Chemical Industry of the Future

Technology Roadmap for Computational Chemistry

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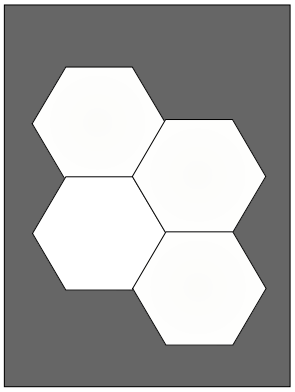
This is the final approved version of the roadmap for Computational Chemistry, derived from the workshop held March 16-17, 1998 at the University of Maryland, with support from the U.S. Department of Energy Office of Industrial Technology (Brian Volintine, 202-586-1739). Sponsorship of this roadmap is by the Council for Chemical Research (CCR), with a task force led by Dr. David Dixon (Pacific Northwest National Lab). The initial rough draft of this document was prepared by the workshop facilitators, Energetics, 7164 Gateway Drive, Columbia, MD 21046 (attn: Joan L. Pellegrino, 410-290-0370). The present document was edited by Dr. Tyler B. Thompson (Research Partnership Leader, The Dow Chemical Company, External Technology Department, Midland, MI 48674, 517-636-0330, tbthompson@dow.com), with major contributions from some of the members of the workshop organizing committee. The committee, which accepts responsibility for the content of this roadmap, consists of H. D. Cochran, Jr. (Oak Ridge National Lab), P. T. Cummings (University of Tennessee), D. A. Dixon (Pacific Northwest National Lab), J. T. Golab (BP Amoco), G. S. Heffelfinger (Sandia National Laboratories), B. K. Peterson (Air Products), A. Redondo (Los Alamos National Lab), T. B. Thompson (Dow Chemical) and P. R. Westmoreland (University of Massachusetts, Amherst).

This final version incorporates revisions suggested by a number of qualified individuals in response to an earlier draft (April 14, 1999), posted on the internet web site of the Council for Chemical Research (CCR). This version was approved and accepted by CCR at their annual meeting Saturday, September 25, 1999. Comments and suggestions continue to be welcome. Please send all comments to the editor by e-mail, tbthompson@dow.com.



1 Introduction

Meeting the Challenges of the 21st Century

The chemical industry faces considerable economic, environmental and societal challenges as the 21st century approaches. Technology research, development and deployment will be vital to meeting these challenges and seizing opportunities for future growth. Increased globalization of markets, for example, will create many new market opportunities, but will require the development of advanced technology to ensure the industry is globally competitive. The industry will also need to balance societal demands for improved environmental performance with the need for increased profitability and capital productivity in a global, highly competitive market place. Manufacturing processes that are resource efficient, cost-effective, and environmentally sound will be a cornerstone in maintaining this balance. Strategically-driven investments in technology R&D can help to move the industry toward higher levels of financial performance while keeping pace with technological change and meeting environmental goals.

Between 1994 and 1996 the chemical industry, with the participation of several representatives from academia and the U.S. national laboratories, reviewed and analyzed the factors affecting the competitiveness of the industry and its ability to meet future challenges. The study resulted in *Technology Vision 2020: The U.S. Chemical Industry*, a visionary document that identifies major needs and challenges over the next two decades [Vision 2020]

To meet industry goals for the 21st century, *Technology Vision 2020* advocates that R&D be conducted in a number of areas, including new chemical science and engineering technologies that will promote more cost-efficient and higher performance products and processes. An important element of chemical science and engineering is the development of "enabling" technologies -- technologies that improve the application of fundamental chemical sciences throughout the industry's process environment (see Exhibit 1-1). Enabling technologies identified in *Technology Vision 2020* as essential to the industry's future include process science and engineering (e.g., engineering scale-up and design, thermodynamics and kinetics, reaction engineering); chemical measurement; and computational technologies (e.g., computational chemistry, simulation of processes and operations, smart systems, computational fluid dynamics).

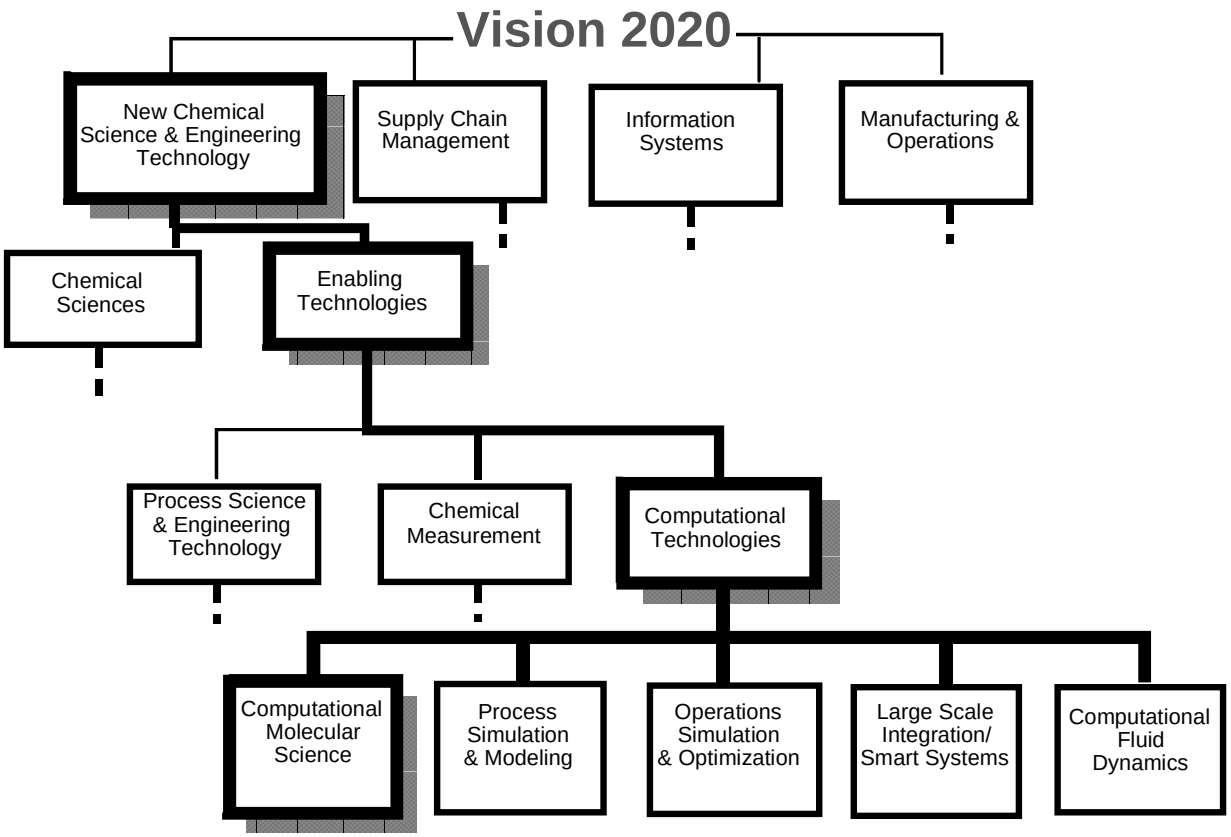


Exhibit 1-1. Selected R&D Areas Identified By *Technology Vision 2020*

The Role of Computational Chemistry

Computational technologies are embodied in nearly every aspect of chemical research, development, design, and manufacture. They have a broad range of applications, from molecular modeling to the simulation and control of chemical processes. The aspects of computational technology that are most critical to the chemical industry include computational molecular science, process modeling and simulation, optimization of operations, process control, and computational fluid dynamics. The field of **computational chemistry**, broadly defined, includes computational molecular science, empirical correlations such as linear free energy relationships and Quantitative Structure Property Relationships (QSPR), and aspects of process modeling and simulation.[1] The focus of this report is on computational molecular science, sometimes called molecular modeling. This involves models of chemical systems at the molecular or atomistic level, as well as predictions of quantum effects. At the most basic molecular level, this involves the solution of the Schroedinger equation for electronic (and nuclear) motion or the solution of Newton's equations of motion. Among other applications, it supplies quantitative estimates of engineering parameters such as heats of formation and heats of reaction, entropies and heat capacities, reaction rate constants, and transport properties like viscosity and thermal conductivity that are needed to construct macro-scale models of complete chemical processes.

[1]Research needs in computational fluid dynamics are discussed separately in the *Technology Roadmap for Computational Fluid Dynamics*, draft available from Los Alamos National Laboratory at http://www.lanl.gov.

And molecular modeling gives valuable insight into the properties of new materials so necessary for the efficient design of new products.

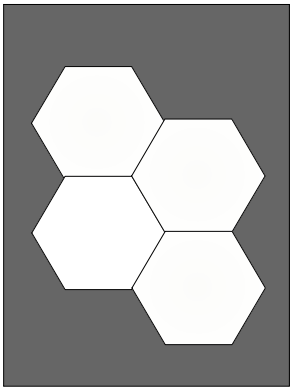
Advances in computational chemistry have contributed, and will continue to contribute, directly to the goals stated in the chemical industry vision. Specifically, the increased application of computational technologies will promote:

- Shortened product-process development cycles;
- Optimization of existing processes to improve energy efficiency and minimize production of waste;
- Efficient design of new products and processes; and
- Improvements in health, safety, and environment.

Following the publication of *Technology Vision 2020* in 1996, the chemical industry began to define its needs in computational chemistry through a series of workshops [NSF 1997, PNNL 1997], culminating with the Computational Chemistry Roadmap Workshop held at the University of Maryland March 16-17, 1998, facilitated by the U.S. Department of Energy Office of Industrial Technology. The scope of this workshop included the manufacture by chemical and petroleum companies of materials (plastics, elastomers, thermoset resins, polymer composites, etc.), industrial chemicals, and the chemical process interests of pharmaceutical, agrichemical, and other life sciences companies. It specifically excluded the molecule discovery and molecular biology functions of life sciences companies. These workshops were attended by representatives from the chemical, petroleum, and computer (both software and hardware) industries, along with participants from industry trade organizations, federal agencies, and the national laboratories.[2] The purpose of the workshops was to identify the needs of the industry, and to define some of the challenges faced by the chemical process industry in modeling specific chemical systems. The results would then serve to build an industry-wide consensus on the R&D needed to develop advanced computational chemistry capabilities and facilitate their use in the chemical processing industries.

Together the results of these workshops provide the foundation for a technology roadmap in computational chemistry. It is one of many such efforts to provide a link between the broad-based goals defined in *Technology Vision 2020* and the research portfolio that will be pursued through cooperative R&D partnerships. The research priorities outlined in this roadmap will be used as the basis for making new research investments by government and industry. It is a dynamic document, and will be reevaluated periodically to incorporate new market and technical information and to ensure that the research priorities remain relevant to the needs of both the chemical industry and its customers. The intent is to make this roadmap document generally available on the World Wide Web so that it can provide not only guidance but also inspiration that will lead to significant advancements in this important area for the chemical process industries.

[2] A complete list of participants and contributors to this roadmap is provided in Appendix A.



2 Computational Chemistry: An Overview

What is Computational Chemistry?

Computational chemistry involves a mathematical description of systems of chemical species. The goal is to solve the complex equations such as the Schrodinger equation for electronic and nuclear motion which accurately describe natural phenomena. In a practical application of computational chemistry, mathematical equations or algorithms are devised to quantitatively describe the physical and chemical phenomena (e.g., energy states, structures, reactivity, positions and momenta of atoms) that occur in a particular system. These algorithms are then programmed in the appropriate computer languages and linked together so that the many millions of calculations required to effectively describe the phenomena can be quickly computed. For example, it might be necessary to evaluate billions of integrals to accurately describe the repulsion of electrons in a complex molecule. The end result is a set of computational tools that predict the characteristics and behavior of the chemical system.

Computational chemistry can be used to describe a diversity of chemical systems with a wide range of complexity. At the quantum molecular level, chemical systems of hundreds of atoms can be modeled today, and highly accurate calculations are possible for up to 10 atoms. More approximate classical atomistic methods can handle systems up to millions of atoms, depending on the time scale. At the upper end, the mesoscale involves systems of billions or trillions of atoms which still manifest molecular effects.

There are many potential applications of computational chemistry in chemical processes where predicting the characteristics and behavior of a system may be beneficial. By predicting a system's behavior, computational chemistry can potentially be used to improve the efficiency of existing operating systems as well as the design of new systems. It can help to shorten product and process development cycles, optimize processes to improve energy efficiency and environmental performance, and solve problems as they arise in plant operations.

Applications for Computational Chemistry in Chemical Processing

- New Bioprocesses
- Catalyst Design
- Improved Reaction Mechanisms
- Product Development (polymers, pharmaceuticals)
- Efficient Process Design
- Materials and Polymer Design
- Polymer Processing
- Environmental modeling and remediation

Components of Computational Chemistry

Computational chemistry describes chemical systems at various size scales.

Quantum Scale - Solves the Schroedinger equation for electronic motion in atoms and molecules either by molecular orbital or density functional theories. Predicts molecular structure, energetics, bonding, reaction rates, and spectroscopic data.

Atomistic or Molecular Scale - computes interactions between atoms or groups using classical Newtonian mechanics and empirically determined force fields. Calculates structure and thermodynamic and transport properties, and time dependence of the structure.

Mesoscale - in between atomistic calculations and the continuum assumption of traditional materials engineering. Typically applies to systems of millions of atoms which still reflect molecular scale phenomena.

Bridging Scales - theory and models to provide an interface between scales.

Computational chemistry can also play an important role in the design of molecules (e.g., new chemical products, materials, catalysts). For example, by reliably predicting thermochemistry (the energy associated with the chemical reaction), it is possible to examine the feasibility of reaction pathways to determine whether a reaction is thermodynamically allowed. Computational chemistry can also be used to reliably predict a wide range of spectroscopic properties (IR, Raman, UV-Vis, NMR, EPR, photoelectron) to aid in the identification of chemical species (e.g., reaction intermediates). Electronic structure calculations can also provide useful insights into bonding, orbital energies and shapes, which can be used to target the design of new molecules with selective reactivity.

Computational chemistry involves calculations at the quantum, atomistic or molecular, and mesoscales, as well as methods that form "bridges" between scales.

At the **quantum scale**, computations seek to solve the Schrödinger equation[3] and describe the ground state (and sometimes the excited state) energies of chemical species. Other properties (e.g., molecular geometry, vibrational and nmr spectroscopic data, multipolar moments) can be obtained from the quantum level energy calculation. Quantum effects are particularly important in chemical reactions and spectroscopy, and provide the basis for predicting interactions at the atomic and molecular scale. The results of quantum mechanical calculations are often used in the design of molecular force fields providing a connection to the next scale, that of atomistic simulations.

The **atomistic or molecular scale** encompasses a wide variety of computations. Calculations are usually done by molecular dynamics or Monte Carlo methods using classical "ball and spring" force fields. Properties described at this scale might range from thermodynamic properties (critical points, pressures) to transport properties (mass and heat transfer) and phase equilibria. Using statistical mechanics, the results of atomistic or molecular scale calculations can then be applied to describe behavior at the mesoscopic and macroscopic scale (e.g., process or bulk properties).

[3] Theory developed by Erwin Schrödinger to describe the motion of an electron in an atom in terms of three-dimensional wave functions (i.e., the probability distribution of the electrons can be described in terms of waves similar to sound waves).

Mesoscale computations describe behavior and properties of systems that reflect the molecular composition of materials, but consist of far too many atoms to compute atom by atom.

Finally, **bridging** techniques attempt to provide continuity and interface between the various scales, allowing the results of calculations at one scale to be used as input parameters to calculations at another scale.

Current Situation

Computational Techniques

Computational techniques have improved dramatically over the last two decades along with the revolutionary advances in computing power. It is now possible to use computational methods to address a number of practical engineering and design issues in chemical processing. Computational techniques are being used to complement, guide and sometimes replace experimental measurement, reducing the amount of time and money spent on research to bring ideas from the lab to practical application. The potential advantages associated with using computational techniques have led to the formation of computational chemistry groups in many major chemical companies as well as numerous pharmaceutical firms. The growing interest of larger firms in computational techniques has resulted in the growth of software vendors that specialize in user-friendly modeling packages for chemical, biochemical, and biological applications.

Current Applications of Computational Chemistry

- Atmospheric Chemistry
- Drug Design
- Catalyst/Biocatalyst Design
- Materials Design
- Physical Properties for Process Simulation
- Polymer Structures/Properties
- Adhesives/Coatings Design
- Lubricant Properties/Chemistry
- Surfactant Chemistry

Computational chemistry initially began in academic chemistry and physics departments with the development of quantum mechanics in the 1920's and significant efforts have continued in the development of methods and codes. Nobel Prizes in chemistry have been awarded to Pauling and to Mulliken for their respective developments of valence bond theory and molecular orbital theory. The 1998 Nobel Prize in chemistry went to Prof. John Pople and Prof. Walter Kohn for their respective work in developing computational chemistry methods (Pople) and density functional theory (Kohn). A dramatic change in the academic world has been the involvement of chemical engineering faculty in the development and application of computational chemistry tools, especially at the atomistic scale. Today at least fifty academic chemical engineering groups are doing research in this field. In the last ten years involvement in computational chemistry activities by organizations such as the American Institute of Chemical Engineers has also risen dramatically. The first Topical Conference on Applying Molecular Simulations and Computational Chemistry at the 1998 Annual Meeting of the AIChE was one of the largest and most successful topical conferences ever. Such symposia regularly occur at American Chemical Society meetings, at national

international conferences focussed on computational chemistry, and at the Gordon Conference on Computational Chemistry.

In the pharmaceutical industry computational methods have played an important role in structure-based drug design, most recently in the development of the current generation of HIV protease inhibitors. In the chemical industry, considerable effort has been expended on using computational techniques for the design of homogeneous and heterogeneous catalysts. While useful, the application of computational techniques to hetereogeneous catalysts has met with somewhat limited success because of the types of atoms involved (often transition metals) and the lack of techniques available for dealing with them in commercial codes, although significant successes have been found in modeling zeolites and homogeneous catalysts. Recently 2D and 3D periodic quantum mechanical codes have improved this situation. In addition, there have been significant successes in the chemical industry in the use of computational chemistry for chemical process design and even in the design of chemical plants as well as in providing information on safety issues. Computational tools have also been used with varying degrees of success for a diversity of practical applications involving adhesives, coatings, polymers, and surfactants and for the prediction of the toxicity of chemicals. Molecular computations are also currently used for modeling atmospheric chemistry (e.g., the fate of chemical species after release to the atmosphere), and thus have an important role in the study of climate change. New work is being focussed on the use of computational chemistry to address other environmental issues such as ground water and subsurface remediation.

Computing Power

The availability of computer hardware capable of handling highly complex computations has increased rapidly over the last five years to support the development and use of advanced computational software. Computational tools available today are greatly improved from those developed just a few years ago, and are easier to use. Development of vector and vector/parallel machines, RISC architectures and powerful desktop computing, and more recently, highly parallel computing systems, is allowing the solution of problems that were previously impossible to solve. With the availability of new high performance computers, new algorithms and new theoretical methods have been developed to take advantage of the increased computational power offered by these systems. Further, the development of moderate cost, high performance workstations has made it easier to generate input data and to analyze and view the results of large calculations as well as perform reasonably complex calculations at the desktop.

Computing Hardware and Terminology

Supercomputer - A system at the forefront of the computer industry's evolving standard for performance at any particular time. It would typically cost more than one million dollars and would be among the 200 largest and fastest computer installations. The present standard is a computer capable of a peak performance of 100 Gigaflops (100 billion floating point operations) per second - and the associated memory and data (I/O) processing technology to make the high speed of the computer useful.

Vector Processing - Calculations are performed in batches that fill a vector pipe, in which each instruction generates many operations. Supercomputers based on Vector Architecture include special processor hardware to stage and rapidly execute the repetitive calculations that are typical of matrix arithmetic, as found in most scientific computer programs.

Parallel Architecture - At least two (and usually more) processors linked together, and controlled by hardware and software for efficient use of the maximum number of processors at any time. Processors may cooperate or work independently to solve a problem. The highest performance computers today are massively parallel processor (MPP) systems with thousands of processors, terabytes of memory, tens of terabytes of disk, and greater than a Teraflop of peak performance.

Distributed Architecture - A technique to use the capabilities of more than one computer (processors and memory) simultaneously. The technique is usually applied with software controls.

RISC Architecture - Reduced Instruction Set Computer, which is designed to execute commands more efficiently than a Complex Instruction Set Computer like the Intel Pentium processor.

Symmetric Multiprocessing Architecture - System in which multiple processors share a single memory address space.

Flops - Floating point operations per second.

Distributed and Shared Memory - Distributed memory is locally accessible only to the processor or node that "owns" it. Shared memory is directly accessible to multiple processors.

At present, the highest available computing performance is found on massively parallel processing (MPP) computers with more than one teraflop (1000 gigaflops) of peak performance (using highly tuned code will give about 30 to 50% of peak). These systems have terabytes of memory and tens of terabytes of disk storage. The current (1999) cost for a system with these capabilities is in the range of $50 - $100 million. A system with this performance may have distributed memory with several thousand processors (e.g., the Intel computer at Sandia National Laboratory); it may be based on symmetric multiprocessors (SMPs) in which 4 to 16 processors share the same memory, and all

processors are connected by a high speed switch (the IBM SP computers at Lawrence Livermore National Laboratory); or it may consist of a cluster of larger shared memory multiprocessor machines (e.g., the Silicon Graphics "Origin" computer at Los Alamos National Laboratory, which has 48 nodes, each with 128 processors). Each of these systems has demonstrated sustained performance of one teraflop on linear algebra benchmarks and some production codes. Present high-end workstations with up to four processors are available with several hundred megaflops of peak performance, up to four gigabytes of random access memory and more than 20 gigabytes of disk space. The cost of such a workstation, including complete peripherals and software, is well under $100,000.

The next generation of single processor workstation performance (those of reasonable cost and available to a wider group of users) is approaching that of the Cray C90. By combining such workstation processors into MPP systems with distributed memory, it will be possible to attain cost-effective sustained performance greater than 250 gigaflops for a reasonable cost. More important, such computational power is no longer restricted to the sole use of specialized practitioners. With the advent of easier-to-use software, coupled with user-friendly graphical user interfaces, access to high performance computing is becoming available to a much broader community of users. In the longer term, the next step for large scale computers will be MPP systems based on symmetric multi-processors (SMPs), with a goal of 100 teraflops of peak performance in less than ten years. This level of performance is expected to be achieved through improvements in the speeds of individual processors (doubling every 18 months), as well as improvement in memory speeds, bandwidth to memory, interprocessor communication, and general input/output capability. These advances in scientific computing are being driven by the Department of Energy's ASCI (Accelerated Strategic Computing Initiative) program. A similar program has been proposed for non-defense applications.

Advances have also been made that facilitate the handling of the immense amount of data generated by a complex simulation. Distributed and shared-memory computer architectures have both emerged as effective ways to increase computational power. Three-dimensional visualization of molecular structure is a commonplace and practical tool for obtaining useful information from simulations.

Trends and Drivers

Modeling and Simulation in the Chemical Industry

The chemical industry has been highly successful in remaining globally competitive. Part of the reason for the industry's success is its ability to meet new technological and societal needs through research and development. The chemical industry currently leads the industrial sector in investments in R&D (over $18 billion in 1995), and is responsible for one in every eight patents issued [CMA 1996].

In recent years the industry has increased its focus on the development of high-valued specialty chemicals as well as products for the biomedical and materials industries. Development of these products, as well as the ability to create new products that have targeted properties, requires more precise control and understanding of physical and chemical properties. Computational chemistry

will increasingly be used to meet these needs by providing an understanding of how molecular, collective, and mesoscopic features influence macroscopic behavior.

The spectacular rate of developments in computational chemistry will potentially become even greater over next decade. Since the passage of the High Performance Computing Act of 1991, government investments valued at more than $1 billion/year have created extraordinary computational and networking environments that may be used to apply computational methodologies to practical problems. These investments are expected to continue, and could contribute to a dramatic expansion in the range of problems that can be solved through computational chemistry [NSF 1997].

Historically, the body of knowledge in computational chemistry has been generated largely through academia and the national laboratories, then distributed to industry by third party vendors at a relatively slow pace. In the future, increased collaboration between industry, academia, and government researchers could help to develop a more efficient mechanism for providing robust, highly useable versions of new computational techniques to the user community. Chemical engineering researchers are becoming more and more involved in both application and development of molecular modeling methods, and this trend should also contribute to their power and usability on practical problems.

The desire to improve manufacturing processes and the need to rationally design new materials will be major driving forces in the chemical industry over the next two decades. The development of new technology for manufacturing will be motivated by the need for "Green" processes that minimize the use of energy and the production of waste streams. The rapid and efficient design of new materials, chemical intermediates and products will be necessary to achieve goals for energy efficiency and increased productivity while minimizing environmental impacts. The design of new catalysts (chemical as well as biochemical) will become increasingly important as the industry strives to improve yields, reduce emissions and effluents, and develop alternative "Green" chemical processes. Modeling and simulation will play a critical role in the development of both new manufacturing technology and material/product design.

Advances in modeling and simulation, particularly computational chemistry, could have a significant impact on reducing the cost and time involved in designing chemical processes and new materials or catalysts. Accurate molecular modeling tools would allow researchers to more quickly predict the properties and performance of chemical species prior to the process design stage. Significantly, this speed-up of calculations will make feasible calculations that were previously beyond practicality, making the overall R&D investment more efficient. The attractive economic advantages of using advanced, more accurate models will help to promote the increased use of these tools.

Many new developments in computing methodologies will be driven by the rapid advancement that is occurring in computer technology. New software (advanced numerical algorithms for parallel machines, object oriented modular programming) and theory will be needed to keep pace with the revolution in computer architectures.

Computer Technology

New computing technology is entering the marketplace almost daily. The speed of high performance computing platforms has increased dramatically, and in 1999 will reach over three tera flops in some models. Dramatic advances have been made in highly parallel processing and parallel numerical algorithms. The rate of improvement in computing technology is not expected to slow, and will lend further support to the development and effective use of computational tools.

A critical variable for computational chemistry will be the ever-changing world of computer hardware. The development of massively parallel supercomputing systems will have a dramatic but indirect impact on the use of computational chemistry in industry. Massively parallel resources will provide the computing power needed to develop highly complex models (e.g., intermolecular potentials) which will serve as input to the computational tools applied by industry, government, and academic users. The development of these complex models will be critical to improving the utility of computational chemistry for practical industrial applications. Massively parallel systems will also be essential for complex computations that are too large for a single research entity to perform (e.g., traversing of time and spatial scales, protein folding) [NSF 1997]. These very large calculations will provide essential validation for some of the methods used to bridge from quantum to atomistic scale or from atomistic to mesoscale.

The chemical industry is not likely to adopt highly sophisticated massively parallel machines in the next few years but will continue to adopt moderately parallel supercomputers with symmetric multiprocessing architecture (i.e., multiple processors share a single memory). Many of the computational codes used by the industry have already been ported to this architecture [NSF 1997]. However, based on ASCI and the President's Information Technology Initiative for the 21st Century, this could change as MPP systems become easier to use, the cost is lowered, and software becomes more generally available.

Energy Price and Supply

The availability and cost of fossil energy for use as fuel and feedstock is of vital importance to the chemical processing industries. For some products, energy for heat, power, and feedstocks can account for up to 85 percent of total production costs (overall, chemical industry energy costs are about 8 percent of the value of shipments) [DOC 1994, CMA 1996]. Feedstock availability is also a primary concern for many chemical producers — nearly 50 percent of energy consumed is in the form of petroleum-based feedstocks. The industry is highly susceptible to volatility in energy feedstock price and supply, a fact made evident during the oil embargo of 1973. Although energy prices are currently low, history shows they can be subject to rapid change with devastating impacts. Advances in technologies like computational chemistry, which have the potential to directly impact process and feedstock energy consumption, will be of increasing importance to the industry as it strives to maintain its competitive edge in the world marketplace.

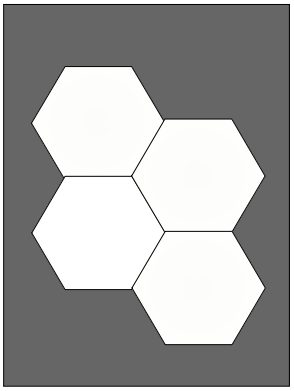
Government Regulations and Public Policy

Chemical production, use, storage, transportation, and disposal are heavily regulated by Federal and state laws and regulations. Compliance with these statutes (e.g., Clean Air Act and its Amendments, Toxic Substances Control Act, Resource Conservation and Recovery Act, and others) places an enormous financial burden on the chemical industry in terms of capital and

operating expenses. In 1994 the industry spent about $4.6 billion on pollution abatement and control, nearly double the costs incurred in 1984 [CMA 1996]. New environmental programs are continually being proposed at the Federal, state and other levels of government, and will likely further increase the difficulty and cost of compliance. Consequently, cost-effective technologies that improve the environmental performance of processes will be increasingly important.

Computational chemistry will become an increasingly important tool in the industry's strategy for improving environmental performance. As accurate computational techniques are developed, they will be used to assess the environmental and safety aspects of chemical species and new chemical processes (e.g., byproducts, toxicity, fate and transport in the environment), and will assist in the design of more environmentally-benign materials and products.

As we progress into the 21st century, industry will continue to emphasize shareholder return, globalization, and the efficient use of capital, people, and the implementation of technology. According to the Technology Vision 2020 report, the two major driving forces of the chemical industry are the desire to improve manufacturing processes and the need to design new materials rationally. Modeling and simulation is a critical technology for achieving these goals because it can provide the detailed technical understanding needed to design useful and profitable materials and processes. In the future, models created by multi-disciplinary teams will be developed more quickly and will be more indicative of reality.



3 Quantum Scale

Current Situation

Advances in computational quantum chemistry are pursued worldwide by a large number of researchers based in the disciplines of chemistry and physics. These researchers contribute to the refinement of existing methods (e.g., Hartree-Fock, perturbation and density functional theory) as well as the development of new techniques. Several well-known quantum chemistry software packages (GAMESS, GAUSSIAN, MOPAC, UniChem, TURBOMOL, NWChem) are available to academic and industrial users directly or through commercial vendors. At the present time, the translation of new developments into readily available codes occurs relatively rapidly and through well-established networks. Currently, there is significant research in academic institutions and in national laboratories on new theoretical methods, algorithms, basis sets, and approaches in computational quantum chemistry. There is also significant research focussed on applied systems of practical interest such as catalyst design, reaction pathways, organic and inorganic molecules, etc. [NSF 1997]. There is no part of chemistry which is now not impacted by computational chemistry. Continued improvements in theory and algorithms are resulting in the continued expansion of the range of molecules that can be treated with computational quantum chemistry techniques as well as higher accuracy of results. One can calculate the heats of formation of small molecules to significantly better than 1 kcal/mol and can calculate accurate charge distributions at the ab initio level for molecules with >700 atoms.

Over the next few years computer codes available through general release will include most aspects of *ab initio* molecular orbital theory and density functional theory for molecular electronic structure and molecular dynamics. Currently, *ab initio* molecular orbital theory provides the most accurate prediction of molecular properties. High quality basis sets are available for first and second row (of the periodic table) atoms as well as for main group third row atoms. Correlation methods such as coupled cluster theory with large basis sets that can be extrapolated to the complete basis set limit (such as the correlation-consistent basis sets) can provide chemical accuracy (i.e., values for properties such as structure and energy that are as accurate as the best available experimental methods) for many small molecules. Using density functional theory and other correlation treatments, one can obtain somewhat lower but still useful accuracy for much larger systems.

The Language of Computational Quantum Chemistry

***ab initio* Molecular Orbital Theory** - describes the electronic structure (e.g., electrons, nuclei) of molecules using rigorous quantum mechanical principles. A solution of the Schroedinger equation for electronic motion in the fixed nuclei approximation using orbitals.

Basis sets - a complete set of known functions which represent the atomic orbitals.

Car-Parrinello - an approach to finding the energy and structure simultaneously by performing molecular dynamics simulations while optimizing the energy. Usually used in a density functional theory approach.

Density Functional Theory (DFT) - a theoretical model by which the energy of an N-electron system can be described as a functional of the density.

Electron Correlation - defines the treatment of electron-electron interactions. These interactions are missing in the simpler Hartree-Fock approximation.

Hartree-Fock - a theoretical model which solves the Schroedinger equation, self-consistently, using an antisymmetrized, linear combination of atomic orbitals and a single arrangement of electrons within those orbitals.

Heavy Atom - any atom other than hydrogen. The number of non-hydrogen atoms is used loosely to characterize the difficulty of a quantum calculation.

Perturbation Theory - a size-consistent, systematic procedure for finding the correlation energy neglected by Hartree-Fock methods based on a perturbation expansion of the energy**.** Other approaches to finding the correlation energy include coupled cluster methods and configuration interaction.

Scaling - describes the rate of increase in computational cost with problem size proportional to N^m where N is the number of basis functions and m is an exponent which is method-dependent.

Electronic and optical properties, including nonlinear optical properties can be predicted with semi-quantitative to quantitative accuracy for small molecular systems. For large systems (e.g., macromolecular aggregates and materials) optical and magnetic properties can be predicted with qualitative or semi-quantitative accuracy. Electronic excitations and ultraviolet properties for small and large systems can currently be predicted with qualitative or semi-quantitative accuracy. For nuclear magnetic resonance (nmr) spectra, calculations for up to 1000 basis functions can be done. Depending upon the molecule, 5-10 ppm accuracy can be obtained for many nuclei and approaching 1 to 2 ppm for smaller systems with up to 20 atoms. [NSF 1997, PNNL 1997]

Accurate methods are available for the prediction of transition state geometries and energies associated with gas phase reactions at the same electronic structure theory level as used in accurate calculations on ground states. Rates can be calculated from this information by using transition state theory or variational transition state theory to within a factor of 2 over a broad temperature range. It is however, presently difficult to deal with coupled low amplitude motions, anharmonicity, and quantum mechanical (tunneling) effects. For reactions in other phases, currently obtainable accuracy is lower where specific solvent effects or reactions at interfaces are important.

For solid-state computations, codes based on Hartree-Fock or density functional theory are available but are slow and difficult to use. Chemistry applications in the solid-state are currently not well-integrated with the solid-state physics community. Calculations for solid state systems can not yet be done with chemical accuracy, especially for chemically reacting systems. As a result, most calculations aimed at the design of heterogeneous catalysts with accurate energies are now done on model clusters.

The reliable prediction of solvent effects is needed for studying reactions occurring in solution, for both chemical and biochemical processes. If one treats the solvent explicitly, this can lead to a very large increase in computational expense because of the need to average over solvent configurations and because of the need for large numbers of solvent molecules. It is possible to

use continuum dielectric models to treat solvent effects, which eliminates the need to average over solvent configurations, but doing so requires the introduction of more parameters in order to get accurate results. A variety of combined methods are being developed mixing quantum results with molecular mechanics and continuum models but these are not yet generally available.

Interpretive Summary of Performance Targets, Barriers, and Needs

Detailed lists and discussion of the performance targets, technology barriers, and research needs for the quantum scale are presented in the following pages. The basic themes can be summarized by calling for the ability to compute a full range of molecular properties from first principles (*ab initio*) on larger systems, more accurately, faster, and cheaper. We use the term "larger systems" rather than "larger molecules" because such methods need to be equally applicable and reliable for arbitrary assemblies of atoms, including transition states, excited states, cluster of molecules and reactive intermediates, and fragments of polymer systems or inorganic crystals.

There are two broad performance targets: (1) to be able to calculate highly accurate properties for small-to-medium size systems, consisting of up to about thirty heavy atoms; (2) to obtain good accuracy and reliability for medium-to-large systems, consisting of 500 heavy atoms or more. The second target allows (or requires) help from appropriately validated and calibrated empirical factors, corrections, and hybrid methods. The following figure depicts the correspondence between the performance targets and the barriers listed in Exhibit 3-2.

The principal barriers to achieving high accuracy on small-to-medium size systems are:

- the extremely rapid increase in computational resources required as the size of the system increases, referred to as the "N^7 scaling problem" for present high-accuracy methods;
- the need for experimental validation[4] of new methods;
- the need for convenient, practical access to cost-effective high performance computing;
- the need for a high level of expertise in order to obtain reliable results and avoid "ugly surprises" due to mis-application of advanced methods.

The principal barriers to achieving good accuracy on medium-to-large size systems are:

- lack of adequate basis sets for all atoms of the periodic table;
- the need for validation;
- the need for more accurate, consistent functionals for the density functional theory methods, which are appropriate for larger systems;
- the need for better, more fundamental and universal empirical factors, corrections, and hybrid methods;

[4] The purpose of validation is not really to show agreement between experiments and computational models. It is, rather, to challenge the model - - to discover the limitations and range of applicability of the model. A “validation” project which merely demonstrates agreement with experimental data is much less useful than one that shows where the model fails, as well as how it performs under a variety of conditions. “All models are wrong. Some are useful for the purpose for which they are intended.” (source unknown)

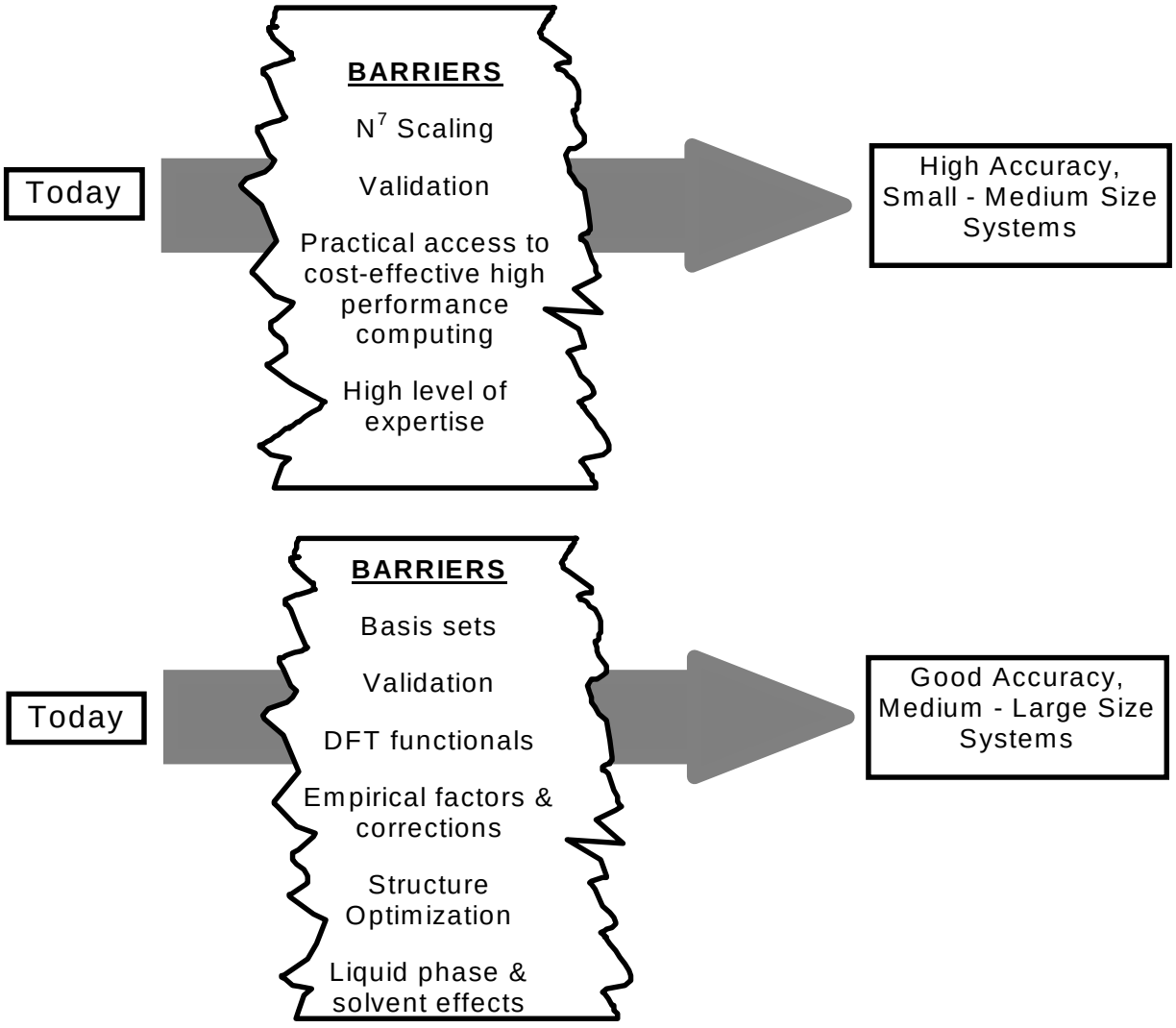
- the need for better methods to compute the best structure or ensemble of low-energy structures for large, flexible molecules;
- the need for better methods of modeling the liquid state and the interactions of target molecules with solvents.

Four of the highest priority responses called for in Exhibit 3-3, Research & Development Needs, are equally applicable to both targets. These include:

- create methods with better scaling and better solutions to the fundamental causes of error;
- combine quantum methods with other models to solve larger problems;
- create accessible benchmark calculations and experimental results for selected "gold standard" reference molecules;
- design expert advisory systems and more usable robust software.

Two other high priority R&D needs are more specific to the second target:

- develop robust methods for solvent calculations;
- develop better structure optimization methods.



Performance Targets for the Quantum Scale

Quantitative performance targets have been identified for computational quantum chemistry, as shown in Exhibit 3-1. These targets represent significant advances over current capability, and would greatly enhance the utility of quantum scale calculations for practical applications. They also represent what is anticipated to be the state-of-the-art in this field by the year 2020.

Exhibit 3-1. Performance Targets for Quantum Scale by 2020 (Absolute Thermochemical Energy)

Size of the Problem	Accuracy	Performance
30 heavy atoms	0.2 kcal/mole	Increase speed by 300,000 or 2^{18} Cost < $1,000 per case
500 heavy atoms	1-2 kcal/mole	
Intermolecular/relative energetics	Increase accuracy by a factor of 5-10	

By 2020, the most important performance targets are to increase the size of the systems that can be addressed as well as the accuracy of results. The current accuracy of quantum calculations with existing methods is 0.5-2 kcal/mole for small molecules in the first and second row of the periodic table; transition metal systems and heavier elements fall in the range of 5-10 kcal/mole for the best cases but can be significantly outside these limits. The ability to address some large systems is currently not available, and for those systems that can be treated, accuracy decreases considerably.

The targets shown in Exhibit 3-1 require several orders of magnitude improvement over what is achievable with existing techniques. It is currently not possible to treat systems effectively containing more than about 10 heavy atoms with great accuracy and reliability without help from empirical methods and correction factors. Being able to do so would open many new opportunities and greatly expand the types of systems that can be simulated using quantum chemistry techniques. Many of these are industrially important (e.g., polymers, homogeneous and heterogeneous catalysts).

Another useful way to characterize both the present state of the art and the performance requirements for the future is in terms of the full cost of obtaining a reliable and useful answer. For example, highly accurate molecular energies, such as heats of formation or transition state energies, are sometimes required for engineering reaction simulations. An expert with ready access to a supercomputer or a high-end multiprocessor workstation (i.e., an R&D department compute server) can now calculate the required result for a molecule with five or six heavy atoms within a week or two at a cost of $3,000 - $5,000. This cost is roughly evenly divided between personnel labor and computer charges. Some projects can bear this cost, which is now competitive with experimental methods. However, typical projects require many such calculations on perhaps dozens of molecules. Industry needs to be able to perform such computations on molecules with 20-30 heavy atoms for less than $1,000 per molecule.

Computing speed (the ability of the computer architecture and hardware to process calculations) is a critical element in the advancement of quantum computational tools. To keep pace with the desired increase in accuracy and size of systems modeled, the speed of computing performance will need to increase at least by a factor of several hundred thousand. Current computing speeds for a single processor have been roughly doubling every 18 months, and this trend is expected to continue in the near future, but it cannot continue indefinitely. It is evident that the performance targets in Exhibit 3-1 will not be achieved by hardware speed alone. It will also require improvements in theoretical methods, algorithms, and more efficient use of multiple processors. For systems of hundreds or thousands of atoms, it will also require further development and judicious use of empirical corrections. And, for the practical use of computational tools, such speeds need to be found in systems that are available at reasonable cost to the industrial user.

Quantum Scale Technology Barriers

There are a number of barriers that inhibit the development and use of computational methods at the quantum scale. These are shown in Exhibit 3-2, organized by topic.

Data/Basic Knowledge

The greatest barrier inhibiting the use of computational tools at the quantum scale is the lack of a consistent set of reliable and efficient basis functions for the entire periodic table, coupled with the lack of experimental validation of computed results. Current basis sets allow for the treatment of molecules with up to ten first or second row (of the periodic table) atoms and associated hydrogen atoms with relatively high accuracy. For larger systems the level of accuracy is much lower, and many systems involving transition metals are difficult to model. For example, molecules containing transition metals have many electrons requiring many basis functions to describe; they can have multiple spin states; and they exhibit relativistic effects. However, there is work ongoing to develop correlation-consistent basis sets for the first row of transition metal atoms. Significant work needs to be continued on developing effective core potentials and basis sets for transition row elements, especially those important in catalysis. In addition, semi-empirical methods for treating organometallics or metals need improvement in accuracy and applicability.

Exhibit 3-2 Technology Barriers
Quantum Scale
(◆ = Most Critical Problem Areas/Barriers)

Computational Limits of Current Modeling Tools	Data Basic Knowledge	Computer Hardware Architecture	Institutional Educational
N^7 scaling ◆◆◆◆◆◆ Insufficient validation for specific problems ◆◆◆ Lack of methods for structure optimization of large molecules ◆◆◆ Lack of accurate/consistent DFT functionals ◆◆ Poor prediction of uncertainties (Occurrence of pathologically wrong answers from current methods) ◆ Limited ability to interpret results ◆ Lack of techniques for dealing with excited states ◆ Inability to apply quantum mechanical information in kinetics (as a function of temperature) ◆ Inability to find important conformations in large molecules ◆ Lack of consistent multi-reference methods to be used in building databases ◆ Lack of general purpose methods/codes for solid state calculations Insufficient empirical parameters for computational methods Lack of availability of methods to incorporate relativistic effects No way to optimize use of options to arrive at desired results Lack of readily obtainable electronic record of results	Lack of basis sets to cover the entire periodic table ◆◆◆◆◆ Lack of data and validated models for solvent effects ◆◆◆ Lack of fast methods for predicting transition states ◆◆ Lack of useful semi-empirical methods for organometallics or any metals (all of the periodic table) ◆◆ Poor understanding of organics containing mixed/multi halogens ◆◆ Insufficient methods for dealing with the Hindered-Rotor problem ◆ Inadequate understanding of transition states of floppy molecule structures (coupled low energy nodes) ◆ Length of time required for data accessibility Lack of data mining tools	Un-availability of cost-effective computing power Insufficient computer speed to apply quantum calculations to dynamical problems. Lack of practical access to high-end power	High level of expertise required to get good results Lack of management understanding and support for quantum chemistry Inability and/or reluctance of industry to share success stories in computational quantum chemistry Problems in communicating results and receiving recognition for activities in quantum chemistry

Adequately accounting for solvent effects is a severe challenge. Treatment of solvent effects can increase the computational expense significantly, primarily because of the need to average over solvent configurations to obtain converged results, as well as the need to treat explicit

interactions with solvent molecules. The ability to incorporate solvent effects is essential for treating chemical reactions in solution, and especially in biochemical processes.

Adequate methods are currently lacking for easily predicting transition state geometries and energies, particularly for floppy molecules (i.e., coupled low energy modes). Understanding of how to treat certain types of halogen-containing systems, although improving, limits capabilities for modeling these systems, which are common throughout the chemical process industry.

Computational Limits of Current Modeling Tools

Currently available codes at the quantum scale are limited by a number of factors. The most significant of these is the N^7 scaling of the most theoretically rigorous and accurate methods (CCSD(T)or multireference CI) and the fact that one needs very large basis sets with high angular momentum functions to get accurate results. The N^7 scaling property means that, as the number of electrons and atoms in a system goes up, the required computing goes up as the seventh power of the number of basis functions used to describe the locations of the electrons. For example, doubling the number of non-hydrogen atoms may require $2^7 = 128$ times the computing resource.

Other factors limit the type and size of problems that may be solved using available quantum scale tools. Methods for treating large molecules are seriously limited within the existing set of quantum scale computations, decreasing the usefulness of these tools for many systems of practical importance due in part to the complexity of optimizing the geometry of these molecules. There is also a lack of general-purpose methods for treating solid state systems. Current solid state issues include: the ability to predict reactions on surfaces; the need to include low levels of dopants and different morphologies; the ability to treat macroscopic shapes and natural materials; and the ability to predict accurate binding energies.

The inability to predict or model certain properties or states of molecules is also a limiting factor for currently available tools. The most important of these include a lack of techniques for dealing with excited states easily; the lack of accurate and consistent functionals for DFT methods; the lack of chemically general multi-reference methods that are easy to use; and the approximations of present methods to incorporate relativistic effects. An overarching problem involves difficulties in applying the minimum number of quantum mechanical energetic results to predict kinetics (obtaining accurate reaction rate constants as a function of temperature and pressure).

In terms of usability of currently available tools, several factors are limiting. For example, there is no way for the non-expert user to optimize the available modeling options to arrive at the desired results. This often means that numerous unnecessary computations are performed at considerable computing expense. Efforts are underway to develop a more accessible database of computational results to alleviate this problem. Empirical parameters are lacking for a number of computational methods, requiring the use of estimation methods that increase the possibility of erroneous results and the occurrence of pathologically wrong answers. Another major barrier is the lack of validation for specific problems of interest to the user community. In these cases the reliability (and hence utility) of results is highly uncertain. Other limitations to current models include inadequate methods for predicting uncertainties in calculations as well as interpretation

of results, particularly for non-expert users. These shortcomings limit the widespread acceptance and usefulness of quantum scale tools to solve practical problems in the chemical plant.

Computer Hardware/Architecture

In spite of the many advances in computer hardware and architecture, computer hardware still places limits on highly complex computational tools. Current computer systems are still not fast enough to perform the many billions of calculations required for some simulations. Another problem for the industrial user (indeed, for most users) is that supercomputing systems require a large investment that may be difficult to justify.

Institutional/Educational

Advances in the development and use of quantum scale tools is further limited by industry perception of computational quantum chemistry and its results. In general there is a lack of understanding and a reluctance to support quantum chemistry as a useful industrial tool among many senior chemical industry managers. This often translates into problems in communicating results as well as recognition for activities in quantum chemistry. The problem is exacerbated by the high level of expertise required to properly run currently available quantum scale models and obtain and interpret results for problems of industrial importance. One of the main problems faced by the industrial practitioner is the need to convert the question being asked by the bench chemist or design engineer into one that can be addressed by computational methods. Another institutional barrier that inhibits acceptance of quantum computational methods is the inability and/or reluctance of industry to share their success stories in quantum chemistry and the potential benefits. However, future prospects look bright because of a general increased awareness of computational chemistry methods among younger scientists and new hires.

Quantum Scale Research Needs

Research needed to overcome barriers to the development and use of computational quantum chemistry are shown in Exhibit 3-3, with priority levels and time frames for research identified. Time frames indicate the period in which the results of various R&D activities are expected to be available for use by the modeling community at large, assuming sufficient R&D funding.

Computational Methods

Ultimately, the goal is to develop computational capabilities at the quantum scale that are efficient, accurate, usable, and allow simulation of a broad range of chemical and biochemical systems by a broad range of chemists and engineers. Research in computational methods will help to overcome some of the more critical barriers associated with current computational limits. For example, the integration of quantum results with other models will further the ability to solve problems involving larger systems. Research to develop computational methods with much better scaling will allow one to treat much larger molecules with high accuracy and lower the most critical technical barrier to the use of highly accurate quantum tools.

In terms of time frames for R&D, early progress in developing tools for integrating statistical mechanics and kinetics with quantum mechanics is needed to improve the linkage with engineering modeling and enhance the usefulness of computational tools for a wider range of problems. Closely related to this effort will be the cross-fertilization of simulation levels, requiring the movement of data from raw quantum calculations into engineering codes. The design of more general expert systems that increase the utility of quantum tools will be needed throughout the time span between now and 2020. This includes the development of query capability and other functions that optimize the computing time as well as user time. Research to improve the computational scaling of treatments of electron correlation also needs to be pursued over the entire time frame.

Exhibit 3-3. Research & Development Needs
Quantum Scale
(✪ = Top Priority; ● = High Priority; ○ = Medium Priority)

Time Frame	Computational Methods	Data/ Basic Knowledge	Computer Hardware & Software	Institutional/ Educational
NEAR (0 - 3 Years)	Successfully integrate quantum results into other models/methods to solve larger problems ●●●●●●●○ Establish links between combinatorial chemistry and computational chemistry Develop tools for integrating statistical mechanics and kinetics with quantum mechanics Accomplish cross-fertilization of areas -- move data from raw quantum mechanics into engineering codes		Develop generally accepted standards - information storage - data interface ●	Develop generally accepted standards - information storage - data interface ● Improve accessibility of codes
MID (>3 - 10 Years)	Develop robust methods for solvent calculations ✪●●○○ Develop better, more efficient structure optimization methods ●●●○○○○ Develop easy to use relativistic methods in addition to effective core potentials ●○ Devise good embedding schemes (hybrids like QM/MM) for large systems ○○ Incorporate automated generation of potential functions (force fields)	Create accessible benchmark calculations and experimental results for molecules ✪✪✪○○○		

Exhibit 3-3. Research & Development Needs
Quantum Scale
(✪ = Top Priority; ● = High Priority; ○ = Medium Priority)

Time Frame	Computational Methods	Data/ Basic Knowledge	Computer Hardware & Software	Institutional/ Educational
MID - LONG	Produce general, accessible and consistent multi-reference methods ○	Study detailed kinetics of reactions at surfaces and in solution ✪●●		
LONG (>10 Years)	Develop reliable accurate functionals for density functional theory ○○			
SPANS ALL TIME FRAMES	Design more general expert systems - user query capability - optimized computing/ human time ✪✪●●●●●○ **<3 — 20 years** Create improved methods (e.g., better treatment of correlation, etc.) with better scaling ✪✪✪✪●●● **<3 — 20 years**	Establish centralized, public-access electronic source for theoretical/ experimental benchmark data ✪●○○○ Create greater diversity of "gold standard" reference molecules - experimental thermo-chemistry in agreement with multiple computational approaches ●○○○○○ Expand range of typical industrial problems that can be treated - incorporate exptl and field data	Develop transparent parallel computing ●●●○○○ Create faster computational codes ○ Develop software that is appropriate for the evolving computer environment ○ Develop accessible, optimized codes for existing/new architectures	Decrease disconnect between organic/ physical chemists to obtain better interpretive tools and analysis ✪✪✪●●○ Conduct modeling activities especially with chemists - enhance connectivity - improve mind set ✪✪✪○○○ Create mechanisms for improving usability of models for "non-experts" - education in the field, both undergraduate and graduate level - improved codes ●●●●●○

In the mid-term, computational techniques that permit the incorporation of solvent effects are a high priority. The inability to effectively model solvent effects limits the accuracy and usability of current models for many reaction systems. This effort will depend greatly on the increased

availability of basic data and knowledge obtained through fundamental research and experimentation. The development of better methods to optimize the geometry of flexible molecules is also a critical mid-term goal. The development of better methods to treat relativistic effects will continue throughout the mid-term, and will help to resolve current limitations in this area.

The development of reliable, accurate functionals for density functional theory, noted as a critical barrier, can only be accomplished through long-term research. The same is true for the generation of consistent multi-reference methods (also a critical barrier), although research could provide some results in this area in the late mid-term (8 - 10 years).

Data/Basic Knowledge

Establishing a centralized, public-access electronic source for theoretical and experimental benchmark data is of the highest priority in the area of data/basic knowledge research needs. Such a source would enhance the utility of current models, increase the ability to interpret results, and enable more rapid advances in existing methods. Closely related to this effort is the creation of a greater diversity of "gold standard" reference molecules that can be used to correlate results from multiple computational approaches. Another important effort is the collection and incorporation of experimental data to help expand the range of industrial problems that can now be treated with quantum scale computational tools. All these activities could occur and provide continuing results throughout the time frame between now and 2020.

Early progress in the building of data and knowledge for treating solvent effects and transition states will be essential to the further advancement of computational quantum methods. Research to study the kinetics of reactions as they occur at surfaces and in solution is also a high priority research need and could be accomplished by the mid-long term. Research is needed to better integrate methods for predicting kinetics and quantum mechanical energetic information in computational methods, a capability which is significantly limited in current widely available tools.

Computer Hardware/Software

Computing power will continue to evolve independently of the research done in computational chemistry. However, some advances will be critical to the increased use of computational tools by the industrial, government, and academic user community. The most important is the development of transparent parallel computing. Faster computational codes and the development of software that is appropriate for the higher performance computing environment will also be vital to the advancement of quantum methods. This will include the generation of accessible, optimized codes that are compatible with existing and new computer architectures. One must develop codes that are high performance, portable and scalable on a variety of computer architectures in order to maximize their usability and minimize the cost of their maintenance.

Institutional/Educational

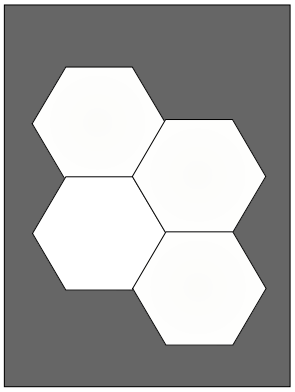
The current disconnect between organic and physical chemists should be overcome to allow the development of better interpretive tools and analysis of quantum chemistry results. This could be accomplished through more cooperative research activities and the exchange of results. This

is a high priority activity that should be on-going across the entire time span from now through 2020.

Other activities are needed to improve the acceptance and usability of quantum tools. Conducting modeling activities with chemists is a high priority research need that would enhance connectivity between the theoretical and the practical and improve the perception of quantum models and the validity of their results. Another high priority need is the creation of mechanisms geared specifically to improve the usability of these models for "non-experts" in the chemical enterprise. Such mechanisms include more user-friendly codes, improved problem solving environments, and increased education about quantum models at both the undergraduate and graduate level. Many of the programs currently available are not user-friendly and may be difficult for a non-theoretician without specialized expertise to use and interpret.

Education about model capabilities would provide new graduates with the information needed to make choices related to computational techniques once they are working in industry. This will become increasingly important as chemical engineers in the field are faced with the challenges of further optimizing processes and developing new chemicals and materials.

Another important activity is to increase interaction between researchers working in computational molecular science and those working in fluid dynamics. The synergy possible when the two methodologies work together on a common goal is enormous and shouldn't be disregarded. The disconnect between these two disciplines results in the slow dissemination of advances in methods that could be used in both fields.



4 Atomistic Scale

Current Situation

Simulations performed at the atomistic or molecular scale are much more diverse than those typical of computational quantum chemistry. A wide range of properties from thermodynamics (e.g., equation of state, phase equilibrium) to bulk transport properties (e.g., viscosity, thermal conductivity) and even the rheology of fluids can be calculated. The systems modeled may be reactive, undergoing phase changes, and consist of heterogeneous or homogeneous components (both chemical and biological). As a result of this diversity, researchers in a broad range of disciplines (e.g., physics, chemistry, chemical engineering, biology, biochemistry, geochemistry) around the world contribute to the development and refinement of atomistic scale methods (e.g., Monte Carlo, molecular dynamics). Many industrial groups are also users of these techniques, ranging from commodity chemical to pharmaceutical manufacturers.

Atomistic/Molecular Scale Terminology

Molecular Dynamics Methods - atomistic molecular simulation methods in which Newton's classical equations of motion are solved numerically for a system of atoms or molecules

Monte Carlo Methods atomistic molecular simulation methods in which the equilibrium configurations of systems of atoms or molecules are sampled statistically

Non-equilibrium Molecular Dynamics - molecular dynamics method in which systems that are not at equilibrium are simulated

Gibbs Ensemble Method- Method in which the conditions of phase equilibrium are directly simulated

Gibbs-Duhem Method - method of determining phase equilibrium by integrating the Gibbs-Duhem equation

Intermolecular Potentials - force fields existing between atoms, molecules, or sites within molecules.

Car-Parrinello Methods - molecular dynamics methods in which the intermolecular potential is approximately calculated quantum mechanically at each time step.

One of the consequences of the diversity of researchers and users of atomistic methods is that many research calculations are performed by special purpose codes rather than commercial codes, and adoption of new techniques into commercial codes is relatively slow. A few groups and software companies have developed atomistic scale software (GROMOS, AMBER, CHARMM, DISCOVER) that is more easily usable, but most of these are focused on biological systems at ambient or near-ambient conditions in aqueous solution. Furthermore, it requires a real effort to input the data. The transferability issue for software and force fields is exacerbated by the dichotomy between researchers whose focus is

biological (prediction of properties near ambient conditions) and those interested in chemical processes (wide ranges of temperature and pressure, as well as phase equilibria) [NSF 1997].

Third party vendors (software developers) have been reluctant to incorporate the latest developments in atomistic simulation into commercial packages primarily because of the fractured nature of the user community. The result is that commercial packages are frequently as much as a decade behind leading edge atomistic simulation technology. Examples of this are the Gibbs ensemble method (a decade old) and non-equilibrium molecular dynamics (two decades old), which have yet to be implemented in commercial packages.

An increasingly important component of research at the atomistic scale is the development of intermolecular potentials suitable for a wide variety of compounds and temperature/pressure conditions. Such potentials are critical to the prediction of properties of practical importance to chemical process and product design (e.g., critical point properties, vapor pressure curves). Unlike other advances in atomistic simulation, third party vendors have been relatively quick to implement leading edge codes relating to intermolecular potentials and most commercial packages reflect the current state-of-the-art.

Simulations over long periods of time relative to the shortest time scale motion cannot be accomplished with current computational methods at the atomistic scale, even with parallel supercomputers, due to limitations in single processor speed and in bandwidth and latency. Modelers currently perform simulations at some appropriate time scale and represent other motions using empirical methods and simplified models. Examples include ignoring C-H vibrations in a polymer model, or treating the slow diffusion of molecules in a polymer matrix or a zeolite pore using activation energy barrier concepts.

Thermophysical properties for gases can be predicted now with reasonable reliability based on the interaction potentials of dimers and transport theory. For liquids, such properties can be predicted by using molecular dynamics and Monte Carlo simulations. The reliability of such predictions is very dependent on the quality of the potential functions used, and is less certain for mixtures or if ions are present because accurate interaction potential models are less likely to be available.

At present, it is routinely possible to study atomistic systems (or systems represented as interacting atoms, such as polyatomic and polymeric systems) for periods on the order of nanoseconds. The record for the longest simulation using MD techniques is on the order of 1 μsec for a biochemical system. However, much longer time scales are needed to study phase transitions, rare events, kinetics, and long-time dynamics of macromolecules.

Interpretive Summary of Performance Targets, Barriers, and Needs

Detailed lists and discussion of the performance targets, technology barriers, and research needs for the atomistic scale are presented in the following pages. The basic themes can be summarized in four categories of need:

- to be able to simulate larger systems, consisting of many more atoms than now possible, covering larger size scales, and to simulate dynamic phenomena on much longer time scales;
- better methods and potential functions, particularly those that govern the forces between molecules;
- validation and applicability to complex problems of industrial importance;
- availability and usability of codes.

The diagram below shows the relationship between the performance targets of Exhibit 4-1 and the technology barriers of Exhibit 4-2. The specific barriers are discussed in more detail below.

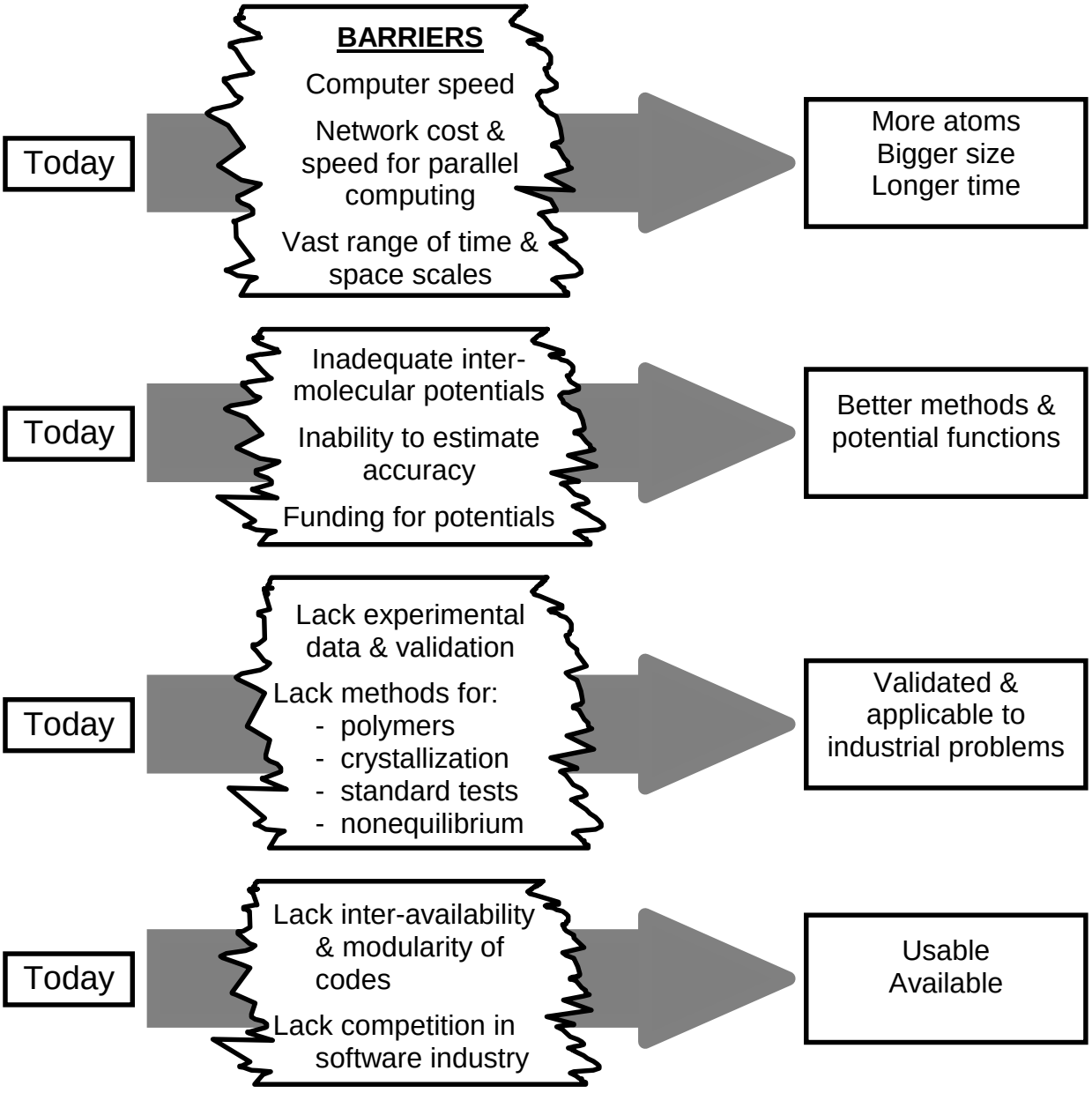


Exhibit 4-3 and the attendant discussion list a number of R&D needs. Several of these in the category of "Human and Institutional Factors" are applicable to all four performance targets. These include encouraging better communication between communities of scientists, supporting

consortia and other sorts of collaboration mechanisms, and improving the relationships between commercial software developers, their customers, and the more fundamental research institutions.

The thrust toward bigger systems and longer time scales is supported by the call for a common software framework built upon standards for modularity, portability, and scalability on parallel computing platforms. The longer term needs for new theories and models and innovation in the computational methods for handling very long time scales are identified.

The second performance target of better methods and potential functions is supported by a straightforward call for more support and better reward mechanisms for those engaged in such research. A call to increase interactions with researchers in quantum mechanics and molecular dynamics is also particularly apropos.

The third target (validation, industrial applicability) is supported by a call to more clearly define what experimental results are useful for validation, to choose some critical systems, and then embark on an extensive experimental and computational program directed specifically toward validation.

The fourth target (usability, availability) is supported by the call for a common software framework, and by encouraging more open release and publication of codes and results. Encouraging better relationships between the basic researchers who discover and develop new methods and the software vendors who deliver to the market is also required.

Performance Targets for the Atomistic Scale

Quantitative and qualitative performance targets have been identified for simulation at the atomistic scale, as shown in Exhibit 4-1. These targets address many of the elements that limit the use of molecular simulations for solving practical problems of interest to the chemical processing industries. They also provide a perspective on leading edge molecular modeling capability by the year 2020.

In 2020, a key performance target is to be able to address systems larger than 1 million atoms and length scales of 100 - 1000 angstroms as routinely as systems of a 1000 atoms are addressed today. This would permit modeling of systems in some cases at the application size. For example, accurate simulation of thin films (about 0.1 micron thickness) would be possible. By way of illustration, a cube of material 0.1 microns (10^{-4} mm, 1000 Å) on a side contains about a billion (10^9) atoms. A thin film only 100 Å thick over an area of one square micron contains about ten billion atoms. A single particle of microcrystalline zeolite (one micron diameter) contains on the order of a trillion (10^{12}) atoms.

The development of methods usable by bench chemists for atomistic simulations a microsecond in duration is a target for 2020 and perhaps before. Work is being published now reflecting time scales of 50 - 100 nanoseconds (0.0001 microseconds). While massive parallelization of computers will help to address the size scale issue, it will not eliminate the time problem.

Exhibit 4-1. Performance Targets for Atomistic Scale Computational Chemistry

- Be able routinely to address systems of 1 million atoms/100-1000 angstroms
- Access longer time scales with methods that are usable by bench chemists
- Have access to validated intermolecular potentials with quantifiable accuracy
- Be able to calculate energy differences between states in large systems at the millisecond time scale
- Be able to address polymer systems with large molecular weight distribution
- Ability to simulate ASTM[5] tests computationally within 2 days
- Expert advisory system to steer computations

An important target is the development of intermolecular potentials for a wide variety of systems and states with known accuracy that have been validated through experimentation or by highly accurate calculations. Currently, the intermolecular potentials needed to solve specific problems often simply do not exist, and many existing potentials have received only limited testing.

Rather than using energy differences between states obtained from quantum theory, a goal is to use atomistic simulation to determine the differences, on a millisecond time scale, and for large systems. An example would be determining energy differences between an amorphous and crystalline state, even though the transition cannot be simulated directly.

The capability to address macromolecular systems with a large molecular weight distribution is essential for many applications. It is particularly important in the simulation of polymer properties and processes, which are treated less than adequately with existing methods. The goal is to be able to simulate macromolecular systems with large molecular weight distributions as routinely as smaller systems are currently modeled today.

Industrial representatives to the Roadmap Workshop suggested the ability to simulate computationally ASTM tests on materials. This target is really a proxy for a much improved ability to compute a wide range of materials properties like the ones that industrial researchers typically have to contend with. These are usually complex performance measures that depend on several underlying properties, and are not directly or simply related to any single fundamental physical or chemical property. Examples include flammability, ignition resistance, melt flow index of polymers, toughness tests, and adhesion. Conducting these tests with current methods is very difficult in some cases (e.g., determining the pour point of a lubricant) and could be

[5] American Society for Testing and Materials

greatly facilitated with computational predictive techniques. Even for empirical tests that are relatively easy to perform, simulations could be of great help in interpreting and understanding them.

In many cases there is no clear-cut guidance for which computational path to take to address a specific problem and obtain the desired solution. The choice of computational methods is mostly addressed through a combination of past experience and guesswork. A goal for 2020 is the built-in expert advisor capability for a researcher or computational user to request the solution in the most expeditious fashion, and with specified accuracy. This would include the ability to verify the accuracy of a result in a quantified way, a function that is virtually non-existence with current methods.

Atomistic Scale Technology Barriers

There are a number of barriers that inhibit the development and use of computational methods at the atomistic or molecular scale. These are shown in Exhibit 4-2, organized by topic.

Computer Hardware and Software

The greatest barrier limiting the more widespread use of atomistic scale simulation tools is the poor inter-availability of codes between various research and user groups. Atomistic scale codes from different research groups have limited inter-operability, are lacking in modularity, and often have poor non-standard graphical user interfaces (if any), all elements that would promote transfer of use between groups. For example, modularity (linkage) between force fields is lacking or insufficient in currently available codes. Industry is also reluctant to use codes that are university-based, even though they may be widely used in the academic community, for all the reasons stated above. Another factor is that simulation tools developed by academia do not have commercial-level technical support available to industrial users.

In the commercial software industry, refinement and incorporation of advances in molecular simulation is limited by the relatively small, specialized customer base, a lack of competition, and the small number of interested developers. Computing hardware limitations include the cost of fast networks capable of running a group of personal computers as a multi-processor distribution system, and computing speed, which has increased exponentially but is still too slow for the enormous number of calculations required for many desirable atomistic scale computations.

Computational Limits

Applying atomistic scale calculations to the time scales present in complex molecular systems remains a problem even with the fastest parallel supercomputers. Molecular vibrations and collisions can occur on a time scale of femtoseconds, but the motion of a polymer chain may occur on a time scale many orders of magnitude longer (milliseconds or longer), for example. Methods for bridging this wide range of time scales are vitally needed; they are addressed in Section 6 of this roadmap.

There is a lack of appropriate atomistic computational methods for some of the phenomena that are important to the chemical processing industries (e.g., crystallization), which contributes to an inability to apply these tools to practical problems. There are also various ASTM tests for which interpretive computational tools do not exist but would be very useful.

Data/Basic Knowledge Limitations

The lack of intermolecular potentials that accurately predict pressures and chemical potentials is the most critical barrier to the more widespread use and applicability of atomistic tools for chemical processing. Intermolecular potential functions are needed for all atomistic simulations (e.g., molecular dynamics, geometry optimization of large systems, Monte Carlo, Brownian dynamics) but are not currently available for all systems and states. One approach has been to develop transferable potentials, but such potentials are not available for all atoms and are generally not transferrable to different state conditions. In general, potential functions are very time-consuming to construct, and are not thoroughly validated by a variety of experimental data. In spite of the importance of intermolecular potentials to the practical use of atomistic methods, little industrial effort and research funding are currently focused on this area, primarily because of its long-term nature and expense.

Methods of estimating the intrinsic accuracy of calculations and results are significantly lacking, and this is a critical barrier to the more widespread use of these methods for solving practical engineering problems. This inability to ascertain accuracy is linked to a number of other factors, including the limited availability of relevant experimental data, as well as a shortfall in basic science and theories underlying some of the computational methods used.

Experimental validation is crucial to the acceptance and use of all computational tools. The validation of some atomistic methods is currently limited by experimental data that is either fragmented or non-existent, making it nearly impossible to verify solutions once achieved. Ideally, simulations should be developed and then verified experimentally. Numerous cultural and institutional barriers stand in the way. Incentives are needed to encourage collaboration between experimentalists and researchers performing molecular simulations. Cooperation between industry, academia, and government could provide such incentives. Within the research community in general there is a lack of effort being expended on validating the results of atomistic scale models with experimental data. Part of the problem is the tendency of experimentalists to pursue experiments that are project-specific rather than those that will expand fundamental knowledge. On the other hand, the measurements that would be most helpful in developing and verifying computational methods are often perceived as having little practical application value for the experimentalist. There is a cultural barrier (disconnect between disciplines) between theorists, experimentalists who measure properties, and synthesis chemists.

Essential theory and computational methods are currently inadequate for addressing several important phenomena at the atomistic scale. Importantly, however, parallelization at the atomistic scale is reasonably well-advanced and careful implementations can currently take full advantage of the most massively parallel supercomputers.

Exhibit 4-2. Technology Barriers
Atomistic Scale
(◆ = Most Critical Problem Areas/Barriers)

Computer Hardware and Software	Computational Limits	Data/Basic Knowledge/Experiment	Institutional/ Educational
Poor inter-availability of codes ◆◆◆◆◆◆◆ - transfer of code across groups (portability) - modular software development - lack of modular force-fields Inadequate computer speeds ◆◆ Lack of methods for non-equilibrium properties in commercial codes ◆ Lack of fast, cost-effective networks to run PCs as multiprocessor distribution machine Lack of competition in molecular modeling software industry Academic codes that are not available to industry Lack of involved commercial software developers Poor scaling of parallel methods of calculating pairwise forces	Inability to bridge time scales from femtoseconds to milliseconds or longer ◆◆ Lack of appropriate computational methods - crystallization - some ASTM tests - polymer MW distribution	Unavailability of inter-molecular potentials for a wide variety of systems and state conditions ◆◆◆◆◆◆◆ Lack of methods to define the accuracy of a result ◆◆◆◆ Inadequate funding for development of potentials ◆ Lack of validation for inter-molecular potentials and research toward that end Inadequate treatment of periodic boundary conditions for amorphous systems Lack of understanding of physical and chemical process energy barriers Inadequate understanding of mechanisms of phase transitions Lack of methods to calculate phenomena based on energy data (hyper MD simulations) Lack of methods for dealing with multiple local minima Experimental data inadequate & fragmented Lack of people willing to validate simulation data with experimentation Changing relationship between experimental and computational fields Tendency toward project development experiments vs. fundamental knowledge experiments	Lack of people working in the field - computational chemistry is competing with software industry - Shortage of U.S. residents that can be hired - Lack of success stories - Lack of big impact projects to get management attention - Unclear ownership of intellectual property Steep learning curve Management confidence is lacking Industrial/ academic/ government time-scales vary

Institutional/Educational

The limited number of people working in the field is one of the major problems hindering more rapid advances in atomistic computational methods. There are many reasons for the lack of researchers dedicated to this area, including the shortage of U.S. scientists trained or expert in this and related disciplines. Many of the bright, qualified students leaving undergraduate

schools are opting for readily available careers in the software development industry, where careers are more lucrative or glamorous. Many are also lured into bioengineering or what is perceived as more high-profile careers than theoretical chemistry. The result is a general shortage of people that can be readily hired or that go on to graduate school to develop the computational expertise needed for working in the molecular simulation field.

Contributing to the lack of skilled professionals willing to work as theoretical chemists is the lack of (or lack of publication of) success stories and high impact projects that garner the attention of management and gain recognition for researchers. In addition, the ownership of the intellectual property rights of the products created (as well as economic benefits) is often unclear, making efforts difficult to justify. The learning curve for atomistic scale methods is steep, which discourages many from entering the field.

Atomistic Scale Research Needs

Research needed to overcome barriers to the development and use of atomistic or molecular simulations are shown in Exhibit 4-3, with priority levels and time frames for research identified within categories. Time frames indicate the period in which the results of various R&D activities are expected to be available for use by the modeling community at large, assuming sufficient R&D funding.

Computing Power/Software

The highest priority research need in the area of hardware and software is to develop a single framework and standards for several important aspects of the computer codes. This includes developing modular codes, parallel codes that will run on heterogeneous systems, and portable, scalable codes that can be readily adapted to run on different computing platforms. Successful research in these areas will address the critical barriers of inter-operability and portability that are prevalent in existing codes. Research is also needed to develop software architectures that allow separation and modularity of force field calculations.

Exhibit 4-4 illustrates the chronology and path of activities supporting the development of a single framework and standards. Efforts in modularization and portability will occur concurrently with those in parallelization and force fields. Activities beginning within the near term are expected to produce viable results by the end of the mid term, or within ten years.

Techniques for bridging the wide range of time scales, from femtoseconds to milliseconds or more, are also vitally needed; these are addressed in Section 6 of this roadmap.

Fundamental Science/Experimental Validation

Research activities spanning the near- to the long-term will be needed to overcome the current limitations imposed by lack of experimental validation of some atomistic methods. A well-planned effort is needed for coordinated molecular simulations and experiments aimed at validating the results of approximations used in some atomistic methods.

Support should also be given to investigators focussed on conducting research to develop and test intermolecular potentials applicable to a wide variety of chemical systems and state

conditions. The lack of accurate intermolecular potentials was cited as the most critical barrier facing developers and user of atomistic methods. As shown in Exhibit 4-4, results in this area are needed in the near term to support efforts to develop modular, extendable force fields (see discussion under Computation Methods/Algorithms).

Exhibit 4-3. Research & Development Needs
Atomistic Scale
(✪ = Top Priority; ● = High Priority; ○ = Medium Priority)

Time Frame	Computing Power/Software	Fundamental Science/Experimental Validation	Computational Methods/ Algorithms	Human/ Institutional Factors
NEAR (0 - 3 Years)		Create list of what experimental data is desired ●● Identify new types of properties to measure ●		Institute reward mechanism for scientists (funding, tenure) working on intermolecular potentials ●●●●●●○ Increased interaction between people in quantum mechanics, molecular dynamics, and simulation ●●●○○ Encourage open release and publication of codes and results of simulations ●○○ Create mechanisms for consortia (industry, labs, DOE) ●○○ Define unifying visionary target for modelers to rally around ●○○ Simplify intellectual property issues dealing with the release and licensing of codes (DOE/NSF) ○ Sustain funding to complete projects ○ Support industry-university-national labs joint projects ○ Create partnerships with software companies Establish market potential Develop methods to instruct/inform management Use DOE - ASPEN project as model for future partnership to focus molecular modeling on chemical industry Encourage molecular modeling in undergraduate programs make codes available for instructional purposes

Exhibit 4-3. Research & Development Needs
Atomistic Scale
(✪ = Top Priority; ● = High Priority; ○ = Medium Priority)

Time Frame	Computing Power/Software	Fundamental Science/Experimental Validation	Computational Methods/ Algorithms	Human/ Institutional Factors
NEAR - MID	Develop single framework with agreed upon standards to unify the following: ✪✪✪●●○○○ - modular codes ✪ - portable, scalable parallel codes for different platforms ● - software architecture that will separate software from force fields	Support investigators whose focus is on developing and testing intermolecular potentials		
MID (>3 - 10 Years)		Develop new methods for measuring properties ○	Develop modular, transferable intermolecular potentials ✪✪✪✪●●● ○○	
LONG (>10 Years)		Choose critical systems, synthesize molecules and compare rigorously (compare real and computational molecules)	Develop software solution for scaling of time dimension (handling of complexity) ✪✪✪●○○ ○○○○	

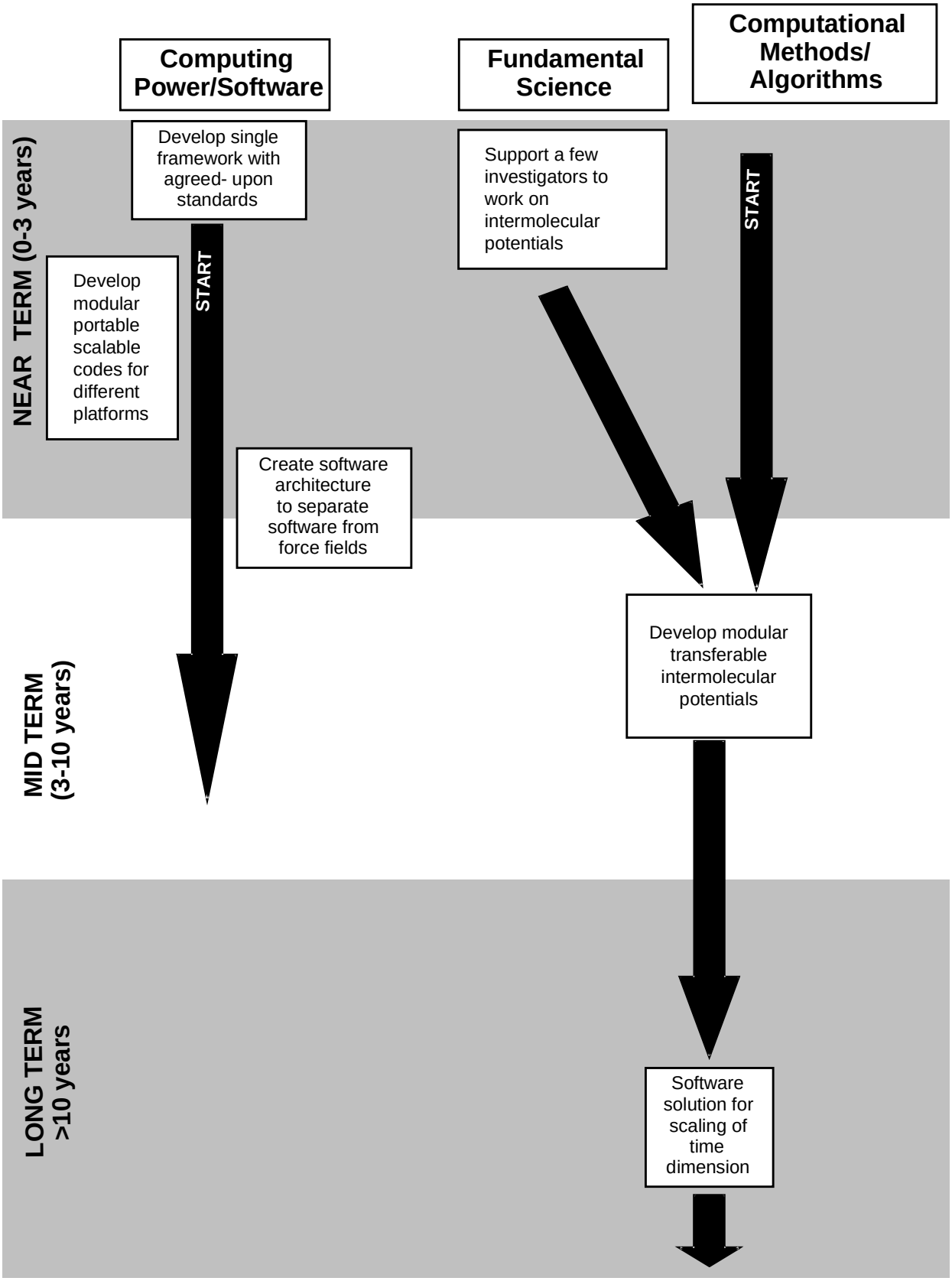


Exhibit 4-4. Research Pathways - Atomistic Scale

Long term research is needed to conduct a coordinated experimental and computational program to validate modular, transferable intermolecular potentials.

Computational Methods/Algorithms

One of the most critical research needs is the development of modular, transferable intermolecular potentials. Accomplishing this research will serve to broaden greatly the applicability and use of atomistic models for many practical applications. As shown in Exhibit 4-4, research beginning in the near term should produce results by the middle of the mid term, within five to eight years.

A long term, high priority research effort is needed to address the scaling of time dimensions (and handling of complexity of various systems). The time scale problem is a critical issue that must be addressed to enable significant expansion in the types and sizes of systems that can be effectively handled using atomistic scale methods. As illustrated in Exhibit 4-4, results from force field development will be necessary to support efforts to resolve the time scale issue. This issue is discussed in Section 6 of this roadmap.

Human/Institutional Factors

Many near-term efforts are needed to overcome some of the critical institutional and educational barriers to the development and use of atomistic methods. The most important is to provide incentives for long-term efforts by academic groups to develop and test modular, transferable intermolecular potentials applicable to a wide variety of chemical systems over a wide range of state conditions.

Another important activity is to increase interaction between researchers working in quantum mechanics and molecular dynamics. The disconnect between these two disciplines results in the slow dissemination of advances in methods that could be applied and/or used in both fields.

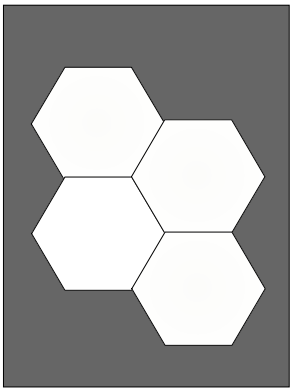
Incentives should be provided to encourage the publication and release of new codes as well as the results of simulations. This would provide a broader means for dissemination of useful information as well as successes that could be used to justify R&D to management. Increased cooperation and sharing of results within the research community could be fostered by defining a visionary target for modelers to rally around.

A consortium between industry, national laboratories, and government agencies is needed to increase collaborative activities (e.g., joint industry-university-national laboratory projects). There is a need and an opportunity to coordinate support for this field between the programs of the DOE/Basic Energy Sciences, the DOE/Office of Industrial Technology, NIST, and NSF. Government also needs to improve incentives and simplify the intellectual property issues dealing with the licensing of codes developed with federal support.

A number of other activities will help to promote the more widespread use of atomistic methods. Partnerships with software companies could help to get commercial code and technical support networks in place. Establishing market potential for some codes could help to facilitate software company buy-in of development efforts. A partnership (similar to the DOE-ASPEN project)

could be designed to help focus molecular modeling activities on chemical industry problems and could help to develop the market for commercial codes.

In the academic arena, molecular modeling should be incorporated as an element in undergraduate programs. Existing and new codes should be made more available for instructional purposes to increase the number of students with potential interest in the field on graduation, and to foster more graduate work in this area. Efforts sponsored by the National Science Foundation through the CACHE Corp. of AIChE have already made a significant beginning to these ends. Academic researchers should also take the lead in finding partnership funding from industry partners for research in atomistic methods.



5 Mesoscale

Current Situation

Applying results from calculations at molecular levels to problems at macroscopic levels is essential for studying real materials (e.g., polymers, catalysts). Many real systems have structures much larger than can be studied atomistically which strongly impact properties at the macroscopic scale. For example, the properties of materials made from block-copolymers are strongly influenced by the molecular segregation into mesoscale domains. Quantitative, predictive methods for dealing with such systems are only now on the horizon. Some current approaches include linear statistical modeling, fractal models, re-normalization models, lattice-Boltzmann approaches, wavelets, homogenization solutions of partial differential equations, self-consistent mean field theory, dynamic mean-field density functional methods, and dissipative particle dynamics. Current models rely heavily on either atomic-scale or continuum assumptions.

Interpretive Summary of Performance Targets, Barriers, and Needs

The lists of barriers and R&D needs for mesoscale modeling portrays a methodology in its infancy. This is not a problem that will be solved just by bigger and faster computers. The field requires major advances in fundamental theories and creative methods, and it needs to accumulate a track record of validation and successful application to realistically complex situations.

The performance needs listed in Exhibit 5-1 are in two categories:

- to qualitatively model system properties and trends in a way that contributes to understanding and predicting how the molecular architecture determines measurable macroscopic properties;
- to compute accurately the properties of systems that are far larger and phenomena that occur over far longer periods of time than can be approached by atomistic methods.

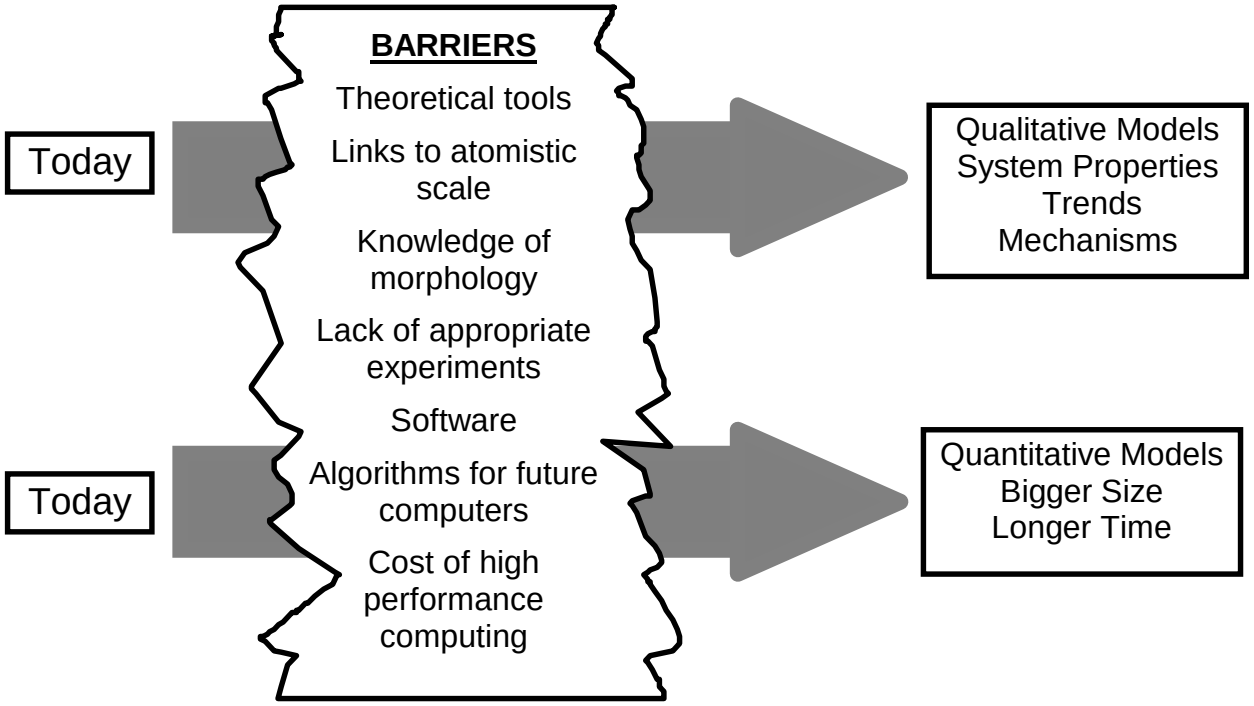
These two categories are not easily separated, and the barriers that stand in the way of one also pertain to the other. The barriers are represented together in the diagram below. Those later in the list are perhaps more pertinent to the second performance category, but the division is by no means clear.

The most prominent barriers listed in Exhibit 5-2 are summarized as follows:

- Lack of theoretical tools for the mesoscale;
- Lack of links to atomistic models;
- lack of knowledge (data) of morphology of materials;
- lack of experiments designed to validate modeling;
- lack of software for the best available methods;
- lack of algorithms to take advantage of future computers;
- cost of high performance parallel computing

These barriers are addressed by R&D needs identified in Exhibit 5-3. The highest priority of these can be summarized as follows:

- collaboration between theorists and experimentalists;
- Support discovery & development of theory, models and methods that are linked to atomistic knowledge but incorporate creative new ideas;
- Support experimental research, particularly aimed at analysis of multiphase phenomena, morphology, and dynamics.



Performance Targets for the Mesoscale

For purposes of discussion it is useful to identify the time scales and length scales which characterize mesoscale systems. The upper bound of the mesoscale is the length-scale at which the material behaves as an effective continuous medium. The lower bound of the mesoscale generally refers to what can be calculated using atomistic methods. Mesoscale calculations generally occur on the physical timescale greater than 100 nanoseconds. The length scale is usually on the order of 10 nanometers to 10 micrometers.

Exhibit 5-1. Performance Targets for the Mesoscale

- Qualitative goal: model and predict system trends given specific chemical structures, compositions, and process conditions
- Quantitative goal: predict continuum properties on scales as large as 10,000 nanometers (10 μm) with accuracies similar to atomistic level calculations
- Model larger systems on a physical timescale greater than 100 nanoseconds

The first goal for computational chemistry tools on the mesoscale is to identify the qualitative trends in a system given specific chemical structures, compositions, and process conditions (see Exhibit 5-1). This really means the ability to model the effect of molecular architecture and dynamic conditions on the macroscopic continuum properties, and to do so in a way that reflects and helps to understand the molecular-level mechanisms responsible for observable properties. The next goal is to quantitatively predict the continuum properties of the system on scales as large as 10,000 nanometers (10 microns) with accuracies similar to what are currently being obtained in atomic level calculations. By way of illustration, a cube of material 10 μm on a side contains on the order of 10^{15} atoms! It will not become possible to compute such systems atom-by-atom even on the massively parallel computers that are foreseeable. Systems of this size usually embody processes with correspondingly long time scales. For example, responses to a local stress typically propagate through a system no faster than the speed of sound. However, the duration of detailed atomistic simulations that can now be achieved routinely, even for relatively small size systems (e.g., 200 carbon atoms in a unit cell with periodic boundary conditions), is too short for a sound wave to propagate a distance of 10 microns. To illustrate: the speed of sound in ordinary liquids and solids is on the order of 1000 m/s or higher — equivalent to 1000 nm/ns, or 1 μm/ns. Thus simulation of a dynamic phenomenon propagating over a distance of 10 μm would require about 10 ns of simulation time, or ten million time steps of one femtosecond (10^{-15} s) each. Of course, many relaxation processes are orders of magnitude slower than the speed of sound. And mesoscale modeling is about simulating systems that are much larger in length scale or number of atoms. Thus, the third performance target is to accurately model larger systems on the physical timescale much greater than 100 nanoseconds.

Mesoscale Technology Barriers

There are several identifiable barriers to the increased use of computational chemistry tools at the mesoscale. These barriers fall into the categories of Computational Limits of Current Modeling

Tools, Data/Basic Knowledge Limitations, Computer Hardware/Architecture, Theory, and Other. A full listing of the technology barriers is included in Exhibit 5-2.

Computational Limits of Current Modeling Tools

Current modeling tools only allow researchers to study the mesoscale on short time scales, which results in the need for a considerable amount of assumptive reasoning and introduces inherent flaws in model predictive capability. There are few algorithms that take advantage of current and advanced computing platforms, and little effort is being expended to plan for further advances in computing power.

Theory

The most critical barrier to the use of computational chemistry tools at the mesoscale is the lack of the proper theoretical tools. Mesoscale computations are unique in computational chemistry because the theory to fully describe the phenomena has not yet been developed. Mesoscale refers to the length scale that lies between the atomic and bulk scales. Materials demonstrate both atomic and bulk phenomena at this scale, while often being in a non-equilibrium state due to processing conditions. The defining equations linking these regimes are complex. Current models extrapolate calculations from either the atomic or bulk scales, and involve much empiricism. This generally does not produce results that accurately describe mesoscale phenomena. Results can be difficult to interpret and link to experimentally observable properties. The few validation experiments that have been conducted at this scale show quite a difference in results between the theoretical models and the actual data. Part of this problem can be attributed to the poor sensing equipment that is used in these experiments. It is very difficult to accurately measure physical properties such as temperature and fluid velocity at this scale.

Given a complex molecular structure such as that of a polymer, it is now possible to predict at some level what the properties of the material are likely to be. The accuracy of the results depends critically on the complexity of the structure as well as available information on similar structures. For example, various QSPR (quantitative structure property relationship) models are available for the prediction of polymer properties. However, the inverse of this process (designing structures given a set of properties) is far more difficult and is practiced today by synthetic chemists using mostly heuristic methods, based on individual knowledge and experience. A significant amount of effort is currently being expended to develop “reverse engineering” software to solve the problem of going backwards from a set of desired properties to chemical structures. These efforts are primarily based on artificial intelligence techniques and have met with limited success.

Data/Basic Knowledge Limitations

The next most important barrier is limitations related to available data. Presently there are not enough good validated measurements of the morphology of mesoscale systems. Methods to measure mass, heat, and momentum transfer in such systems have not been developed. The lack of specific experiments geared towards validating the results of molecular modeling is part of the reason that such methods have not yet been developed. One of the reasons is the fact that there is very little collaboration between molecular modelers and experimentalists, resulting in a scarcity of the data that is required by modelers.

Computer Hardware/Architecture

Other barriers to the use of computational chemistry tools at the mesoscale include a lack of low cost parallel computing capabilities. Calculations on this scale are currently run on expensive and massive supercomputers. The slow processing speeds of current desktop computers and small workstations are insufficient to conduct computations with the kind of accuracy necessary to fully describe mesoscale phenomena.

Exhibit 5-2. Technology Barriers
Mesoscale
(◆ = Most Critical Problem Areas/Barriers)

Computational Limits of Current Modeling Tools	Data/Basic Knowledge Limitations	Computer Hardware/ Architecture	Theory	Other
Unavailability of software embodying the best available theory for mesoscale modeling	Not enough good (validated) measurements of the morphology of materials ◆◆◆◆◆	Unavailability of low cost parallel computers for desk tops ◆	Lack of proper theoretical tools ◆◆◆◆◆◆◆◆	Tools that are too expert specific
Lack of anticipation of future computing capabilities	Limited ability to observe how molecules reorganize on long time - scales		Lack of understanding the partitions of free energies ◆	No link between technical simulation and plant-friendly tools
Lack of algorithms that take advantage of current and future machines	Lack of basic inputs		Lack of methods to average from atomic-scale to mesoscale	Poor understanding of when mesoscale needs to be stepped back to the atomistic level
	Lack of specific experiments geared towards validating molecular modeling ◆◆◆		Lack of links between microscopic thermodynamic models and atomistic molecular models	Lack of unifying language, organization, problem definition, and vision
			Lack of good theories for inter-molecular interactions of large molecules	

Mesoscale Research Needs

Research needed to overcome barriers to mesoscale computational methods falls into the five categories of Theory, Experiment, Collaboration, Enabling Technologies, and Vision Education. Exhibit 5-3 illustrates the research needs, time frames, and priorities in the area of mesoscale computations.

Collaboration

There is an opportunity in collaboration to build on lessons that have been learned from the successes and mistakes made in atomistic and quantum-scale modeling. The need for strong collaborations between theoreticians and experimentalists is the most important lesson. Experimentalists and theoreticians must work together in order to devise both models and verification experiments that will accurately describe mesoscale phenomena.

Exhibit 5-3. Research & Development Needs
Mesoscale
(✪ = Top Priority; ● = High Priority; ○ = Medium Priority)

Time Frame	Theory	Experiment	Collaboration	Enabling Technology	Vision Education
NEAR - NOW			Support strong collaboration between theoreticians and experimentalists ✪✪✪✪✪✪✪ ○ - review current experiments to validate mesoscale theories		Develop better definition of mesoscale ●●● Determine impact of mesoscale research/conduct market research ●○○ Educate experimentalists in mesoscale science ●●
NEAR (0 - 3 Years)	Learn how to apply statistical and stochastic methods to the mesoscale ●● Increase knowledge of how to work with multi-phase systems at the mesoscale ● Explore inputs and outputs of current theories Improve force-field computations for heterogeneous systems	Develop in-situ physical characterization of multi-phase mesoscale features ●●●●○○ - combine micro-fabrication techniques and physical property measurements - experiments geared to specific molecular modeling needs - scattering experiments (light, x-ray, neutron) Develop standardized data to ensure/improve data quality ○○ Understand how to work with multi-phase systems ○ Develop data on morphology evolution in semi-crystalline polymers as a function of processing	Support multi-disciplinary collaboration between molecular modelers and theorists ○○○ Create better access to available data ○		

Exhibit 5-3. Research & Development Needs
Mesoscale
(✪ = Top Priority; ● = High Priority; ○ = Medium Priority)

Time Frame	Theory	Experiment	Collaboration	Enabling Technology	Vision Education
MID (>3 - 10 Years)	Develop mesoscale calculations with respect to bulk-scale properties	Create benchmark materials and morphologies for property measurements at the appropriate time and length scales ○		Explore new paradigms for producing faster computations	
LONG (>10 Yrs)				Develop easy access to cost-effective high performance computing ✪	
ONGOING (All Periods)	Support advances in mesoscale theory ✪●●○ Ensure models are based on atom-level detail ●●○ - apply massive atomistic computations to validate theories Ensure dynamical theory of mesoscale systems is consistent with macroscopic laws ○○ Encourage innovation/movement away from strict atomistic or bulk models ○ - consider the possibility of analytical solutions - other approaches, e.g. neural nets	Study interactions between chains/ interacting species and their phases	Build on lessons learned from successes and mistakes in atomistic and quantum models Encourage and support collaboration between chemists and engineers		

Experiment

The development of in-situ physical characterization of multiphase mesoscale features is a high priority need. In order for this to be accomplished, for example, micro-fabrication techniques

might be combined with physical property measurements. Improved techniques for gathering physical information is key to accomplishing this research. More experiments geared towards specific molecular modeling needs (input data and validation) are necessary for advancements in model accuracy.

Theory

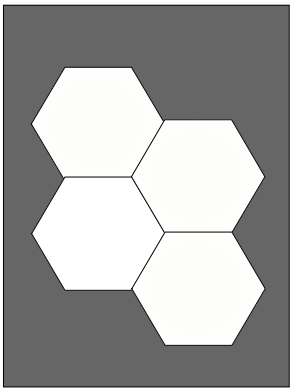
Research investments to advance theory in mesoscale systems and models that are based on atom-level detail are of the highest priority in the area of theory. Massive atomistic computations to validate the theories are also necessary. Generally, the theory that is currently being used to conduct calculations on this scale are derived from both atomistic and bulk models. Extrapolations from these models are highly inaccurate, and therefore mesoscale theory is an area in which study is needed.

Enabling Technologies

Enabling technologies can be defined as technologies that are necessary for conducting and implementing research. This can include computing capabilities, sensing equipment, and control mechanisms. Massively parallel computing capabilities are frequently necessary in the field of computational chemistry. This holds true for the mesoscale area. Developing easy access to cost-effective high performance computing power for a wide range of users is a high priority long range need.

Education Vision

Since mesoscale chemistry is still a very vaguely defined area, a better definition and understanding of mesoscale science is necessary to improve modeling and experimentation. Increased interest in the area of mesoscale calculations must be developed. Students should be introduced to the field as part of their education. Computational scientists must also become more familiar with the area. Communicating the potential impact of this research on commercial products will significantly increase interest in the field.



6 Bridging Techniques

Current Situation

Bridging techniques are computational methods used to bridge the range of spatial and temporal scales, from quantum to atomistic to mesoscale and from femtoseconds to minutes or hours. The goal of bridging techniques is to enable the use of results from calculations at one scale as inputs to calculations at another scale. Two types of bridging techniques are currently under investigation — seamless data interfaces and coarse-graining methods.

Bridging Techniques and Terms

Seamless Data Interfaces - permit interactions between calculations performed at different size scales (e.g., between quantum and atomistic scales).

Coarse-Graining Techniques - theory-based techniques which allow knowledge gained from calculations or experiments at a small scale to be usefully applied at a larger scale.

Seamless data interfaces enable software which performs calculations at one scale to exchange data "seamlessly" with other software performing calculations at a larger, smaller or equivalent scale. This interface allows the user to extend the results of calculations across several size scales, and enables interaction with commercial products as well as developmental software still in the research stage. These data interfaces could also permit interaction between process simulation codes and various physical property codes. Seamless data interfaces are now common only among the products of a single software vendor, and no vendor offers a complete suite of codes for all the calculations needed for the chemical processing industries. However, it may soon be possible to create seamless data interfaces between software products from different vendors running on machines with different architectures using familiar software technologies such as consensus standards, public domain libraries, and daemons.

Theoretically-based coarse graining techniques could potentially provide another means of bridging size scales by allowing knowledge gained from calculations or experiments at a small scale to be usefully applied at a larger scale. These techniques (e.g., coarse-grained potential models where dynamics is obtained by Brownian dynamics simulation) remain an integral part of computational chemistry, largely because of the lack of rigorous methods for connecting the dynamics of femto-second time scales with macroscopically long time scales. It has recently become possible to test the validity of many theoretically-based coarse-graining techniques that have been used to reach beyond the limits of brute-force atomistic calculations. Advances in computer technology today may provide the means for a theoretically-based "bootstrapping" approach to develop and test better and more powerful coarse-graining techniques. The use of these techniques could grow in importance, gradually supplanting the empirical constitutive models that are used in process-scale calculations today.

Bridging Techniques Technology Barriers

There are a number of barriers limiting the development of techniques for bridging the various size scales. These are shown in Exhibit 6-1, organized by topic.

Computational Limits

The lack of good statistical techniques for moving between scales is the most critical computational limit inhibiting the development of bridging techniques today. Contributing to this problem is the disconnect and disagreement between results at the various scales, and the lack of a common language that would permit communication between scales. The lack of a methodology for deriving materials-based force fields from quantum mechanics is also an important limiting factor.

As with all the computational scales, the inability to handle more than one time scale places limits on current computational capability. Another issue with time scales is the lack of capability for making predictions about how properties will change over time (e.g., decomposition, aging of materials). These issues are often of paramount importance for users interested in simulating practical problems in the chemical plant.

Data/Basic Knowledge

The lack of theory linking atomistic and mesoscale computations represents the most important knowledge limitation facing developers of bridging techniques. Without this essential theory, it remains difficult or impossible to translate and mesh results between these two scales. In general, there is also a significant lack of understanding in how to move between scales. In many cases, results from one scale are not easily transferable to another scale (e.g., potentials from quantum mechanics do not translate to the atomistic scale).

There are number of critical limitations in the area of physical phenomena and data analysis. There is a significant lack of understanding of the phenomena occurring at interfaces, which is essential for predicting the behavior of many industrial problems. Generally available knowledge and data on physical and chemical aging is also virtually non-existent.

A number of factors affect the ability to develop techniques that bridge to the mesoscale. The most important of these is the lack of experimental methods and results for validating mesoscale results (e.g., stress/strain curves for semi-crystalline materials). The result is the inability to observe phenomena that occur at the mesoscale. There is also a lack of general theory and understanding of the morphology of materials at the meso-level.

Exhibit 6-1. Technology Barriers
Bridging Techniques
(◆ = Most Critical Problem Areas/Barriers**)**

Computational Limits	Data/Basic Knowledge	Institutional/Educational
Lack of good statistical techniques to go from scale to scale ◆◆◆◆	Lack of theory linking atomistic and mesoscale ◆◆◆◆◆◆◆◆◆	Lack of programs and computing power capable of going from quantum to atomistic scales
No methodology for materials-based force field from quantum mechanics ◆◆	Lack of understanding of phenomena at interfaces ◆◆◆	Lack of knowledge across scales in the scientific/user community
Lack of standard data structures and data interfaces applicable at different scales	Lack of experimental methods at meso-level (e.g., stress/strain curve for semi-crystalline materials) ◆◆	Lack of hands-on experience in industry, particularly at the mesoscale
Difficult links when local average does not represent bulk	Potentials from quantum scale results are not transferable in many cases to atom scale	
Disconnect and disagreement between scales	Poor level of detail for microscopic properties	
No common "language" between scales	Lack of general consensus/theory/ understanding of morphology of materials at the meso-level	
Inability to bridge load scales dynamically	Non-observability of phenomena at the mesoscale	
Inability to handle more than one time scale	Lack of fundamental theory and quantity of unknowns at the mesoscale	
Lack of capability for simulation over long time scales - decomposition - aging of materials/chemicals	Lack of understanding in how to move between scales Lack of knowledge/data on physical and chemical aging	

Institutional/Educational

Currently there is little effort being expended in the research community aimed at developing the means to move between the quantum and the atomistic scales. In general, there is a considerable lack of knowledge and expertise relating to movement between scales in the scientific community at large, although it is becoming apparent that issues dealing with scaling will play a dominant role in science over the next few decades. In the industrial area, hands-on experience in bridging techniques (as well as computational chemistry methods in general) is relatively limited. The most significant lack of experience is found at the mesoscale. The lack of effort

being conducted toward bridging techniques in general contributes largely to the slow pace of developments in this field.

Research Needs in Bridging Techniques

The research needed to overcome barriers to the development of bridging techniques is shown in Exhibit 6-2, with priority levels and time frames for research identified. Time frames indicate the period in which the results of various R&D activities are expected to be available for use by the modeling community at large, assuming sufficient funding.

Exhibit 6-2. Research & Development Needs
Bridging Techniques
(✪ = Top Priority; ● = High Priority; O = Medium Priority)

Time Frame	Computational Methods	Data/Basic Knowledge	Institutional/Educational
NEAR (0 - 3 Years)	Conduct more research on the use of stochastic methods (e.g., Monte Carlo simulations) ○○ **3 — 20 years** Develop theoretical techniques for stochastic and statistical methods for averaging over large number of atoms ●○○ Propose standards for data structures and data interfaces useful at different scales	Explore and gain knowledge of topology and morphology interaction of materials - strain/stress - temperature - time - characterization of materials at same scale - well-defined physical systems ●●●●○○○○	Create an organization to propose standards for data structures and data interfaces useful at different scales.
NEAR - MID		Expand theory and knowledge of long-time evolution in molecular models ●●●●●○ **3 — 5 years**	
MID (>3 - 10 Years)	Explore how large an atomistic simulation is necessary to link to the mesoscale ✪ Study and incorporate non-equilibrium kinetic effects on ●●○○ Develop a set of standards for results between scales ●● Study and resolve the ensemble-size issue ● Develop coupling methodologies, codes, and data structures ●	Develop theories for - multi-component mixtures - chemical composition - morphology ✪●○○	

Exhibit 6-2. Research & Development Needs
Bridging Techniques
(✪ = Top Priority; ● = High Priority; O = Medium Priority)

Time Frame	Computational Methods	Data/Basic Knowledge	Institutional/Educational
LONG (>10 Yrs)		Develop better understanding of constitutive equations O	
SPANS ALL TIME FRAMES	Develop methods for deriving potentials that are valid between quantum and atomistic scales and between atomistic and mesoscale ✪✪✪✪●O **0 — 3 years**	Improved force fields at the atomistic level based on highly accurate quantum calculations - reacting force fields - improved intermolecular potentials Bridging theory to span scales Quantum → Atomistic → Mesoscales **0 — 3 years** Develop new theoretical approaches to reducing the complexity of the problem	Conduct collaborative R&D projects across industry, academic, and national labs ●●●OOOOO **now — 2020** Increase cooperation in the scientific community through creation of multi-disciplinary teams OO **0 — 20 years**

Computational Methods

The development of bridging techniques is in a fledgling state, and research is needed mostly in developing theory and new computational techniques. Research is needed to develop theoretical methods for averaging over large numbers of atoms. In general, more research is needed on stochastic methods such as Monte Carlo methods. Early progress in this area is needed in the near term, but sustained effort is required over the long term. These activities will provide a basis for developing statistical techniques for going from scale to scale. The development of methods to describe bridging different scales will be an ongoing activity that should produce results in a time span ranging from three to twenty years. Research is also needed to expand theory and knowledge of long-time evolution in molecular models.

The development of bridging theories for multi-component mixtures, chemical composition, and morphology is a high priority. This activity will help to facilitate the development of methods for linking properties simulated at different scales. Investigating how large an atomistic simulation is necessary to link to mesoscale calculations is also an important research need, and will help to define the scope of advanced bridging techniques. To create an effective interface between the scales, a set of standards should be developed for results between scales. In addition to standards, coupling methodologies, codes and data structures need to be developed to allow linkages between scales. Results in all the above are expected in the mid-term, and will address many of the problems associated with differences and disconnects between the various scales.

One of the most critical research needs is the development of methods for deriving intermolecular potentials that are valid for all scales, spanning the quantum to the atomistic to the mesoscale. While early progress is needed in this work, it should be an on-going research activity spanning the next ten years and perhaps beyond.

Efforts are needed to develop consensus standards for data structures and data interfaces used in computational chemistry codes at all scales which will permit results of calculations performed at one scale to be used seamlessly at other scales.

Data/Basic Knowledge

The most important research needed to expand basic knowledge and support the development of bridging techniques is the study of the topology and morphology of materials. Research should include the study of strain/stress, temperature, and time, as well as other relevant topics. Exploration is also needed to characterize materials at the same scale, and studies should include the evaluation of well-defined physical systems. Progress in this activity is needed in the near term, within three years.

Another critical research need is the resolution of time scale issues, a problem that is common to all the size scales. Research should begin in the near term, but is expected to achieve on-going results over the next ten years.

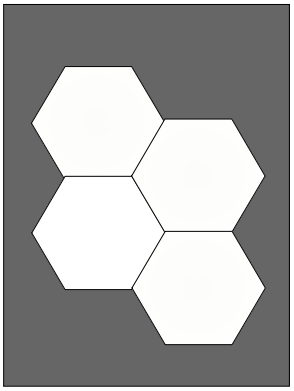
Improved methods for using the results of highly accurate quantum calculations in atomistic force fields need to be developed. This will enable improved descriptions of intermolecular interactions in atomistic simulations. In addition, force fields for reacting systems need to be developed for simulations at the atomistic level.

Research is needed to study and incorporate non-equilibrium effects on properties. Methods for accomplishing this are essential for applying bridging techniques to chemical processes. Results achieved in the mid-term could facilitate the development of techniques that are highly usable by the private sector.

Institutional/Educational

Over the next twenty years, efforts should be made to facilitate collaboration between researchers in the many disciplines needed for the development of bridging techniques. The top priority will be to conduct collaborative research projects that involve scientists from industry, government and academia. Increased cooperation in the scientific community, fostered through the creation of multi-disciplinary teams, will also be vital to the successful development of bridging techniques.

Effort is needed to establish an organization to propose and maintain consensus s standards for data structures and data interfaces used in computational chemistry codes at all scales which will permit results of calculations performed at one scale to be used seamlessly at other scales.



7 Enabling the Use of Computational Chemistry

Current Situation

Computational chemistry tools are currently in use throughout industry and are applied to a variety of industrial problems. Some of these are commercially available packages that have been developed by software vendors who are able to provide technical support. Commercial packages are more readily available for computations at the quantum scale. Commercial packages at the atomistic scale are few in number and apply mostly to ambient or near-ambient conditions (such as those encountered in biological systems). A number of large companies (e.g., Alcoa, Air Products, BP Amoco, Dow Chemical, DuPont, Exxon, Shell, Phillips, Proctor and Gamble, Xerox, and most major pharmaceutical companies) also have in-house molecular modeling groups that use computational tools and may do some method development to aid in product design or in solving industrial problems. Any methods or codes developed in a company are usually for applications of specific interest to the individual company, and are not easily accessible or transferable to users outside the originating firm, especially as they provide a competitive advantage.

Problem-solving environments (PSE) or expert advisory systems, in which the software guides the computational strategy, is an important new concept coming from computer science. PSEs are needed by both experts and non-experts to use new, high performance computer architectures effectively with advanced software. PSEs include access to databases on a hierarchical mass storage system, intelligent graphical user interfaces, interactive job control, and data analysis and visualization. It is also advantageous for PSEs to include data browsers and "Computational Advisors" that assist the user to make choices about methodology. PSEs are currently under development and some components are already available in commercial codes.

Process modeling is currently practiced extensively by the chemical industry. Modeling software such as ASPEN and SPEEDUP (Aspen Technologies) are in widespread use for a diversity of chemical production processes. The complexity of process simulations can be as large as desired depending on whether a steady-state or dynamic simulation is used and how effects such as fluid flow and mass transfer are included. As engineering models become more detailed and useful, computational chemistry can provide input parameters of increasing accuracy that enhance the robustness and reliability of these simulations.

Property data bases that provide information on chemical and physical properties at the molecular as well as bulk and process level are an essential component of computational chemistry. They provide source data for numerous algorithms and enable comparison of

predicted with experimental values. There are many data bases currently available, but most are not easily searchable and have no interface for connecting with current modeling tools.

Barriers Limiting the Use of Computational Chemistry

There are a number of barriers that inhibit the more widespread use and acceptance of computational chemistry for designing new products and materials as well as solving practical engineering problems. These are shown in Exhibit 7-1, organized by topic. Numbers in brackets next to individual barriers indicate that the barrier is also an important factor or has a direct relationship to another category.

Practical Usability for Non-Experts

For the non-expert user of computational chemistry tools, the greatest obstacle is the lack of expert help in choosing the most effective options necessary for running the computation and achieving the correct result. Non-expert users also have little familiarity with the specifics of the computational tool itself (e.g., how it works, the algorithms used), and have difficulty in trouble-shooting problems or anomalies when they arise or even in recognizing that they have arisen. This lack of familiarity contributes to the long start-up time and steep learning curve for new users, given the inherent complexity of computational tools and the fact that the primary job of the non-expert user is generally not computational work. Of course, in this respect such computational tools are no different from complex experimental measurements, for which there are similar start-up problems.

Perhaps the most immediately effective remedy would be to improve communications between the computational experts and the chemists and engineers who are their clients. Tightening this interface has been effective at Dow Chemical, DuPont, Union Carbide, Lubrizol, and several other leading companies, but it depends on the individuals involved. Removing barriers, encouraging communication, and motivating effective teamwork where it doesn't exist, while cultivating and rewarding individuals, is a significant management challenge.

Other barriers for non-experts are related to the limited accessibility of "known" results. The literature of computational chemistry is fragmented. Experimental validation or subsequent refutation of computational results sometimes appears much later. There is in the literature a great deal of fortuitous (accidental, undeserved) agreement between selected computational and experimental results. This misleads the non-expert regarding the degree to which methods are reliable and can be extended to other situations. There have been several attempts to provide comprehensive data bases of computational results, pre-dating the World Wide Web, but the products have not been easy to use or widely supported. Research has produced a variety of valuable interpretive tools for properties such as effective bond order, electron density distribution, polarity, various kinds of spectroscopy, and so forth, but many of these tools have not been incorporated into commercial codes, and are available only as academic programs and subroutines.

Practical Usability by Experts

Even for the expert user, currently available codes can be difficult to use, especially at the high end, which often hinders their use and application to real problems. Currently available codes

(many of which are developed in academic groups and are, thus, not fully supported commercial software) are not designed to be easily transferable and usable by a wide spectrum of users. Training tools for these codes are not comprehensive enough, which leads to trial-and-error (and inherently inefficient) use and application of the codes.

Applicability to Real Problems

In general, the greatest barrier to the application of computational chemistry is the limited ability to obtain results that are quantitative enough for practical problem resolution. Both non-expert and expert users often have difficulty linking the computational methodology with real applications, and in deriving meaningful knowledge from the results. This problem is exacerbated by a lack of good accessible benchmarks that could be used for comparison. The lack of published information on the successful application of computational tools by others in the field is also constitutes a critical barrier -- without some proven past success, many engineers are reluctant to expend the considerable cost and effort needed to apply these complex tools to their real problems.

Exhibit 7-1. Technology Barriers to Increased Use of Computational Chemistry
(◆ = High Priority Areas/Barriers)

Practical Usability For Non-Experts	Practical Usability By Experts	Applicability To Real Problems	Commercial Software Development	Education	Other
Lack of expert help in choosing options needed to run computations ◆◆ Lack of familiarity with specifics of computational tools Lack of readily accessible database of computational chemistry results Start-up time for new model users	Molecular simulation codes are not easy to use ◆ Current training tools are not comprehensive enough Lack of frame-work for implementing results Realistic solution behavior is not routinely accounted for in quantum calculations Difficulty in deriving meaningful knowledge out of data	Lack of sufficient quantitative accuracy ◆◆◆ Lack of force fields for problems of interest ◆◆ Lack of many demonstrated successes ◆ Lack of good accessible benchmarks Difficulty in linking with real applications Lack of easy to use tools to integrate time and length scales Simulations limited by time, length and number of units Lack of computing power Lack of links between molecular simulations and engineering correlations/models No direct links between comp. tools and analytical measurements Lack of commodity solution inhibits access to a larger market Validity of results is not clear	Small market size/insufficient funding ◆◆ Commercial codes do not keep up with science ◆ Lack of understanding of the software development company/process ◆ Too much of the software is UNIX based Too little new science is included in codes, despite increased costs of development Industry only feels comfortable using commercial codes Lack of desktop accessibility (language barriers) Software manufacturers make too many decisions without user input	Not enough education for non-modelers with regard to model capabilities Chemists think in terms of valence bonds rather than molecular orbitals.	Computational chemists are not included in initial process design team Management is not familiar with the value of computational chemistry Successes are proprietary and are not made public Lack of critical mass of people inside companies/ insufficient staff

The limited availability of input data such as general purpose, reliable force fields as well as easy-to-use methodologies is a major barrier to the application of computational chemistry to practical problems. One major issue is the lack of force fields (intermolecular potentials) that can be applied to solving problems of industrial interest. Many industrial problems require the ability to deal with liquids and solutions — a situation that is not routinely accounted for in currently available computational tools at the quantum scale. Current models also lack the capability to integrate time and length scales, and most simulations are limited by time, size, and number of units that can be handled.

To solve real problems or design new materials, it is often important to be able to link and/or compare computational results with experimental data. This capability is quite limited at the present time. There is also little ability to link the results of molecular simulations with engineering correlations and process models. Developing this capability would greatly extend the utility of computational results for problems arising in chemical plants.

Commercial Software Development

The small size of the market (as well as insufficient corporate funding) for computational chemistry is a significant barrier to the development of commercial software packages in this field. In general there is a disconnect between the developers of code in the research community and commercial software developers. Commercial software developers often make decisions without consulting the users and/or original developers. The result is that commercial codes do not reflect the advances that are made in the scientific community in terms of computational methodology as well as theory. Too little new science is included in commercial codes, especially for atomistic simulations. On the other side, users of computational chemistry methods have a poor understanding of the processes used by software development companies to bring codes to a commercial level. However, most industrial users only feel comfortable using commercial codes, primarily because they have limited in-house training and consulting, and need immediate, on-going technical support when difficulties arise.

In terms of computing capability, few computational methods have desktop accessibility, since accuracy does come with a significant computational cost. Most methods require sophisticated, costly computing systems and software. Another barrier is that too much of the currently available software is UNIX-based, a platform that is not always available to the non-specialist. However, the advent and acceptance of new, powerful, NT workstations will start to lessen this problem.

Education

The lack of education in modeling capabilities for non-experts is a significant barrier to the use of computational methods for solving plant problems. Without sufficient training, most research engineers would not attempt to set-up and use a complex modeling package.

Other Barriers

The mind-set of management within many traditional chemical companies has not been overly conducive to the routine use of computational chemistry as a problem-solving tool. Management is typically not familiar with the results and/or the value of computational chemistry — successful application of these tools in industry is often proprietary and never

publicized. One result is the lack of critical mass of people on staff at chemical companies that are expert in computational sciences and capable of applying tools to real problems. The company may not have a computational chemist on staff, and even if one is available they are typically not included as part of the initial design team on new projects.

Research Needed to Enable the Use of Computational Chemistry

Research needed to overcome barriers to the greater use of computational chemistry tools are shown in Exhibit 7-2, with priority levels and time frames for research identified within categories. Time frames indicate the period in which the results of various R&D activities are expected to be available for use by the modeling community at large, assuming sufficient R&D funding.

Problem Solving Environments

Much of the research needed to develop effective problem solving environments (PSEs) will be on-going over the next ten years. There is a critical need to develop a PSE that is specific to chemistry, particularly one that is comfortable for non-expert users. This should include the ability of the PSE to adapt to the expertise level of the individual user as well as the complexity of the problem being solved. Closely related is the need to develop expert systems that can facilitate the solving of specific problems. Ideally, the system should provide a mechanism for identifying where computations have failed to provide a reasonable result. Expert systems should also have the capability to provide users with an appropriate selection of computational methods based on problem parameters. Along with expert system development is the need to create accessible, linked databases that contain information on inputs as well as outputs with selection and search options for users.

The development of an easy-to-use framework that permits the user to move from *ab initio* molecular orbital electronic structure results to predicting accurate reaction rate constants and thermodynamic properties is an area of critical need. Such a framework will provide an enabling interface that promotes the use of computational chemistry for real problems. Research is also needed to enable the application of computational chemistry to very large real systems (e.g., development of hybrid techniques). Results in both these areas could be obtained in the short to mid-term (3 to 10 years).

Long-term efforts are needed to develop computational methods at the quantum scale that apply to the entire periodic table (good accuracy is currently only obtainable with the first two rows of the period table and the third row main group elements). Along with this activity, research is needed to support broad advances in model capabilities to improve efficiency and accuracy, to address large molecule systems, and to effectively model transition states and transition metals. Obtaining results in these high priority areas will be critical if computational chemistry at the quantum scale is to become a routine method for solving industrial problems as well as designing new products and materials.

Exhibit 7-2. Research & Development Needs
Enhancing Usability of Computational Chemistry By Industry
(✪ = Top Priority; ● = High Priority; ○ = Medium Priority)

Time Frame	Problem Solving Environments (PSE)	Development of Computational Tools	Experiment, Validation &Testing	Institutional/ Educational
NEAR (0 - 3 Years)		Develop commercial software that delivers engineering properties of interest to process design engineers - phase diagrams - viscosity - surface tension ●●●●○○○○ Develop more rigorous methods to estimate errors ●●○ Study statistical mechanics of hindered rotors and floppy systems ○○	Establish a benchmark database that is highly accessible and widely published ✪●●○○○○○○ Support widely published demonstration projects ✪✪●● - provide detailed information on the demonstration projects - develop case studies ● Produce results in the language of experienced chemists ●	Develop curricula (software and support material) for educational purposes ✪ Implement structure or overseeing body to coordinate R&D efforts ● Define size of market for computational tools ○
MID (>3 - 10 Years)	Develop framework to go from *ab initio* molecular orbital results to accurate rate constants and thermodynamics ✪●●●●● ○○○ Pursue application to very large real systems ●○○ - hybrid techniques	Studies to explore the environment around the molecule at the quantum scale (solvation and solid-state effects) ✪✪●○○ - methods to handle extreme environments Generate better potential functions ●		
LONG (>10 Years)	Develop quantum scale methods that apply universally (e.g. to the whole periodic table) ✪●●●○○ Support broad advances in model capabilities - efficiency - accuracy - large molecules - transition states - transition metals ✪●●○ Develop methods that can scale with theory ●○	Describe bond - breaking through reactive force fields ✪○ Studies in mesoscale modeling ✪○		Provide more support for application of molecular modeling to real problems ✪✪● Appropriate pricing for educational use Good, well worked tutorials

Exhibit 7-2. Research & Development Needs
Enhancing Usability of Computational Chemistry By Industry
(✪ = Top Priority; ● = High Priority; ○ = Medium Priority)

Time Frame	Problem Solving Environments (PSE)	Development of Computational Tools	Experiment, Validation &Testing	Institutional/ Educational
ONGOING (All Periods)	Develop a problem - solving environment for chemistry (including non-expert use) ✪✪✪●○○ Develop expert system to solve specific problems ●●●●○○○ - know where certain computations have failed ✪ - quantify "what is something" as opposed to "how do I do something"○ Create databases and expert systems for method selection ●○○○○○ Develop problem solving environment that adapts to the user and level of the problem ●●● - incorporate backward compatibility	Develop transferable force-fields ✪●●●●○○ - to use over a wide - range of conditions Develop public domain standards for creating inter-operable codes ✪● Develop standards for potentials ●● Develop flexible user interface for expert users ●○	Disseminate information on demonstrated success stories ✪✪✪✪✪✪ ●●○○ Include validation as an integral part of modeling efforts ✪○○ Quantify uncertainties through benchmark calculations ●●○○○ Develop experimental data for validation	Develop better mechanisms for technology transfer ✪✪●○○○ - standard application interfaces - more easily available Lower barriers to entry ●●○ Develop ways for academics and vendors to better understand markets and industrial problems ●○ Develop in-house training for casual users ●

Development of Computational Tools

The development of transferable force fields (intermolecular potentials) that can be used over a wide range of conditions is a high priority for advances in computational methods (and is also listed as a priority in the chapter on atomistic methods). Complementary research is needed to develop the capability to describe bond-breaking through reactive force fields. Research is also needed to generate better potential functions, as well as standards for potentials that will facilitate transferability. Efforts in force fields in general will be on-going over the next twenty years and will produce results continuously throughout that time.

Research is needed in a number of areas to develop theories that will expand the range of systems that can be modeled at the quantum scale. The most important of these is the need to describe the environment around the molecule, particularly solvation and solid-state effects. These are essential for predictive modeling of systems involving solvents (a vast majority of industrial problems) and transition metals, such as those in homogeneous and heterogeneous catalysts. Research is also needed to develop the capability to model the extreme environments (high temperature and pressure, corrosive) found in many chemical processes. Supporting research should be conducted to better address the statistical mechanics of hindered rotors and floppy

systems, which are not adequately addressed by existing methodologies. Research in these important areas could be accomplished by the mid-term.

In the area of practical usability, there is a critical need to develop commercial software that generates engineering properties (e.g., phase diagrams, viscosity, surface tension) that are useful to process design engineers. Complementary research is needed to develop more rigorous methods for estimating errors in results and to increase the validity and certainty of computational techniques.

To expand the utility of computational methods for more expert users, research is needed to develop flexible user interfaces and enable communication of results between scale levels. A broad research effort is also needed in mesoscale modeling, which is still in a very fledgling stage of development but represents a critical link between quantum chemistry, atomistic modeling, process simulation, and *de novo* materials design.

In general, as new theories and codes are developed, on-going efforts will be needed to develop public domain standards for inter-operable codes. This will ensure the usability of new codes and facilitate commercial development by software vendors.

Experiment, Validation and Testing

A critical element in promoting the more widespread use of computational chemistry is the increased dissemination of information about these techniques to the potential user community. A high priority activity is to establish a benchmark data base of computational results that quantifies uncertainties, and is easily accessible on the World Wide Web. Another critical effort is the aggressive dissemination of information on demonstrated success stories (i.e., where computational chemistry has been used to solve practical engineering problems or design new products and materials). Support should also be provided for widely publicized demonstration projects where detailed information on the nature of the project and/or case studies can be generated and distributed to the user community. These activities would provide expert as well as non-expert users with examples of how to apply computational chemistry, historical results for comparison with new projects, and a basis for justification in using these tools that could be effectively presented to management. We do note that there are difficulties here due to the competitive nature of the industry and the value of proprietary intellectual property.

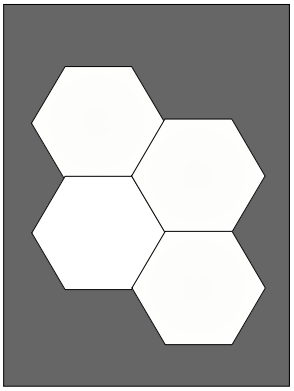
Experimental data is also critical in promoting the usability of computational chemistry. Predicted results need to be experimentally validated to ensure reliability and practicality. Experimental validation, including the collection of experimental data and development of measurement techniques, should be incorporated as an integral part of modeling activities.

Institutional/Educational

Mechanisms for more effective transfer of technology are needed to broaden the user community for computational chemistry. This includes the development of standard application interfaces to allow transferability of models between developers and users, which is a significant limitation to the use of existing tools. There should be an effort to better connect the needs of researchers, practical industrial users, and commercial software developers. Complementing these activities would be long-term support for promoting the application of molecular modeling to real problems (e.g., providing tools at a discount to potential new users, developing good tutorials).

To promote software vendor commercialization and ultimately greater use of computational chemistry, the size of the market for computational tools needs to be continually reevaluated. Ways to lower the barriers to entry (cost of development) need to be found. A contributing factor is the lack of education and curricula in this field at both the undergraduate and graduate level. There is a need to develop software and support material that could be integrated into curricula at both levels to increase the number of graduating scientists and engineers interested in working in the field.

Above all, there is a need for better coordination and communication among all of the stakeholders. The field spans the scientific disciplines of chemistry, chemical engineering, polymer science and engineering, materials science and engineering, and applied physics. It includes both basic and applied research. The funders, developers, and customers of computational chemistry include industrial companies in several sectors, universities, and several government agencies. If one could imagine an organization or society to "take responsibility" for the field, it would have to encompass all of these interests. Its role should include coordinating the dissemination of technology, communicating needs, exchanging scientific progress, and connecting across scales. No such organization currently exists.



8 Summary

Goals for Computational Chemistry

Computational chemistry can assist in the design and optimization of new and existing processes and products. It can be used to reduce the costs of development, improve energy efficiency and environmental performance, and increase productivity and profitability. Although computational chemistry is currently being applied in the chemical industry to some degree, it is difficult, costly, and could see much greater use. There are significant limits to the type and size of problems that can be modeled, as well as the validation and reliability of the results. There are considerable barriers to entry for development of commercial software packages available to the broad user community, and many codes that are available are difficult or impossible for non-experts to use. Contributing to these limitations is the lack of people qualified or willing to work in the field, and the lack of published information and education about the benefits and use of computational tools.

Ideally, computational chemistry tools for the chemical industry need to be:

- Applicable to a wider range of systems — larger systems, over greater time scales, liquid or solid-state systems
- Flexible — inter-operable between various computing platforms and software, graphical user interfaces, scalable
- Affordable — capable of running on desktops or lower-cost parallel computing platforms
- User Friendly — technical support mechanisms, expert systems for non-experts and experts
- Experimentally-validated — computations validated through experimentation
- Widely publicized — publication of benchmarks, demonstrated successes
- Included in the educational curricula — undergraduate and graduate level software, course work

Pathways for Success

The results of the workshop have demonstrated that pre-competitive research and development is needed to advance the state-of-the-art and to build capabilities for computational chemistry. Considerable effort needs to be expended to develop new theories, increase computational capability, remove predictive uncertainties, and educate decision makers about the benefits of these potentially powerful tools. Management is starting to expect applied computational chemistry to aid their businesses. Although some keep looking for the “killer application” that will "prove" the technology and also provide the direction for future profitable applications, computational chemistry is rarely employed single-handedly to solve a problem, just as no single experimental method is used to solve complex problems.

The Vision 2020 problems are really big. Their efficient solution depends on getting the right people together, doing the right things, at the right time, for the right reasons. Exceptional results from individual contributions will become less important in the future. The real challenge is turning disparate information into organized, exploitable, implementable knowledge. The Vision 2020 report points to the importance of the future coordination, integration, and deployment of a focused, multidisciplinary national team concept.

For effective resource leveraging, risk minimization, and providing a stable baseline for funding, pre-competitive research should be cooperatively supported through the chemical industry, commercial software developers, and the federal government. For maximum use by industry, the users of computational technology in the chemical industry should provide significant input to the development process, particularly regarding the types of problems that need to be addressed. Research may be conducted by industrial research laboratories, software development companies, through the federal R&D laboratory system, and by the academic research community. Project selection, control and evaluation should be carried out with input by a broad cross-section of potential industrial users. Federal laboratories could partner with individual companies for technology development, and for addressing fundamental issues. Computational chemistry cannot be widely applied in the chemical process industry without the customer service and support base of the software industry, and these businesses must be brought into the technology program as soon as possible.

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