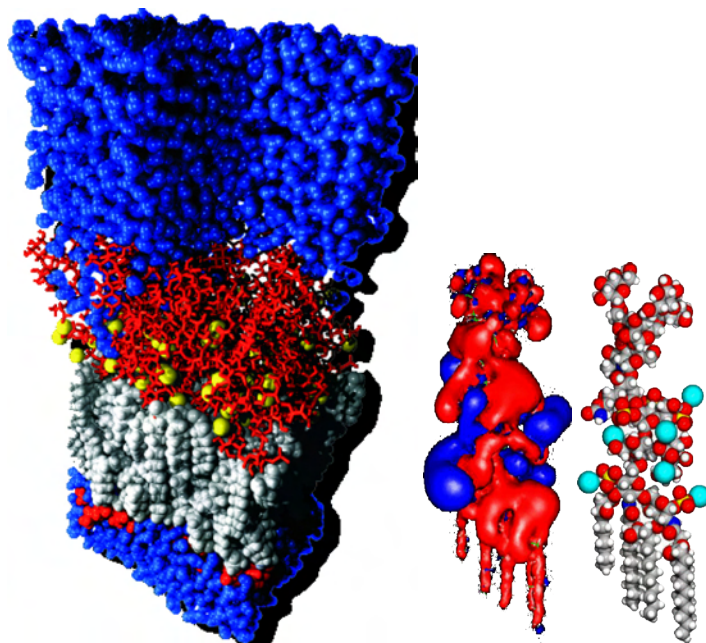
### 6.6.1 Molecular Modeling and Simulation Applications in Biogeochemistry Case Study

Microorganisms represent a significant fraction of all living material on earth. For a long time it has been known that subsurface microbial processes can play an important role in oxidation and reduction reaction rates, as well as in the alteration of mineral dissolution and precipitation reactions. Microbes have been found to adsorb metals and other ions at the microbe surface, and can thrive in heavily contaminated areas including mine drains and beneath the waste tanks in

the Hanford site, where they are able to biomineralize high levels of metals, including radioactive contaminant metals such as uranium, into their cell wall.

Most of these microbially mediated processes occur either directly at the microbial surface or at the microbe-mineral interface. In the last ten years, a combination of experimental and theoretical studies have contributed to a better understanding of these complex interfacial reactions. Much of this work has focused on gram-negative bacteria, especially those important in metal reduction and bioremediation, that are characterized by an extensive outer layer of lipopolysaccharides (LPS), which can account for a significant fraction of the mass of the outer membrane. Because of its physical location on the outside of the microorganisms, and because LPS is the major constituent conferring negative charge to the cell surface, as has been observed in both experimental and computational studies, this outer LPS is believed to be a key factor responsible for the attachment of microbes to mineral surfaces, for the uptake of metal ions, and for microbially induced precipitation and dissolution reactions, including biomineralization.

Much of the detailed atomic composition of LPS outer membranes is known, and molecular models can be designed to study computationally the interaction of these membranes with their environment, using HPC simulations (Fig. 6.3).



*Fig. 6.3. A 3D computer simulation of lipopolysaccharides membranes, a subsurface microbial process that plays an important role in oxidation, reduction reaction rates, mineral dissolution and precipitation reactions. Molecular models can be designed to study the interaction of these membranes with their environment. Courtesy T. Straatsma.*

The complexity of these systems is such that large-scale computing resources are needed to achieve the length and timescales for adequate predictions to be made. Such simulations already have provided insight into the electrostatic character of these membranes. Detailed structural elements in the interactions between key functional groups within the membrane and with solvated ions have also been disclosed. It is of great importance that these simulations are extended to much longer times than is currently feasible, because of the extremely low diffusion within these relatively rigid biological membranes. Moreover, these membranes are expected to have different behavior under extreme conditions of temperature and acidity. The ability to conduct many of these simulation studies for each combination of organism-specific LPS outer membrane and particular species in their environment, and to extend these models to include electron-transfer reactions between organisms and important mineral assemblages is critical.

### 6.7. CONCLUSION

The challenges of long-term geologic sequestration represent a critical obstacle to advancing the U.S.'s new energy future. High-performance computing facilities are very important in the geosciences' search for long-term strategies for geologic sequestration of nuclear wastes and greenhouse gases. Supercomputing is indispensable for the advancement of basic science needs in geosciences research, including simulation of multiscale systems for ultra-long times, for hundreds of years to as long as a million years; to the integration of characterization, modeling, and monitoring of geologic systems; to the computation of the thermodynamics of complex fluids and solids, to predict long-term reaction rates; and to develop better theories of interfacial reactivity and dynamics.

*Andy Felmy, Paul Meakin, Peter Lichtner, Jim Rustad, Tim Scheibe, Greg Newman, and Tjerk Straatsma*

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Hammond, Glenn E., P.C. Lichtner, and C. Lu. (2007) “Subsurface Multiphase Flow and Multicomponent Reactive Transport Modeling using High-Performance Computing.” *SciDAC Review*. June; *J. Phys.: Conf. Ser.* 78 012025 (10pp). doi:10.1088/1742-6596/78/1/012025.

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## SCIENTIFIC IMPACTS AND OPPORTUNITIES FOR COMPUTING WORKSHOP PROGRAM

### WORKSHOP GOALS

The goal of this workshop is to understand how the computing systems currently deployed are being used to advance scientific objectives in several key domains, as well as how these same systems and the multiple petaflops systems to be deployed by Department of Energy (DOE) and National Science Foundation (NSF) can be used to maximize scientific impact in the next 12-18 months. The research opportunities will be explored in half-day sessions engaging panels and workshop participants in discussion in Nanoscience, Superconductivity, Combustion, Energy Storage, and Geosciences.

#### Goals:

1. Identify expected science outcomes in key scientific domains (nanoscience, superconductivity, combustion, energy storage and geoscience) that will utilize computing - especially those systems currently deployed at the three Office of Science Advanced Scientific Computing Research (OASCR) facilities: Argonne Leadership Computing Facility (ALCF), National Energy Research Scientific Computing (NERSC) and Oak Ridge Leadership Computing Facility (OLCF).
2. Identify expected science outcomes utilizing those systems to be deployed at the three OASCR facilities in the next 12-18 months.
3. Identify the impact of having all scientists dedicating 50% of their effort to performing computational experiments - what would those simulations entail?

#### Outcome:

1. Greater understanding of the impact and opportunities of computing in producing today's science
2. Greater awareness of what computational experiments should be performed upon delivery and acceptance of computer hardware (a more Basic Energy Sciences (BES)-like facilities approach)
3. Workshop report - derived from short reports (~5 pages) from each of the sessions

#### How can you maximize your contribution?

There are five half-day (3 -hour) sessions on the various scientific topics. Each session is roughly organized into (1) a plenary talk which broadly outlines opportunities and impacts of computing in the subject area, (2) a panel discussion in which panel participants will be asked to provide specifics on the questions to frame the session's discussion, followed by (3) an open discussion moderated by the session chair.

Participants have the opportunity to contribute to all five discussions and to explore the role of supercomputing at the petascale in advancing science in each of these science areas. We have an opportunity to help set the research agenda in the next five years in these exciting interdisciplinary fields.

Note that for each of these topics there have been prior workshops (not necessarily focused on computing) and workshop reports are available (see <http://www.sc.doe.gov/bes/reports/list.html>). This workshop is specifically designed to answer the question of how computing can have an impact and build new scientific opportunities in each of these science areas.

***Panel objectives:***

The purpose of the panels is to identify and define a set of high value R&D studies for each key scientific domain with accompanying focused research questions and expected outcome(s) from a focused 5-year effort. The efforts will use a novel approach which integrates the physical and virtual studies into a single unified effort conducted by a focused interdisciplinary research team. The research would draw heavily on ongoing studies in each key scientific domain and current virtual capabilities at centers such as the Leadership Computing Facilities at ORNL and ANL. The R&D studies will have high relevance to meeting needs to assure high impact on each of the domains.

***Example questions to be addressed by the panel members for each domain might be:***

- A. What ongoing research is already underway that could form the core of an expanded study or support for a new study?
- B. What research question(s) would be the focus of your study?
- C. What intermediate results or progress could be reasonably expected after the first year and third year of effort and what high value result(s) could be reasonably expected at the end of a focused five-year effort?
- D. What level of budget would you anticipate needing to achieve these results?

***DETAILS:***

The workshop dates are January 10-12, 2008.

Participation is by invitation only.

A room block has been established at the Maui Prince Hotel for the nights of January 9-12 under "Oak Ridge National Laboratory." Each person is responsible for his/her own room reservations and costs. Hotel reservations can be made by calling 1-866 PRINCE6 (1-866-774-6236).

Maui Prince Hotel

Speedy Shuttle is available to transport you from the airport to your hotel. The phone number for Speedy Shuttle is 1-877-242-5777.

# AGENDA

## Wednesday, January 9, 2008

- 6:30 p.m. Welcome networking session.....Holokai Pavillion  
 Welcome and introductions.....Walt Polansky/Thomas Zacharia

## Thursday, January 10, 2008

- 7:15 a.m. Morning networking and breakfast.....Haleakala Room  
*Workshop goals/expected outcomes*.....Jeff Nichols, ORNL  
*Hardware systems currently deployed and expected in 12-18 months*  
ALCF.....Ray Bair, ANL  
NERSC.....Jonathan Carter, LBNL  
OLCF.....Buddy Bland, ORNL
- 9:30 a.m. Session I: Scientific Impacts and Opportunities in Computing: Nanoscience  
 Session chair.....Clare McCabe, Vanderbilt  
 Plenary.....Berend Smit, UC, Berkeley  
 Panelists: *Clare McCabe, Thomas Schulthess, Roland Faller, Paul Kent, and Berend Smit*  
 Moderated session.....
- 12:30 p.m. Lunch and continued discussions
- 1:30 p.m. Session II: Scientific Impacts and Opportunities: Superconductivity  
 Session Chair.....Thomas Schulthess, ORNL  
 Plenary.....Peter Hirschfeld, Univ. of Florida  
 Panelists: Thomas Schulthess, Peter Hirschfeld, Thomas Maier,  
Pengcheng Dai, and Doug Scalapino (remote)  
 Moderated session.....
- 4:30 p.m. End of Day 1

**Friday, January 11, 2008**

- 7:15 a.m. Morning networking and breakfast.....Haleakala Room
- Session III: Scientific Impacts and Opportunities in Computing: *Combustion Hardware systems currently deployed and expected in 12-18 months*
- Session chair.....Jackie Chen, SNL
- Plenary.....Andy McIlroy, SNL
- Panelists: Jackie Chen, Joe Oefelein, Al Wagner, Carlos Pantano, Sreekanth Pannala, Robert Harrison, and Angela Violi
- 11:30 a.m. Lunch and continued discussions.....Haleakala Room
- 12:30 p.m. Session IV: Scientific Impacts and Opportunities in Computing: *Energy Storage*
- Session Chair.....Gil Weigand, ORNL
- Plenary.....Yury Gogotsi, Drexel
- Panelists: Gil Weigand, Jim Roberto, Yury Gogotsi, and Jim Davenport
- Moderated session.....
- 3:30 p.m. Session chairs, organizers, DOE program manager round table on workshop report
- Other participants free afternoon
- 7:00 p.m. Reconvene for dinner and continued discussions

**Friday, January 11, 2008**

- 7:15 a.m. Morning networking and breakfast.....Haleakala Room
- 9:30 a.m. Session V: Scientific Impacts and Opportunities in Computing: *Geosciences*
- Session chair.....Andy Felmy, PNNL
- Plenary.....Andy Felmy, PNNL
- Panelists: Andy Felmy, Paul Meakin, Peter Lichtner, Jim Rustad, Tim Scheibe, Greg Newman, and Tjerk Straatsma



Moderated session.....

11:30 a.m. Lunch and continued discussions.....Holokai Pavillion

12:30 a.m. Wrap up and adjourn



## ACRONYMS AND TERMINOLOGY

**3D**—three dimensional (as in modeling and simulation)

**adsorption isotherm**—When a gas comes into contact with a solid surface, molecules of the gas will adsorb (stick) to the surface in quantities that are a function of their partial pressure in the bulk. The measurement of the amount of gas adsorbed over a range of partial pressures at a single temperature results in a graph known as an adsorption isotherm.

**amorphous carbon**—a carbon material without long-range crystalline order; Short-range order exists, but with deviations of the interatomic distances and/or interbonding angles with respect to the graphite lattice, as well as to the diamond lattice.

**AEL**—a crystalline zeolite material that acts as a cation exchanger in energy storage, from which carbon nanotubes can be extracted

**AFI**—an aluminum rich zeolite; See AEL.

**AIMD**—*ab initio* molecular dynamics; a widely used numerical technique for studying structural and dynamical properties of chemically active systems, in which the forces are obtained from electronic structure calculations

**ALCF**—Argonne Leadership Computing Facility

**algorithm**—generally, any well-defined procedure for mathematical calculations; Typically in an algorithm one is given an initial state, a list of instructions for completing a task that proceeds through a well-defined series of successive states, terminating in an end-state. The transition from one state to the next is not always deterministic; some algorithms, known as probabilistic algorithms, incorporate randomness. A computer program is essentially an algorithm that tells the computer what specific steps to perform, in what order, in order to carry out a specified task. In a data processing algorithm, data is usually read from an input source or device, and then written to an output sink or device, and/or stored for further processing.

**AMBER**—assisted model building and energy refinement, a family of force fields for molecular dynamics of biomolecules; AMBER is also the name for the simulation software which implements the force fields.

**AMPI**—adaptive message passing interface; an implementation of MPI code for parallel processors, which builds on MPI by adding dynamic load balancing and multithreading for applications

**AMR**—adaptive mesh refinement simulation code, a technique which enhances both spatial and time resolution by a choice of a particular structured mesh; The technique subdivides the cells which satisfy the refinement criterion recursively. The hierarchical meshes are maintained by a special data structure, and are modified dynamically, for example in accordance with the changes in the distribution of particles followed in a simulation. As the resolution of the simulation increases, the corresponding time step must be shortened, so that more computer time is required to complete the simulation.

**ANL**—Argonne National Laboratory

**ARPES**—angle-resolved photo emission spectroscopy; This is currently the most direct method available for measuring the momentum-dependent electronic structure of solids. ARPES is one of the most important tools for establishing the relationship between electronic, magnetic, and chemical structure of solids, in particular in those complex systems which cannot be described in an independent-particle picture. ARPES is an invaluable tool in both pure and applied condensed matter research.

**ASCR**—Advanced Scientific Computing Research (an organization in the DOE Office of Science)

**BCS**—the theory of conventional (low temperature) superconductivity; BCS theory is named for its developers, John Bardeen, Leon Cooper, and Robert Schrieffer. It explains the ability of certain metals at low temperatures to conduct electricity without electrical resistance (superconductivity) as being the consequence of the formation of pairs of electrons, known as Cooper pairs.

**BES**—Basic Energy Sciences, an office of the DOE which supports fundamental research into new and improved energy technologies and the environmental impacts of energy use

**BRN**—basic research needs of BES

**carbon nanotube**—a nanoscale (1–100 nm) carbon structure, produced by rolling graphene sheet(s) into a tube

**Car-Parrinello**—The Car-Parrinello method is a type of *ab initio* molecular dynamics, usually employing periodic boundary conditions, planewave basis sets and DFT.

**CBH1**—cellobiohydrolase I, a cellulase enzyme

**CI**—compression-ignition engine

**CC**—cross-cutting research themes of BES workshop reports

**CCSD**—Computing and Computational Sciences Directorate (ORNL)

**CDC**—carbide-derived carbon; a carbon material produced by the selective extraction of metal atoms from a carbide crystal lattice by halogens, supercritical water, oxygen at a low partial pressure, other etchants, or in vacuum

**CFD**—computational fluid dynamics, a branch of fluid mechanics which uses numerical methods and algorithms to solve and analyze problems that involve fluid flow (Only approximate numerical solutions can be attained in most such problems.)

**CHARMM**—chemistry at Harvard macromolecular mechanics, the name of a widely-used set of force fields for molecular dynamics; CHARMM is also the name of the MD simulation and analysis package.

**CLC**—chemical looping combustion, a combustion technology with an inherent separation of CO<sub>2</sub>; This technique involves the use of a metal oxide as an oxygen carrier, which transfers oxygen from the combustion gas to the fuel. Two reactors in the form of interconnected fluidized beds are used in the process, a fuel reactor in which the metal oxide is reduced by reaction with the fuel, and an air reactor in which the reduced metal oxide from the fuel reactor is oxidized by air.

**CMD**—classical molecular dynamics simulations; This computational method is used to calculate the time dependent behavior of molecular systems. One of the principal tools used for the study of biological molecules. See also MD.

**CMM**—classical molecular mechanics simulations; Mechanics, a more general term, can include static situations. See also MD.

**CNMS**—Center for Nanophase Materials Sciences, the DOE Nanoscale Science Research Center (ORNL)

**CRF**—Combustion Research Facility, Sandia National Laboratories

**Cryo-em**—Cryo-electron microscopy, or electron cryomicroscopy, is a form of electron microscopy in which the sample is studied at cryogenic temperatures (generally that of liquid nitrogen).

**CSEM**—(marine) controlled-source electromagnetic method; This method was developed to study the electric conductivity structure of the deep ocean lithosphere, which has since found extensive application within the offshore hydrocarbon exploration industry.

**CSM**—Computer Science and Mathematics Division (ORNL)

**DCA**—dynamical cluster approximation; This is an algorithm which treats short-ranged correlations exactly, while approximating the effect of longer ranged correlations. It is used to study the under- and optimally-doped cuprate high-temperature superconductors, which are known to have very strong short-ranged spin correlations.

**DFT**—density functional theory, a quantum mechanical method used primarily to investigate the ground state properties of many-body systems, in particular atoms, molecules, and condensed matter phases

**DMFT**—dynamical mean-field theory, a family of approximate methods used to investigate many-body systems in various fields of physics, in which complicated individual interactions are replaced by a single effective “mean field”

**DMRG**—the density matrix renormalization group, a powerful, recently developed numerical technique which allows one to determine the low-energy properties of certain types of quantum many-body systems with high accuracy; DMRG is typically most useful in studies of one-dimensional systems with strongly local interactions.

**DNS**—direct numerical simulation; in fluid mechanics, the numerical solution of the equations that govern fluid flow. In DNS the whole range of spatial and temporal scales of the turbulence must be resolved in the computational mesh, from the smallest dissipative scales up to the integral scale  $L$  associated with the motions containing most of the kinetic energy.

**DOE**—Department of Energy

**EAMB**—electronic, atomic and molecular based (simulations)

**EC**— electrochemical capacitor

**EDLC**—electrochemical double layer capacitor, a novel energy storage research subject

**EES**—electrical energy storage

**EM**—electron microscopy, a type of microscope which uses electrons to illuminate a specimen and create an enlarged image; Some electron microscopes can magnify specimens up to 2 million times.

**EMSL**—Environmental Molecular Sciences Laboratory, a DOE scientific user research facility (PNNL)

**exascale**—in computer simulations, a reference to problems that require supercomputers capable of a quintillion ( $10^{18}$ ) floating point operations per second (see FLOP/s); a measure of the limits of currently projected supercomputer capability

**FLOP/s**—floating point operations per second, a measure of computer processor speed, in terms of the number of elementary mathematical calculations a computer can perform per second

**Gauss-Newton**—an algorithm used to solve non-linear least squares problems; Unlike Newton's method, the Gauss-Newton algorithm can only be used to minimize a sum of squared function values, but it has the advantage that second derivatives, which can be challenging to compute, are not required.

**GC**—grand challenge initiatives in Basic Energy Sciences (BES)

**Hartree-Fock**—an approximation method in computational physics and chemistry for the determination of the ground state wave function and the ground state energy of a quantum many-body system

**HCCI**—homogenous charge compression ignition, a form of internal combustion in which well-mixed fuel and oxidizer (typically air) are compressed to the point of auto-ignition; This exothermic reaction releases chemical energy in a form that can be translated by an engine into work and heat.

**HDF5**—hierarchical data format, a library and multi-object file format for the transfer of graphical and numerical data between computers; HDF supports several different data models, including multidimensional arrays, raster images, and tables. Each defines a specific aggregate data type and provides an application programming interface for reading, writing, and organizing data and metadata.

**HELIOS**—the HELIOS Research Facility, at Lawrence Berkeley National Laboratory

**HPC**—high-performance computing

**IC engine**—in-cylinder combustion engine

**INCITE**—Innovative and Novel Computational Impact on Theory and Experiment, an Office of Science

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program launched in 2003 to seek out computationally intensive, large-scale research projects with the potential to significantly advance key areas in science and engineering

**Krylov subspace solution technique**—modern iterative methods for finding one (or a few) eigenvalues of large sparse matrices or for solving large systems of linear equations. Such methods avoid matrix-matrix operations, instead multiplying vectors by the matrix and work with the resulting vectors. All algorithms that work this way are referred to as Krylov subspace methods; they are among the most successful methods currently available in numerical linear algebra.

**LANL**—Los Alamos National Laboratory

**lattice Boltzmann**—a powerful technique for the computational modeling of a wide variety of complex fluid flow problems, including single and multiphase flow in complex geometries, based on the Boltzmann equation; It considers a typical volume element of fluid to be composed of a collection of particles that are represented by a particle velocity distribution function for each fluid component, at each grid point. The time is counted in discrete time steps and the fluid particles can collide with each other as they move, possibly under applied forces.

**LBNL**—Lawrence Berkeley National Laboratory

**LDA-GGA**—calculations used in density functional theory (DFT) to calculate the distribution of strongly correlated electrons; LDA, the local density approximation, is an approximation of the exchange-correlation energy functional. GGA, the generalized gradient approximation, a refinement of LDA, can accommodate non-uniform charge densities, in which the exchange-correlation energy may deviate.

**LES**—large eddy simulation, a computer calculation of the motion of large structures in turbulent fluid flow

**lithium-ion battery**—an electrochemical battery that employs a lithium metal anode

**LLNL**—Lawrence Livermore National Laboratory

**LPS**—lipopolysaccharide, a large molecule consisting of a lipid and a polysaccharide (a carbohydrate) joined by a covalent bond; This is a major component of the outer membranes of Gram-negative bacteria, which contributes to the structural integrity of the bacteria and protects the membrane from certain kinds of chemical attack.

**LSMS**—locally self-consistent multiple scattering method, an order-N approach to the calculation of the electronic structure of large systems within the local density approximation (LDA); This method assumes that a good approximation can be obtained to the electron density and the density of states on a particular atom within a large system, by considering only the electronic multiple scattering processes in a finite spatial region centered on that atom.

**MD**—molecular dynamics, a method of molecular modeling and computer simulation, in which atoms and molecules are allowed to interact to give a view of the motion of the atoms; Such systems are so complex it is impossible to find their properties analytically. MD simulation treats this problem by using well-chosen approximations and algorithms.

**MEL**—see AEL

**MFI**—see AEL

**MMC**—Metropolis Monte Carlo; A Monte Carlo method in general is any computational algorithm that relies on repeated random sampling “throwing dice” to compute results. The method is often used when it is infeasible or impossible to compute an exact result using a deterministic algorithm. These methods are especially useful in studying systems with a large number of coupled degrees of freedom, such as liquids, disordered materials, strongly coupled solids, and cellular structures. The Metropolis-Hastings algorithm is a rejection sampling algorithm used to generate a sequence of samples with a probability distribution that is difficult to sample from directly. It can draw samples from any probability distribution  $P(x)$ , requiring only that a function proportional to the density can be calculated at  $x$ .

**MOR**—see AEL

**MPI**—message passing interface, a library specification for message passing, designed for high performance on both massively parallel machines and on workstation clusters

**MPP**—massively parallel processor; Parallel processing is a form of computing in which a large number of activities are carried out concurrently, so that the real time required to solve the problem is considerably reduced.

**MSCF**—Molecular Science Computing Facility (PNNL)

**NCCS**—National Center for Computational Sciences (ORNL)

**NERSC**—National Energy Research Scientific Computing Center, the scientific computing facility for the DOE’s Office of Science (located at LBNL)

**NL**—In computational complexity theory, NL is the complexity class containing decision problems which can be solved by a non-deterministic Turing machine, using a logarithmic amount of memory space.

**nm**—nanometer, one billionth ( $10^{-9}$ ) of a meter

**ns**—nanoscale, at the size or scale of one billionth of a meter or  $10^{-9}$

**NSF**—National Science Foundation

**NWChem**—computational chemistry software capable of molecular dynamics simulations

**OLCF**—ORNL Leadership Computing Facility

**ORNL**—Oak Ridge National Laboratory

**PAH**—polycyclic aromatic hydrocarbons, a class of chemical compounds that consist of fused aromatic rings; These compounds are one of the most widespread types of organic pollutants, and are primarily formed by the incomplete combustion of carbon-containing fuels. PAHs are marker molecules, in that their abundance can be directly proportional to combustion processes in a region.



**PDE**—partial differential equation, a mathematical equation relating a generally unknown function (or functions) of several independent variables to its partial derivatives with respect to those variables; The basic laws of physics can often be succinctly expressed as partial differential equations, which are used to solve problems such as the propagation of sound or heat, electrolysis, electrodynamics, elasticity, fluid flow, and quantum physics.

**PES**—potential energy surface, the set of positions, typically a set of surfaces, on which a particle has a specified potential energy; This concept is used in the Born-Oppenheimer approximation in molecular quantum mechanics. The Born-Oppenheimer approximation itself assumes that the total molecular wave function can be written as the product of an electronic wave function and a nuclear wave function.

**petaflops**—a measure of computer speed; One petaflops is 1,000,000,000,000,000 or  $10^{15}$  (a quadrillion) floating point operations per second. The speed at which the world's fastest supercomputers can perform mathematical calculations is often quoted in petaflops.

**PETSc**—portable extensible toolkit for scientific computation

**PFLOTRAN**—pore reactive flow and transport code

**physical adsorption**—an adsorption process in which the dominant forces involved are long-ranged intermolecular forces (see van der Waals forces), of the same type that are responsible for departures from the ideal gas law in real gases and condensation vapors, and which do not entail a significant change in the electronic wavefunctions (orbitals) of the gas atoms involved;

**PNNL**—Pacific Northwest National Laboratory

**PRD**—priority research directions of Basic Energy Sciences

**QENS**—quasi-elastic neutron scattering, a technique used to study stochastic motions using neutron scattering from a sample with little energy transfer; QENS has been used to study molecular motions and the physical properties of a variety of systems, and provides information on timescales as well as spatial aspects of motion.

**QMC**—quantum Monte Carlo, a large class of computer algorithms that simulate quantum systems and attempt to solve the many-body problem; QMC allows a direct representation of many-body effects in the wave function, at the cost of a statistical uncertainty. This uncertainty can be reduced through longer simulation times. See also MMC.

**RDF**—radial distribution function in neutron scattering

**SEI**—solid electrolyte interphase

**SciDAC**—Scientific Discovery through Advanced Computing, a program within the DOE Office of Science; Collaborations of research scientists, applied mathematicians, and computer scientists are supported through this program to exploit HPC for scientific discovery.

**SiC**—silicon carbide, a wide band gap material for novel energy storage; One such device combines a silicon carbide cathode and an aluminum-lithium alloy anode in an alkali halide electrolyte.

**SIC-LDA**—self-interaction corrected local density approximation, an algorithm used in density functional theory (DFT) to calculate the approximate spatial distribution of strongly correlated electrons; See also LDA-GGA.

**SIE**—self interaction error, an approach used in DFT to refine the accuracy of estimates of electron correlation effects

**SNL**—Sandia National Laboratories

**specific surface area**—When the area of the interface between two phases is proportional to the mass of one of the phases (e.g., for a solid adsorbent, for an emulsion, or for an aerosol), the specific surface area is defined as the surface area divided by the mass of the relevant phase.

**SPH**—smoothed particle hydrodynamics simulations, a Lagrangian method (coordinates move with the fluid) for simulating fluid flows; The resolution in SPH can be adjusted as required to follow the evolution of variables such as density. SPH has been used in many fields, including astrophysics, ballistics, the study of volcanoes and tsunamis.

**STM**—scanning tunneling microscopy, a powerful technique for viewing surfaces at the atomic level; Based on the concept of quantum tunneling, STM probes the density of states of a material, by measuring the tunneling current.

**STS**—scanning tunneling spectroscopy

**supercapacitor**—an electrochemical double layer capacitor, used for energy storage; Electrical energy is stored in the double layer by charge separation, through the electrostatic force between an ionically conducting electrolyte and a conducting electrode. The ions displaced in forming the double layer are transferred between the electrodes by diffusion through the electrolyte.

**teraflops**—a trillion ( $10^{12}$ ) floating point operations per second (See petaflops.)

**Van der Waals forces**—In physical chemistry, these are weak, long-ranged, usually attractive forces between molecules (or between parts of the same molecule) that arise from induced polarization effects. Van der Waals interactions are typically weaker and longer ranged than the usual covalent or ionic chemical bonds, but often play a fundamental role in supermolecular chemistry, structural biology, polymer science, nanotechnology, surface science, and condensed matter physics.

**Voxel map**— a visualization algorithm used to display large data sets in computer simulations

**WL**—Wang-Landau algorithm, a stochastic method for determining finite temperature observables using importance sampling that is determined by an estimated density of states; The density of states is itself estimated by the algorithm during the simulation.

## WORKSHOP ATTENDEES

1. Andrews, Philip L. ....University of Tennessee
2. Bair, Raymond A. .... Argonne National Laboratory
3. Berry, Michael W. .... University of Tennessee
4. Bland, Arthur S. ....Oak Ridge National Laboratory
5. Carter, Jonathan T. ....Lawrence Berkeley National Laboratory
6. Chen, Jacqueline H. ....Sandia National Laboratories
7. Dai, Pengcheng..... University of Tennessee
8. Davenport, James W. .... Brookhaven National Laboratory
9. Faller, Roland..... University of California, Davis
10. Felmy, Andrew R. .... Pacific Northwest National Laboratory
11. Gogotsi, Yury..... Drexel University
12. Harrison, Robert J. .... Oak Ridge National Laboratory
13. Hirschfeld, Peter J. .... University of Florida
14. Kendall, Ricky A. ....Oak Ridge National Laboratory
15. Kent, Paul R. C. .... Oak Ridge National Laboratory
16. Kothe, Douglas B. ....Oak Ridge National Laboratory
17. Lichtner, Peter C. .... Los Alamos National Laboratory
18. Maier, Thomas A. ....Oak Ridge National Laboratory
19. McCabe, Clare M. ....Vanderbilt University
20. McCoy, Debbie D. .... Oak Ridge National Laboratory
21. McIlroy, Andrew..... Sandia National Laboratories

- 22. Meakin, Paul.....Idaho National Laboratory
- 23. Meza, Juan C. .... Lawrence Berkeley National Laboratory
- 24. Newman, Gregory A. .... Lawrence Berkeley National Laboratory
- 25. Nichols, Jeff A. .... Oak Ridge National Laboratory
- 26. Oefelein, Joseph C. ....Sandia National Laboratories
- 27. Pannala, Sreekanth..... Oak Ridge National Laboratory
- 28. Pantano, Carlos A. .... University of Illinois at Urbana-Champaign
- 29. Peterson, Gregory D. ....University of Tennessee
- 30. Polansky, Walt M. ....United States Department of Energy
- 31. Roberto, James B. ....Oak Ridge National Laboratory
- 32. Rustad, James R. ....University of California, Davis
- 33. Scheibe, Timothy D. ....Pacific Northwest National Laboratory
- 34. Schulthess, Thomas C. ....Oak Ridge National Laboratory
- 35. Smit, Berend.....University of California Berkeley
- 36. Stevens, Rick L. .... Argonne National Laboratory
- 37. Straatsma, Tjerk P. .... Pacific Northwest National Laboratory
- 38. Violi, Angela.....University of Michigan
- 39. Wagner, Albert F. ....Argonne National Laboratory
- 40. Weigand, Gilbert G. ....Oak Ridge National Laboratory
- 41. Zacharia, Thomas.....Oak Ridge National Laboratory

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