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Chapter 1

Supercomputer Research in Chemistry and Chemical Engineering

An Introduction

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This chapter gives a selected overview of the current status of supercomputing research in chemistry and chemical engineering and places the research areas discussed in the rest of the book in the context of current work.

The first ACS Symposium volume on supercomputing was published in 1981 (1). That symposium already included mature applications of the Cray-1 machine, usually thought of as the first supercomputer. A more recent supercomputer symposium, the Second International Conference on Vector Processors in Computational Science, held at Oxford in August, 1984, is published as Volume 37 in Computer Physics Communications. In their introduction the editors of the latter proceedings commented that the most notable change in the field over the past few years had not been new hardware but rather the sophistication of the hardware and the maturity of the user community. To a large extent that observation holds for the 1984-87 period as well, especially regarding the use of supercomputer resources in chemistry and chemical engineering.

Multiple processors have been widely discussed as a tool for achieving high compute speeds, but most of the progress on achieving higher computation speeds for applications has been achieved by better utilization of the vectorization strategies that were already possible even in 1981. The hardware available at the time of this writing is about a factor of two-to-four faster, on a per processor basis, than that available on the original Cray-1, and the fastest supercomputers have at most four processors. Since most calculations are still run in the single-processor mode though, we have achieved far less than an order of magnitude in effective top speed in five years. Nevertheless many application fields have advanced to systems much more than five times as demanding, not only because of the increases in user and software sophistication mentioned above, but also because of algorithmic advances and the availability of a greater number of supercomputers, allowing more processing hours to be devoted

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to specific applications and allowing utilization of this kind of resource at a greater number of sites. It is unfortunately true though that this kind of research is still severely underfunded, and this accounts for the fact that its potential is still largely untapped.

Although the increase in speed of supercomputers has not been dramatic in the last five years, there has been a very notable hardware advance in the size of computer memories. Whereas the 1-Megaword memory of the Cray-1 was once considered generous, the opportunities created by the Control Data Corporation Cyber 205, with 8 Megawords of real memory and a huge virtual address space, and the Cray-2, with 256 Megawords of real memory, are much greater and these opportunities are only very recently being appreciated and exploited. Another advance that is rapidly becoming more important is networking. As users get accustomed to taking advantage of the best available hardware, software, and databases in terms of what can be reached easily by network, even if it is across the continent or the ocean, supercomputer capabilities may be expected to have very significant effects on larger and larger areas of chemistry and engineering.

In keeping with the above remarks on the relative importance over the last few years of hardware advances versus utilization and application-mode advances, the present volume centers on the latter. The chapters are arranged in terms of four underlying scientific subfields. First comes the study of electronic structure as based on the Schrödinger equation. Next comes the study of equilibrium systems, based on thermodynamics and equilibrium statistical mechanics, including also some aspects of quantum mechanics, especially with regard to quantized degrees of freedom and spectra. The third application area consists of the study of kinetics and dynamics, either classical or quantal, but at the microscopic level where complications like flow do not come in. Quasiequilibrium theories of rate processes, such as transition state theory, technically belong to dynamics, but may also be considered with equilibrium properties, since the techniques are similar. The fourth and final set of chapters deals with complexities of flow and transport. In general the applications in the later sections must include at least some of those involved in the earlier ones; thus in some sense the organizational principle is one of increasing complexity. For example, the study of dynamics always presupposes some knowledge of interaction energies such as intermolecular forces and binding energies, and such knowledge may usually be traced back to quantum mechanics, spectra, or properties of equilibrium systems. Similarly many problems involving transport also involve chemical reactions and at a detailed level all transport is intimately related to the microscopic atomic and molecular dynamics. This kind of connection is discussed at greater length by Clementi and Lie (Chapter 14), and it comes more and more into play in the large-scale simulations that are made possible by supercomputers. This creates some clear problems in assigning a few of the chapters to one of the four sections of the book. Nevertheless we have

made choices, and in general a chapter is assigned to the farthest down of the sections to which it is directly relevant.

As large-scale computations make their presence felt in more and more areas of chemistry and chemical engineering, and as the context of these applications develops a significant history, it becomes impossible to include a comprehensive discussion in any one volume. Thus the present set of chapters is more illustrative than complete. And although many of the chapters contain reasonably complete introductory remarks, the book cannot serve to put whole subfields into focus. This is all symptomatic of a proceedings in a rapidly developing field. In the rest of this introduction we try to complement the proceedings papers by discussing some of the work in the book and a small subset of other interesting and especially recent work in the field, with the goal of slightly broadening the context in which the proceedings and the current status of supercomputer research in these fields is viewed. The topics will be discussed in terms of roughly the same ordering scheme as used for arranging the topics in the book.

Electronic Structure

In many respects materials science is the branch of chemistry that has the most obvious opportunities to gain from the supercomputer revolution. Experimental, empirical knowledge of materials is difficult to organize without theoretical understanding. For many material properties such understanding is in principle afforded by the analysis of accurate electronic wavefunctions and energies and in favorable cases unknown materials properties can even be predicted. But the calculations require enormous computations even when they are feasible, hence supercomputers are required. An example in the present book is afforded by calculations on metal-containing compounds (Chapter 2). Recent advances in methodology have improved the reliability of *ab initio* calculations on such systems. New calculations give insight into the nature of the bonding and define the two- and three-body parameters used for modelling larger clusters. Comparison of *ab initio* and model results for Al clusters and $Cu_{18}Be$ suggests that composite materials can also be modelled based on parameterization from the *ab initio* calculations. The theoretical calculations are especially useful for obtaining model interactions parameters for interactions of unlike atoms. These are much harder than like-atom interactions to obtain from experimental information on bulk properties, in particular because they don't even occur in single-component metals. The theoretical studies indicate that large clusters are required before the bulk structure becomes the most stable. The study of adsorbates on Be_{13} shows that the chemistry of clusters can be very different from the bulk as a result of the cluster's increased freedom to expand and distort. This leads to interesting insight into the differences between bulk metallic systems and small metallic clusters, which may be very active in catalysis but which are hard to characterize experimentally. The need for powerful supercomputer resources becomes very evident when we consider the

eventual necessity to extend the theoretical studies of multicomponent systems and clusters to include vibrational effects and nonzero temperatures.

Another example from the field of materials science is provided by the chapter (Chapter 5) on conducting polymers and materials with nonlinear optical properties. The potential understanding to be derived from the availability of supercomputers for this research is immense. The materials under study are expected to play a critical role in the future development of molecular electronic and optical devices for information storage and communication. Large-scale *ab initio* simulations lead to detailed understanding of properties which are hard to extract from experimental data or from more approximate and less demanding calculations. The methods of quantum chemistry have reached a point where they constitute tools of semi-quantitative accuracy and have significant predictive value. Further developments for quantitative accuracy are still needed for many purposes though and will require the application of reliable methods for describing electron correlation in large systems. The need for supercomputer power will be very acute for such correlated calculations.

Another area where electronic structure calculations can have an enormous impact on industrial chemistry is the design of efficient catalysts. Very few catalytic systems have been studied so far because of the large computer time requirement, which is where supercomputers come in. The most complete protostudy currently available in this area is the modelling of the full catalytic cycle of olefin hydrogenation by Wilkinson catalyst as calculated by Morokuma, Danie, and Koga with the *ab initio* molecular orbital method. Even though these authors committed about 200 hours of supercomputer time to the project they still had to make several simplifications, such as replacing some phenyl groups by hydrogen, neglecting solvent effects, and ignoring side reactions. Clearly even more resources are required to make the modelling more realistic, but already these authors were able to determine the rate determining step, to predict a possible intermediate, and to illustrate where and why there is a special sensitivity to choice of ligand. This kind of calculation is clearly very stimulating.

One important aspect of the supercomputer revolution that must be emphasized is the hope that not only will it allow bigger calculations by existing methods, but also that it will actually stimulate the development of new approaches. A recent example of work along these lines involves the solution of the Hartree-Fock equations by numerical integration in momentum space rather than by expansion in a basis set in coordinate space (2). Such calculations require too many floating point operations and too much memory to be performed in a reasonable way on minicomputers, but once they are begun on supercomputers they open up several new lines of thinking.

Finally, we mention the very encouraging successes combining atomic natural orbitals and full CI calculations for small molecules (Almlöf, Bauschlicher, and Taylor). With this method the singlet-triplet splittings

of CH_2 and SiH_2 have been computed to an accuracy of about 0.1 kcal/mol, and the dissociation energies of CH and OH are within 0.03 eV of experiment. The extension of these techniques to transition metals will be very interesting.

Equilibrium Properties and Spectra

The rapid advances in electronic structure applications are causing the field to be discussed under many new names, such as computer-aided molecular design or computer-aided materials design (both abbreviated CAMD as a rather obvious variation on CAD/CAM). One especially promising subfield concerns the design of bioactive molecular agents (computer-aided macromolecular design).

The interaction energies important for biological systems are often the weak nonbonding forces that govern such phenomena as conformational changes, tertiary structure of proteins, and the hydrophobic interaction. Because of the weakness of these interactions, the electronic energy cannot be considered apart from such additional factors as the thermal energy and entropy of the substrate and the solvent. Biochemical systems, being complex, clearly require large calculations. Once the possibility of these calculations is opened up, however, interesting approaches become available that illustrate some extremely important advantages of the computational mode of science over the experimental, observational mode. For example, many researchers are very excited about an approach to calculating free energy differences in which one of the compared systems is incrementally "mutated" into the other; this kind of process is clearly impossible in the laboratory, but of course we can nevertheless learn a lot from it theoretically. This technique, whose recent developments are due to Jorgensen and McCammon and their coworkers, is being applied to the binding constants of drugs to macromolecular receptors, the effects of site-specific mutation on enzyme catalysis, and solvent effects (3). This technique is discussed further in the chapter by Berendsen (Chapter 7), who has applied it to the binding of enzyme inhibitors to enzymes.

Another biochemical example (Chapter 8) involves the conformational exploration of an octapeptide with the aim thereby to develop a breast cancer vaccine. Other work by the same author, in this case on the 41-mer of a tetrapeptide, leads to constructive suggestions for a malarial vaccine. It is of course very encouraging to see these humanitarian applications of supercomputers. Rational drug design and protein engineering are clearly fields in which molecular mechanics and conformational analysis combined with interactive computer graphics and molecular dynamics have exciting opportunities to lead to progress. Even though the fields are young, the status of computer-aided drug (and vaccine) design is very greatly advanced compared to its status when an ACS Symposium Series volume (4) appeared on this subject in 1979; that volume may be consulted for a snapshot of this very active field just before the availability of supercomputers.

Most common approaches to simulations, whether biochemical or otherwise, rely on some variant of the Monte Carlo method. In general a Monte Carlo method is a way to compute a quantity by interpreting it as the average of a random sample, usually a computer-generated one. The method was pioneered for the study of small systems and is still very useful for such systems. For example, one of the poster papers at the Symposium concerned vectorization strategies for binary collisions of Ar with CO and He with CH_3CN (5). The Monte Carlo method becomes more important, however, for large, complex systems with many degrees of freedom, for which it may be the only practical simulation technique. Since these systems are often treated classically, a variant of the Monte Carlo method in which the classical equations of motion are used to generate the ensemble, is often used; this is called molecular dynamics. Monte Carlo calculations may require enormous amounts of computer time, taxing any conceivable computer system. The Monte Carlo method yields imprecise estimators with a variance that may be reduced by increasing the size of the sample set. Because the samples may be uncorrelated, Monte Carlo methods are well suited to the next generation of highly parallel computers. A challenge to theorists will be to include quantum effects where required so as not to rely on large classical simulations just because they can finally be carried out. Several groups are now working on large-scale quantum simulations. For example, in one study (6), an excess electron in a sample of 300 water molecules at room temperature was simulated by path integral techniques involving up to 1000-point discretizations of the electron path. The highly quantum nature of this system is obvious from the small mass of the electron, which has a thermal free-particle deBroglie wavelength of about 17 Å.

A repeated theme in discussions of supercomputer simulations is that they allow us to ask and answer questions that cannot be asked experimentally, especially questions about details and about the "why" of various processes. (This same note was struck in the discussion above of electronic properties of materials.) One striking example of this kind of extra detail was provided by a recent classical dynamical simulation of DNA counterion motions in aqueous salt solutions (7). This simulation required calculating the sequence of counterion positions on a very fine time grid, while the total time involved in determining the simulated experimental observable, which was an NMR signal, is very long. Each step requires the calculation of roughly 10,000 interactions among the charged atoms of the polymer and the small ions. The calculation required about 40 hours of computer time on the Minnesota Supercomputer Center Cray-2 computer. Without supercomputers the simulation would have been completely infeasible. Clementi and Lie (Chapter 14) have also considered the counterion structure near DNA, and have considered the time scale question of how long do water molecules near DNA retain their liquid structure as compared to the time scale for those far away; this is clearly another question that would be hard to answer by experiment.

Levy (Chapter 6) has also explored the use of supercomputers to study detailed properties of biological macromolecule that are only indirectly accessible to experiment, with particular emphasis on solvent effects and on the interplay between computer simulations and experimental techniques such as NMR, X-ray structures, and vibrational spectra. The chapter by Jorgensen (Chapter 12) summarizes recent work on the kinetics of simple reactions in solutions. This kind of calculation provides examples of how simulations can address questions that are hard to address experimentally. For example Jorgensen's simulations predicted the existence of an intermediate for the reaction of chloride ion with methyl chloride in DMF which had not been anticipated experimentally, and they indicate that the weaker solvation of the transition state as compared to reactants for this reaction in aqueous solution is not due to a decrease in the number of hydrogen bonds, but rather due to a weakening of the hydrogen bonds.

Supercomputers become more and more useful, and the insights they can generate become more and more unique, as the complexity of the system modelled is increased. Thus interfacial phenomena are a very natural field for supercomputation. In addition to the examples in this volume it may be useful to mention the work of Linse on liquid-liquid benzene-water interfaces, which he studied with 504 H_2O molecules, 144 C_6H_6 molecules, and 3700 interaction sites. He generated over 50 million configurations in 56 hours on a Cray-1A, and he was able to quantitatively assess the sharpness of the interfacial density gradient, which is very hard to probe experimentally, Similarly Spohr and Heinzinger have studied orientational polarization of H_2O molecules at a metallic interface, which is also hard to probe experimentally.

Microscopic Dynamics

The present volume contains only one chapter (Chapter 11) on small-molecule gas-phase dynamics. In this field the role of the supercomputer is diverse, but perhaps the most critical area is allowing essentially exact quantal dynamics to be carried out for previously intractable systems. A recent example is the essentially exact calculation of the reaction threshold for D atoms reacting with vibrationally excited H_2 (8). The same research group has completed the first numerically converged solutions of the Schrödinger for reaction probabilities in a system with an atom heavier than an isotope of H, in particular $O + H_2 \rightarrow OH + H$. Both calculations were carried out with a new basis-set approach that specifically takes advantage of the large memory and high vector speed of the Cray-2. Another new computational approach to small-molecule dynamics that is stimulated in part by the availability of fast vector machines is based on the computation of quantal propagators with very large basis sets by recursive transformation of a large sparse Hamiltonian matrix into a much smaller tridiagonal one; a recent application is to time-dependent energy deposition in a molecule by a laser (9). Abraham (10) has provided an

excellent review of recent simulations on two-dimensional condensation and melting at surfaces and in thin films. His review also provides some relevant background reading for the chapter in the present volume by Gilmer and Grabow (Chapter 13). This review also contains an exciting chapter section entitled "super problems for super computers" (*sic*), in which the author discusses some of the very large computational problems that still defy attack.

We have already mentioned the application of supercomputers to biochemical simulations. Internal dynamics may play an important role in such simulations. An example would be enzyme binding-site fluctuations that modulate reactivity or the dynamics of antigen-antibody association (11). In the specific case of diffusion-controlled processes, molecular recognition may occur because of long-range steric effects which are hard to assess without very expensive simulations (12).

In addition to the already mentioned insights into materials properties obtained through electronic structure calculations, materials science has much to gain from supercomputer simulations of microscopic and macroscopic elements of materials processing. Microelectronic components, optical devices (solid state lasers and detectors), optical fibers and high performance ceramics are artificially microstructured materials made by carefully controlled nucleation, solidification, deposition, and etching procedures. Since the performance of the materials strongly depends on the degree of crystalline perfection and the nature of the interface, a microscopic understanding of the atomic scale growth and etching processes is essential. Direct molecular dynamic simulations of crystal growth from the vapor are discussed by Gilmer and Grabow (Chapter 13). The difficulty in this procedure is the large amount of computation required to obtain the atomic trajectories and the large number of atoms required because of the very slow growth rates. Present computation power may not be sufficient for a direct simulation of molecular beam epitaxy of an elemental semiconductor (e.g. Si) and it limits studies of the many fundamental problems of interface formation and growth found in molecular beam epitaxy of compound semiconductor structures (e.g. AlGaAs/GaAs). Because of the small correlation between samples in molecular dynamic simulations of crystal growth, this application seems well suited for new, special purpose, highly parallel computers.

Metal-hydrogen systems and superionic conductors are examples of other solid systems of great technological importance on which progress has been hampered by the inability to make realistic enough simulations. The reader is directed to recent work by Gillan and Catlow and their coworkers for recent progress in studying these kinds of systems.

Supercomputers can be directed to the study of techniques as well as materials and processes. For example, one can simulate neutron scattering experiments with the goal of elucidating the effects of approximations usually made in "standard" treatments of the experimental data.

The understanding of fluid flow is one the areas where supercomputing has already had a significant impact. General fluid mechanics falls

outside the scope of this volume, but applications of fluid mechanics to chemical problems are characteristic of the chapters grouped under the transport heading. As an interesting transition between the microscopic dynamics and macroscopic transport chapters, Clementi and Lie (Chapter 14) describe the simulation of a macroscopic fluid flow example in terms of constituent molecular motions. Another example of molecular simulation of fluids concerns transport and fluid properties in microporous media as discussed by Davis *et al.* (Chapter 15). Because of the molecular or nanometer dimensions involved in these systems, experimental characterization is difficult. Moreover, fluids can be strongly inhomogeneous in the confined pore space so that the usual macroscopic theories of fluid structure and transport may not be applicable. Thus, supercomputer simulations become an important tool for understanding fluid structure and transport in microporous media as well as for developing appropriate theories suitable for analyzing related macroscopic phenomena, such as processes involving porous catalysts (e.g. hydrodesulfurization), lubrication and wetting, drying of paper products and clay dispersions, and enhanced oil recovery. The study of these practical problems are also natural areas for supercomputer research which will be discussed in the subsequent section.

Transport Processes

Macroscopic analysis of complex chemical processes, including materials processing, requires numerical solution of the equations for local conservation of momentum, energy, mass, and chemical species on irregular domains and often with free boundaries. In their general form, the equations are nonlinear partial differential equations in space and time, where the nonlinearities are introduced by the constitutive equations for fluxes (e.g. multicomponent diffusion, non-Newtonian flow), reaction rates, convective coupling between flow and mass/energy transport, and the dependence of boundary shapes on field variables. These nonlinear interactions severely complicate the numerical solution of the conservation equations by causing transitions in the solution structure, including multiple solutions, spatially and temporally periodic solutions, and even chaotic phenomena. Other complications are caused by multiple length and time scales. Length scales different than those characteristic of the domain arise from the nature of the problem; for example, in the case of a catalytic reactor the active material may be 5 nm metal crystals imbedded in a 5 mm porous particle stacked among thousands of particles in a 0.50 m diameter tube. In addition, different length scales arise as a result of boundary and internal layers caused by rapid changes in the field variables near solid boundaries, interfaces, and reaction fronts. For example, the flame front in a combustion system may be a few mm wide while the characteristic dimension of the system is in order of meters. Multiple time scales originate from the mixing of transport processes and reaction kinetics, which have order-of-magnitude differences in their time scales, and they lead to stiff integration problems that can tax or even exceed the

capabilities of current supercomputer hardware. Ortega and Voigt (13) review numerical methods for partial differential equations on supercomputers along with a brief description of applications to fluid dynamics, reservoir simulation, and weather prediction. They specifically discuss the influence of parallel and vector computing on algorithm design and selection.

The nonlinear nature of detailed models of complex chemical processes is a central issue in their solution and one that contributes heavily to computational demands. If the nonlinearities are strong enough it may be essentially impossible to find a solution for a particular set of parameters from a simple initial guess. In such cases the solution must be found by connecting it by homotopy to a known solution of the same set of equations but with a different set of parameters or perhaps a solution to a simpler, but analogous problem. The procedure involves following the solution family for varying parameters and it is commonly referred to as continuation. Thus, even though a single calculation perhaps could be carried out on a VAX8600 in a few hours, the large number of calculations involved in reaching the desired solution by continuation necessitates supercomputing. Furthermore, because the nonlinearities lead to nonuniqueness of the steady state and a multitude of periodic phenomena, it is necessary to understand the structure of solution space, which again means tracking solution families for varying parameters by using specialized continuation techniques (13–16). If the stability of the solution is also of interest, the eigenvalues of the linearized problem must be determined. For large-scale systems this requires extensive supercomputer calculations and many problems still defy attack.

The nonlinear behavior of physicochemical systems is brought up in several of the application examples in this volume. Brown *et al.* (Chapter 17) consider the evolution of cellular microstructures during directional solidification, which is a nonlinear free-surface problem. Jensen *et al.* (Chapter 19) describe nonlinear flow transitions adversely affecting the growth of compound semiconductor superlattices by organometallic chemical vapor deposition, while Smooke addresses a flame extinction problem (Chapter 20). Both sets of investigators use an arclength continuation technique due to Keller (14). Kevrekidis (Chapter 16) specifically addresses computational issues in the analysis of complex dynamics that cannot be understood through local stability considerations. Because of the nature of the instabilities underlying the dynamic phenomena, it is extremely difficult, if not impossible, to extract an understanding of the transitions between the various periodic behaviors through simple simulations of the physical experiments. Two illustrative examples based on flame front and thermal convection descriptions are presented.

In the remaining parts of this introductory chapter we return to discussion of specific applications of supercomputing -- starting with materials growth and proceeding through increasingly complex physicochemical systems. One of the application areas where large-scale simulations have already had an impact on understanding is the process of crystal growth

from the melt including morphological solidification phenomena. The latter is a classical problem and is addressed by Brown *et al.* (Chapter 17), who use large scale numerical finite element solutions of two-dimensional models to study pattern selection of the solidification front. Central issues in this fundamental problem include the cell shape, the apparent wavelength for the crystallization front, and the evolution to dendritic growth with side branches. The simulations provide significant new insight into the morphological stability phenomena. However, to address the central question of whether the observed dynamics are deterministic or a "snapshot" of a stochastic behavior would require the next generation of supercomputers.

The growth of the thin films from the gas phase by chemical vapor deposition (CVD) involves a complex mixture of homogeneous reactions, surface reactions, fluid flow, heat transfer, and mass transfer that is difficult to understand without a comprehensive model of the process. The work of Kee, Coltrin, and coworkers (17, Chapter 18) represents a significant effort to include detailed kinetic models in CVD reactor simulations analogous to what has been done in combustion modelling. By using sensitivity analysis they derived a mechanism of 20 reactions from a detailed pyrolysis mechanism for SiH_4 involving 120 elementary reactions. Their simulations demonstrated the importance of including detailed descriptions of homogeneous and heterogeneous reactions in CVD reactor models and they compared well to species measurements by laser spectroscopy (18). This type work can only be realized by the use of supercomputers. In addition to treating Si deposition, the authors' contribution to the present volume (Chapter 18) also addresses the implementation of large-scale models of physicochemical processes, e.g. the computation and organization of thermodynamic quantities, transport coefficients, and rate constants. This is an issue that transcends CVD analysis to simulation of other complex chemically reacting systems.

Jensen *et al.* (Chapter 19) focus on two- and three-dimensional transport phenomena as well as transient behavior in the growth of thin films and superlattices of compound semiconductors (e.g. GaAs/AlGaAs). Previous CVD models have been based on simplified transport descriptions unable to provide a complete enough picture of spatial and temporal variations in the deposition rate. However, accurate control of the deposition rate is essential to the further development of advanced optoelectronic and microelectronic devices. Because of the complex gas flows in irregular domains, supercomputing is necessary to simulate the process models. Further analysis will have to consider transient, three-dimensional reacting flow phenomena which will severely tax, and in some cases exceed, the capabilities of current supercomputer hardware. There are many other opportunities for supercomputer applications in materials processing in addition to the crystal growth studies in this volume. For example plasma and laser processing (19,20) could gain considerably from studies of detailed process models. The goal of modelling materials processing should be the theoretical understanding and, eventually, quantitative

prediction of the relationship between macroscopic processing conditions and the microstructure of the materials, which governs the mechanical, optical, and electrical properties.

Combustion of gaseous and solid fuels is another application area that has much to gain from large-scale simulations of detailed processes models. The issues are similar to those in CVD, but complicated by large energy releases and multiphase flows. The questions related to the organization of the database of rate constants, transport coefficients, and thermodynamic quantities are essentially the same as in CVD modelling. In fact, the aforementioned work by Kee *et al.* (Chapter 18) benefits from their extensive experience in combustion modelling. Large-scale computational analysis of combustion involves several critical elements including the chemistry code, the fluid flow treatment, and the resolution of sharp flame fronts. The latter issue, which is part of the general problem of differing length scales in detailed process models, poses significant challenges to numerical procedures. The size of large-scale physicochemical problems combined with the need to accurately resolve local structures (e.g. a flame front) necessitates the use of dynamic, self-adaptive, local grid modifications. Uniform griding on the basis of the length scale of the local phenomenon would lead to finite element/finite difference discretizations with a huge number of equations whose solution would be prohibitively expensive on even the largest supercomputers. Therefore, adaptive griding is a rapidly evolving area in numerical analysis for large-scale models. Two examples from gaseous and solid fuel combustion modelling are included in the present volume (Chapters 20 and 21). A recent survey by Babuska *et al.* (21) shows the principal directions of work adaptive griding techniques.

Atmospheric chemistry modelling to predict the effect of pollutants (intentionally or unintentionally released) on the environment is a natural application for supercomputing. The problem involves a large number of reactions among hydrocarbons, fluorocarbons, nitrogen compounds, and sulfur compounds in sunlight (22,23). In addition, these reactions have rate constants that differ by as much as 14 orders of magnitude. Simulations of the transport processes in the atmosphere require three-dimensional fluid flow simulations with very large grids and many transporting constituents. Furthermore, aerosol particle nucleation and growth play important roles in the overall behavior. Supercomputer simulations of atmospheric chemistry not only increase the scientific understanding of such complex systems but also provide a tool for regulatory agencies to study effects of existing and proposed pollutant emission standards.

There are several other applications where significant gains could be made through the use of supercomputer simulations of detailed physical models. Reservoir simulations was one of the first areas where the value of supercomputing was recognized by industrial companies. It is only possible to measure a few properties of interest to enhanced oil recovery. Furthermore, field tests are extremely expensive, and the monetary

decisions involved in the choice of methods for driving the oil out of a particular reservoir can equal or perhaps even exceed the cost of supercomputer hardware. Thus, supercomputer simulations become a more cost effective method than field experiments (25). Chemical plant design is another area that could benefit from the use of supercomputers. A large chemical plant involves many different units including separation, reactors and heat exchangers, which are interconnected. Some of the units may require the same detailed modelling as the above mentioned applications. Therefore the plant model will involve large numbers of interconnected equations offering considerable challenges to supercomputing (26). The large-scale plant simulations could serve design, optimization, and control purposes.

Conclusions

Many significant applications of supercomputing in chemistry and chemical engineering are emerging as facilities for large-scale computations become more and more accessible. The present volume intends to illustrate recent advances and applications, but already the field is so broad that no single volume can put all the subfields into perspective. The purpose of combining chemistry and chemical engineering applications in a single symposium was to emphasize their strong relationships, and we hope that these relationships will be further strengthened by continuing interactions between these fields.

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