
**Mathematical Research in Materials Science: Opportunities and Perspectives**

Committee on Mathematical Sciences Applied to Materials Science, National Research Council

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# MATHEMATICAL RESEARCH IN MATERIALS SCIENCE

## Opportunities and Perspectives

Committee on the Mathematical Sciences Applied to Materials Science
Board on Mathematical Sciences
Commission on Physical Sciences, Mathematics, and Applications
National Research Council

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# PREFACE

This report is the product of the second phase of a two-phase study by the Committee on the Mathematical Sciences Applied to Materials Science, a committee convened by the Board on Mathematical Sciences (BMS). It builds on the committee's short phase-one survey,[1] which (along with a briefing) was produced in response to a National Science Foundation (NSF) request. That report briefly described general mathematical theory and techniques that have been or show promise of being fruitful for ongoing and future materials science research. It was primarily aimed at and distributed to federal agencies that fund mathematical sciences and materials science research. This more comprehensive technical report documents and presents technical details of fruitful past collaborations between the mathematical sciences and materials science, and it indicates which particular areas of mathematical sciences research hold the most promise for advancing materials science.

Materials research is now undergoing a transformation into a quantitative science.[2] Although interaction between the mathematical sciences and materials science is increasing, many researchers in both communities are unaware that fruitful collaborations are possible and that a broad mathematical theory of materials is already being developed. However, materials science has been a prominent theme of several recent mathematics professional society meetings. Also, materials and processing have become the focus of a major cross-government initiative[3] because they are critical to the success of industries such as the aerospace, automotive, biomaterials, chemical, electronics, energy, metals, and telecommunications industries. In light of the subject's timeliness, and to follow up and build on the brief survey prepared for NSF, the BMS chose materials science as the focus for a BMS cross-disciplinary report. This is one of a series of BMS reports that highlight areas on the interface between the mathematical sciences and other fields.

The purpose of this report is not only to focus on directions for potentially promising collaboration between materials scientists and mathematical scientists, but also to encourage both communities to increase such collaborations. It is written primarily for mathematical and materials science researchers with an interest in advancing research at this interface, as well as for federal and state agency representatives interested in encouraging such collaborations. The opening and closing chapters (1 and 9) are intended for any persons wanting general information on how such cross-disciplinary, collaborative efforts can be successfully accomplished.

To articulate the many mathematical challenges faced by materials scientists, the committee asked a large number of researchers (see appendix) to provide short write-ups briefly describing materials science research areas and identifying mathematical challenges in those areas. The committee incorporated the information received into the committee's descriptions and perspectives presented here. This report emphasizes that both the mathematical sciences and materials science communities have much to gain from an increase in cross-disciplinary collaborations, and it presents the committee's recommendations for facilitating mathematical sciences research that bears on important issues in materials science, including recommendations on how to attract students and young

researchers to this area. These recommendations are general and are not intended to be a detailed "blueprint" for action. It is hoped that this report will encourage research directions in the mathematical sciences that complement vital materials science research, as well as raise awareness of the value of quantitative methods in materials science.

The committee is very grateful to the anonymous reviewers who provided excellent feedback in a short time, and to the many individuals who contributed information at the request of the committee. These colleagues strengthened this report significantly.

## NOTES

1. National Research Council. 1991. *Applications of the Mathematical Sciences to Materials Science.* Board on Mathematical Sciences. Washington, D.C.: National Academy Press. 36 pp.

2. See, for example, National Research Council, 1989, *Materials Science and Engineering for the 1990s*, Board on Physics and Astronomy, and National Materials Advisory Board, Washington, D.C.: National Academy Press.

3. Federal Coordinating Council for Science, Engineering and Technology. 1992. *Advanced Materials and Processing: The Fiscal Year 1993 Program.* Committee on Industry and Technology. Washington, D.C.: Office of Science and Technology Policy.

# CONTENTS

# 1

# SUMMARY AND OVERVIEW

Materials science is broadly concerned with the nature, properties, and use of materials. One materials science area of great significance is solid-state physics, which focuses on the physical properties of solid materials. It addresses such concerns as, for example, the properties that result from the distribution of electrons in metals, semiconductors, and insulators; oscillations in crystals; energy bounds; magnetic phenomena; dielectrics; ferromagnetics; and dislocations. Another materials science area of great importance is that of polymers, for which an additional concern about liquid flow arises. Whatever the context, be it solid, liquid, or some transitionary setting, materials science seeks an understanding of a material's macromolecular structure and properties by drawing on knowledge of its atomic and molecular constituents.

Until recently, the term "materials science" was used primarily to denote empirical study, fundamental research, synthesis, and production in metallurgy and ceramics. Today, the term is used in a broader context that involves interdisciplinary interactions among scientists, engineers, mathematicians, physicists, chemists, and biologists who are concerned with one or more of the four basic elements of modern materials science: properties, structure and composition, synthesis and processing, and performance (National Research Council, 1989). Traditional boundaries between disciplines sometimes needlessly constrain the development of unorthodox ideas and new theories. The National Science Foundation recognized this in establishing a number of interdisciplinary science and technology centers, many of which include several institutions and often several disciplines (National Science Foundation, 1993, 1992). In particular, materials science is today a vast and growing body of knowledge that is based on the physical sciences, engineering, and mathematics but is not obliged to conform to their limits. Interdisciplinary studies encompass all classes of materials, including biomaterials and biomolecular materials, ceramics, composites, electronic materials, magnetic materials, metals, optical and photonic materials, polymers, and superconducting materials (Federal Coordinating Council for Science, Engineering and Technology, 1992). Physics, chemistry, mechanics, and other traditional disciplines are now viewed as an arsenal of complementary scientific approaches serving the common goal of increased knowledge about and understanding of all aspects of materials, from discovery and synthesis to products and uses.

The mathematical sciences, for comparison, originally were developed as an integral part of the physical sciences. Often the same individuals contributed to both areas of research. With the exponential growth of all these areas has come increased specialization such that, in particular, the mathematical sciences and materials sciences are separate disciplines with too little contact between them.

The basic objectives of materials science are the synthesis and manufacture of new materials, the modification of materials, and the understanding and prediction of materials properties and their evolution over time. In each of these areas, the disciplines mentioned above play a role. The mathematical sciences, as a common language for the quantitative description of processes and phenomena, have their own unique role. They provide a

unifying force, reveal underlying structure, offer an avenue for knowledge transfer among disciplines, and serve as the vehicle for computational modeling of the processes and phenomena. Both the mathematical and materials sciences have much to gain from each other. Modern mathematical methods can aid in solving significant problems in materials science, while problems in materials science can suggest fruitful areas for mathematical research. In the larger perspective, however (National Research Council, 1989), it is clear that the scientific vigor, technological strength, and economic health of the nation all argue in favor of universities, government, industry, and professional societies stimulating and facilitating new collaborations between mathematical scientists and materials scientists.

The committee's task was to prepare a broad survey that (1) identifies and describes areas where the mathematical sciences have significantly aided materials research, (2) identifies areas of mathematical research in which increased progress would accelerate materials research, (3) identifies obstacles, if any, to increased collaborative research, and (4) makes recommendations for facilitating this type of cross-disciplinary work, including how to attract students and young researchers to this area. Chapters 2 through 8 of this report address items (1) and (2). This chapter and Chapter 9 address item (3), and Chapter 9 addresses item (4). This report is written for both mathematical and materials science researchers with an interest in advancing research at this interface, for federal and state agency representatives interested in encouraging such collaborations, and for any persons wanting information on how such cross-disciplinary, collaborative efforts can be successfully accomplished.

Concerning obstacles, it should first be noted that despite existing impediments to interdisciplinary work in these areas, there are nonetheless many successful interactions and collaborations between materials scientists and mathematical scientists (some are referred to in the technical Chapters 2 through 8 that follow). However, those impediments do need to be recognized and addressed.

One obstacle to increased collaborative research between the mathematical sciences and materials science concerns the differences in education of researchers in the two disciplines. The education of materials scientists exposes them to varying amounts of mathematics, but it mainly involves classical mathematics and therefore little knowledge of modern mathematics, especially tools that might be beneficial for exploring problems in materials science. In their education, mathematical scientists rarely take physical science courses beyond the elementary undergraduate classical courses, and therefore they generally have little feeling for current research areas and the applications of their expertise to materials sciences. Another impediment is a large jargon barrier that exists between the two disciplines. Similar jargon barriers exist even among different subdisciplines of materials science (and subdisciplines of the mathematical sciences); continual efforts are needed to eliminate jargon as a barrier to interdisciplinary research. Some negative attitudes constitute another barrier and are perhaps best summarized by the comments of, on the one hand, the great mathematician G. H. Hardy, who expressed his pleasure that none of his work had practical applications and, on the other hand, the materials scientist who cautions his students that "too much rigor leads to rigor mortis." University departmental structures that often discourage mathematical research by materials scientists and materials-oriented research by mathematical scientists present another obstacle, as this (and other) cross-

disciplinary research is generally not rewarded in considerations of tenure, promotion, and salary. A minimal level of cross-discipline education couples with the large jargon barrier, some negative attitudes, and a lack of motivating rewards to inhibit cross-fertilization between the mathematical and materials sciences. Chapter 9 presents the committee's conclusions regarding the main obstacles to increased collaboration between the materials science and mathematical sciences communities. It then addresses item (4) with the committee's recommendations to universities, government, industry, and professional societies on how to enhance and further increase collaborative efforts between the two communities.

In making these recommendations, the committee was aware of serious difficulties that exist to developing cross-disciplinary work, difficulties that are not unique to materials science. Progress in cross-disciplinary research, as well as in research within a discipline, can come either incrementally or following breakthroughs. Breakthroughs are often the result of progress on prototype problems, examples being the Ising model of a ferromagnet (the inspiration for the renormalization group work cited in each of Chapters 3 through 6 and 8) or Edward Lorenz's chaos sequence ($x_{n+1} = ax_n - x_n^2$) that Mitchell Feigenbaum studied for his breakthrough on chaos (Lorenz, 1963, 1979, 1984; Feigenbaum, 1978, 1981). These prototype problems provide an excellent vehicle for cross-disciplinary communication and by their elegance and ability to challenge can attract excellent researchers. Areas where such breakthroughs could take place might include, for example, the long time scale behavior of protein folding or the transitions from microscale to mesoscale and from mesoscale to macroscale. Specific candidates for such problems probably already exist, but this committee is not aware of prototypes that have been truly simplified to an irreducible essence.

Therefore, the committee's recommendations focus on enabling incremental advances in cross-disciplinary research that involves mathematical sciences applied to materials science. Some of the main obstacles to cross-disciplinary efforts, such as the reward system, have been and are being addressed in a number of other reports (for example, Joint Policy Board for Mathematics, 1994; National Research Council, 1993, 1991c, 1990, 1989; Boyer, 1990; Sigma Xi, 1988; and Institute for Mathematical Statistics, 1988). The committee attempted to go beyond those general difficulties and offer specific suggestions in its recommendations.

The mathematical challenges in materials science vary with length scale, time scale, and temperature regime (Pantelides, 1992; Baskes et al., 1992). For example, quantum mechanics is the discipline that governs processes and phenomena at the most microscopic level where electronic effects are important. Continuum mechanics and thermodynamics govern macroscopic deformations. Statistical mechanics is one area that connects the microscopic with the macroscopic regime. The basic laws of these disciplines have very different mathematical structures and pose distinct challenges. In each case, the classical mathematical areas such as geometry, differential and integral calculus, and statistics play distinct and mutually reinforcing roles. These different ways of viewing materials science, as well as the breadth and the scope of the modern field, can lead to different ways of breaking up the subject into categories so as to address items (1) and (2). For example, although there are not, say, ten "outstanding problems" in materials science for mathematical scientists, one can identify ten areas with great promise for mathematical applications to

materials science: block copolymers, dynamic fracture, effective moduli of composites, grain boundaries, grain growth, martensite and shape-memory materials, mushy regions, processing of semiconductor chips, stokesian dynamics for complex fluids, and superconductivity. As a basic framework for description, the committee's choice of general categories of focus or themes became the titles of this report's Chapters 2 through 8. This organization of subjects by themes is in contrast to the committee's phase-one survey (National Research Council, 1991a), which was organized around various classes or applications of materials (such as ceramics, electronic and semiconductor materials, polymers, and so on). Extensive cross-referencing has been provided between subjects or chapters when the same or a related topic is discussed elsewhere in this report. Subjects within chapters were chosen for illustration; the lists of subjects are not meant to be comprehensive. Further, the descriptions of those subjects and associated mathematical research opportunities present only a part of the much more wide-ranging totality (for example, cf. Langer, 1992; National Research Council, 1991c, 1989; Psaras and Langford, 1987). In the same way, the references given are intended to help the reader search further into the literature, with no attempt made to be complete. What appears in this report reflects the committee members' expertise and knowledge, that of the cross-section of individuals (see appendix) who were kind enough to provide information to the committee, and the project limits on time and funding.

The committee hopes that this report will help encourage research in the mathematical sciences that complements vital research in materials science, will generally raise awareness of the value of quantitative methods in materials science, and will spur researchers to explore the interface between the mathematical sciences and materials science. The committee also wishes to repeat the perspective expressed in its previous short report on the subject (National Research Council, 1991a): cross-disciplinary collaborations require long-term commitments.

# 2

# ATOMIC SCALE

The properties of all materials ultimately depend on their component atoms. Thus, a fundamental goal of theoretical work in materials science is the description of properties of bulk materials based only on the properties of and interactions between their constituent atoms and molecules. During the last 40 years, tremendous progress has been made toward this goal of understanding and predicting material properties from such a microscopic viewpoint. Research of this nature falls into several broad categories as follows:

- Crystalline materials are characterized by having all the constituent atoms arranged about fixed positions in a periodic lattice. Thus, given the known atomic arrangements, as obtained, say, from x-ray diffraction experiments, theory seeks both to predict and to explain experimental observations concerning the electronic, optical, magnetic, transport, and other properties of these crystalline materials.
- While a number of other materials have their constituent atoms and molecules arranged about fixed positions, these positions are not known in advance and are the desired objects of theory. Such systems involve surfaces of materials, where the surface atoms often rearrange themselves from the bulk configurations, defects in materials (such as dopants in semiconductors), where the host atoms generally alter their arrangement in response to the guest, and folded proteins, where the molecule is found in a complicated equilibrium globular structure that is related to its biological activity. Theories of these materials must first be capable of determining the equilibrium arrangements of atoms before researchers can study a host of other properties of these materials. Liquids and glasses, on the other hand, have more complicated arrangements of the constituent atoms and molecules. Liquids owe their fluidity to the fact that the constituent atoms are not centered about fixed positions but are slowly able to diffuse through the whole system. Thus, theories of liquids seek to determine the statistical properties of the equilibrium atomic and molecular configurations.
- Many systems are not in thermal equilibrium, and the object of theory becomes a desire to calculate the dynamical evolution of a nonequilibrium assembly of atoms and molecules.

The ultimate theory in all three cases would proceed completely from first principles, using quantum mechanics to describe electrons, spins, and nuclear motions. This has been the object of solid-state physics theories for crystalline materials, where the nuclei undergo only small-amplitude vibrations about equilibrium positions. However, when the nuclei are permitted to move over more substantial distances, such as in the examples described in 2 above, it is often adequate to treat the nuclear motion in terms of classical equations of motion, with the forces between atoms and molecules calculated using quantum mechanics or, when unavailable, from empirical potential functions. The latter is the realm of conventional molecular dynamics (Abraham, 1986), which has been applied to a wide variety of systems, including surface reconstruction, liquid and glass structures and dynamics, and others. In many other systems, the interatomic forces depend too intimately on nuclear

positions, necessitating the simultaneous use of quantum mechanics to compute intermolecular forces and classical mechanics to compute the nuclear motions (Car and Parrinello, 1985).

The quantum mechanical description of a bulk material is given by the Schrödinger equation, which is a partial differential equation (PDE) involving on the order of $10^{23}$ degrees of freedom. Cohesive energies, of solids, for instance, are obtained from differences in eigenvalues of this equation for the solid and the separated atoms, but the accuracy of solution required is enormous because this cohesive energy represents only on the order of 10-4 of the total eigenvalue. Thus, mathematical approximations are necessary, and this has led to the development of a wide variety of methods, including model Schrödinger equations that contain within them a set of empirical interactions, pseudopotential methods that likewise rely on empirical information or (more recently) on accurate quantum mechanical calculations for atomic systems upon which curves/surfaces are fitted, and the nonempirical density functional and ab initio quantum mechanical methods.

Density functional theory (Hohenberg and Kohn, 1964; Kohn and Sham, 1965; Callaway and March, 1984; see also Interfaces in Polymer Systems in Chapter 3) provides a framework for the calculation of the electronic structure and total energy of any solid-state or molecular system. However, the underlying Hohenberg-Kohn theorem only proves the existence of the density functional, but does not describe its exact form. Thus, various approximate and heuristic density functionals are used in practice. Rather little has been done to compute these density functionals from first principles theory (Levy, 1991; Freed and Levy, 1982), and mathematical assistance would be welcomed (see Chapters 3 and 8) in proving theorems concerning properties of density functionals (Levy, 1991) and in developing new approximation schemes as means for systematically improving available and perforce approximate density functional methods.

When the atomic positions are assumed known, density functional methods reduce the quantum mechanical description to a nonlinear integrodifferential eigenvalue problem for an effective single-particle Hamiltonian operator whose potential energy depends on the operator's own eigenfunctions. The problem is usually solved iteratively until self-consistency is achieved between the eigenfunctions and the potential energy. The development of fast Fourier transform methods has been a key mathematical contribution to improving the efficiency of this process. The effective single-particle Hamiltonian operator's eigenvalues are identified with the electron energy levels and the eigenfunctions with the electron wave functions. The eigenfunctions and eigenvalues are then used to calculate densities of states, optical spectra, carrier life times, and so forth. Most implementations of density functional methods employ what is called the local-density approximation to incorporate exchange and correlation in the effective single-particle potential energy. In recent years, a number of methods, including quantum Monte Carlo approaches (Zhu and Louie, 1991), have been developed to go beyond this approximation, resulting in significant improvement in the calculated electron energy levels. There is growing use of electronic structure calculations based on approximate solution of the Schrödinger equation for a cluster of atoms (see Chapter 8). The main theoretical problem here lies in extrapolating solutions for small clusters to the bulk or in extracting parameters for model Hamiltonian treatments of, for instance, high-temperature superconductivity.

Density functional theory also yields the self-consistent ground-state electron density and the total energy. A calculation of the total energy as a function of small deviations from perfect crystallinity enables the computation of the vibrational spectra (phonons) of the solid. When the lowest-energy atomic arrangement is unknown in advance and is to be calculated, computation of the electronic energy for this configuration of the atoms enables determination of the total forces on each atom in the system. These forces are then used to calculate the configuration of minimum energy either by employing energy-minimization techniques or by seeking a configuration in which forces on all atoms vanish. Earlier approaches involved the repeated solution of the self-consistent electronic eigenvalue problem for each atomic arrangement encountered in the energy minimization process. Recently, a number of techniques have been developed in which the electronic and nuclear degrees of freedom are treated simultaneously (Car and Parrinello, 1985; Payne et al., 1986, 1992). These techniques have resulted in vast improvements in efficiency for the computation of both equilibrium configurations and dynamics. Other advances enable the treatment of complex materials (Ellis et al., 1990) and consider the use of alternate quantum mechanical descriptions from ab initio quantum computations or ab initio pseudopotential methods.

For perfect periodic crystals, the size of the problem is determined by the number of atoms in the primitive unit cell. When periodicity is broken by the presence of surfaces, interfaces, and defects, the problem becomes mathematically more complex. A number of methods have been developed to handle this reduced symmetry. Some methods are based on scattering theory or Green's functions (Appelbaum et al., 1975; Baraff and Schlüter, 1978; Bernholc et al., 1978). With the advent of very powerful computers, however, these techniques have lost ground to a simpler approach based on supercells. For example, a large cell containing a point defect is repeated periodically. The cells must be large enough so that interactions between defects in neighboring cells are insignificant. Similarly, studies of surface properties or of interfaces use periodically repeated slabs. Solutions are typically constructed by expanding the eigenfunctions in terms of a basis set. A variety of basis sets have proven useful in different cases, but the power of modern computers favors the use of plane waves because the size of the basis set can be increased systematically until convergence is achieved (Ihm et al., 1979). The treatment of dynamical properties, such as conductivity, is generally carried out with semiempirical Hamiltonians, for example, a tight-binding Hamiltonian that is constructed with a localized basis set of atomic orbitals (Khan and Broughton, 1991). The Hamiltonian is defined in terms of its matrix elements, but there are major conceptual and mathematical problems associated with the theoretical determination of these Hamiltonian matrix elements; these offer research opportunities.

When material properties may adequately be computed by first averaging out the electrons, the difficult task still remains of constructing suitable interatomic potentials (Baskes et al., 1992; Smith and Srolovitz, 1992). Analytical expressions are typically assumed that incorporate pairwise interactions plus additional many-body terms, depending on the nature of the material. The parameters in the potentials are tuned to reproduce either experimental data (for example, lattice constants, elastic constants, and so on) or theoretical results calculated by first-principles techniques. Once constructed, the interatomic potentials are used to predict a variety of other equilibrium and dynamical properties of both the

materials whose properties are used to construct the potentials and other materials containing the same constituent atoms. Similar approaches are applied to the description of polymers, proteins, and glasses.

The construction of accurate and reliable interatomic potentials remains a pressing problem that can benefit from new mathematical sciences research. First-principles calculations provide an enormous database concerning the interaction potentials. However, the construction of computationally convenient interatomic potentials involves a many-parameter, highly nontrivial, nonlinear fitting problem.

Currently, the frontiers in atomic-scale theories concern the computation of equilibrium atomic configurations and the evolution of nonequilibrium configurations at nonzero temperatures. The former is usually carried out with direct energy minimization techniques or with Monte Carlo simulation methods (Hayes, 1993). The latter is carried out using molecular dynamics, which can be implemented with a first-principles Hamiltonian, a semiempirical tight-binding Hamiltonian, or with interatomic potentials. The method is in effect an implementation of statistical mechanics. In order to calculate the evolution of a system, externally controlled variables such as pressure or volume, temperature, and so on must be specified. Such specification defines a statistical mechanical ensemble, and the calculation simulates the evolution of a single member of the ensemble in terms of the "trajectories" of all the particle coordinates and momenta in phase space. Equilibrium properties are calculated as time integrals. In addition, elastic constants and linear transport coefficients are obtained using formulas derived from fluctuation theory. Finally, the detailed dynamical evolution allows one to unravel the atomistic mechanisms that underlie a variety of processes and phenomena. For example, studies have been made of dislocation formation and motion, plastic flow, grain boundary sliding and strengthening, crack propagation, tribological phenomena, chemical reactivity, and so forth (Landman et al., 1992; Stillinger and Weber, 1987).

The mathematical sciences have made valuable contributions to the developments described above, especially to the numerical implementations. Examples are fast Fourier transforms, multidimensional integration, curved-space description (Riemannian metric), solutions of nonlinear equations, nonlinear regression, conjugate-gradient methods, and eigenvalue methods for large or sparse matrices.

The main limiting factors in computational atomic-scale research today are the number of atoms that can be treated and the length of the simulation. Parallel computers are becoming an important ingredient in the impetus to study larger systems. The current limits are a few hundred atoms for first-principles calculations and several hundred million atoms for conventional molecular dynamics using interatomic potentials. In time scales, first-principles calculations are limited to picoseconds, whereas conventional molecular dynamics is limited to nanoseconds. Mathematical challenges lie in the development of algorithms to handle large numbers of atoms, in the analysis of instabilities that may arise in the governing equations, and in the development of general asymptotic methods to pass to larger scales.

The above does not exhaust interesting areas involving electronic structure and other atomic-scale theories for properties of materials. One other area is electron transport. In most cases, the classical Boltzmann transport equation is adequate, with the electrons (and

holes in the case of semiconductors) having the energy dispersions dictated by the material's quantum energy bands. Boltzmann's equation can be solved in various degrees of approximation. The drift-diffusion approximation has been the workhorse of the microelectronics industry in modeling devices (Cole et al., 1990). At the next level of sophistication, the hydrodynamic approximation, more accurate solutions are possible (Blotekjaer, 1970; Rudan and Odeh, 1986). Finally, exact solutions of the Boltzmann equation are possible by Monte Carlo techniques (Jacoboni and Reggiani, 1983; Fischetti and Laux, 1988, 1991). Mathematicians played key roles in many of these developments. Computer implementations of the Monte Carlo techniques are, however, extremely time consuming, calling for the development of more efficient algorithms (see Chapter 8 ).

Some currently available mathematical results may provide new inspiration to materials scientists if this well-known mathematics is brought to their attention. A recent example is the study of graphite-like carbon structure with negative Gaussian curvature (Mackay and Terrones, 1991). Construction of such structures depends on the mathematics of periodic minimal surfaces that was developed more than a century ago (Schwarz, 1890; Weierstrass, 1866). These minimal surfaces are also relevant to the study of microphase separation in block copolymer systems (see Chapter 3).

Strong electronic correlations play a dominant role in phenomena such as the metal-nonmetal transition and (probably) high-temperature superconductivity. Standard density functional theory in the local density approximation does not accommodate these strong correlations, and even ab initio quantum mechanical methods encounter difficulties when many electrons must be correlated. Typically, one has to construct a model theory that captures the essence of the strong correlations. Quite often, a model theory, though simple in appearance, may present significant mathematical challenges to obtaining practical solutions to specific problems. Performing direct numerical calculations for the many-body problem of strongly correlated electrons is another frontier. The main limitation is again on the number of electrons that can be accommodated. There are efforts to construct model Hamiltonians with reduced degrees of freedom by introducing a mapping from the true Hamiltonian (McMahan et al., 1990), but these efforts remain heuristic in nature. Some progress, however, is available for small-molecule systems (Freed, 1983, 1989). Further mathematically rigorous developments in this area would be very valuable.

Many workers have explored methods beyond density functional methods in order to describe quantum effects for systems in which material properties involve excited states, be they optical or high thermal excitations. Wiener path integral methods have been extensively used to model (Chandler and Wolynes, 1981; Berne and Thirumalai, 1986) the thermal properties of the solvated electron (Rossky and Schnitker, 1988), the role of quantized rotational and librational motion in liquid water (Kuharski and Rossky, 1985), superfluid transitions in liquid helium (Ceperley and Pollock, 1984), melting in rare-gas clusters (Doll et al., 1990), and the thermal behavior of both nuclei and electrons in sodium clusters (Hays and Hall, 1991; Hall and Prince, 1991; Hall, 1992). Simulated annealing techniques have enabled the computation of electronically excited potential surfaces in conjunction with molecular dynamics simulations of the nuclear motion. The first thermal simulations combining the full electronic Schrödinger equation and molecular dynamics involve simulations of both ground and electronically excited states of metal atoms solvated in rare-

gas clusters, and yield both structural and optical properties of clusters exhibiting isomerization and phase transitions (Tsoo et al., 1990, 1992; Estrin et al., 1992). Simulated annealing has been applied to the $Na_4$ cluster using a generalized valence bond electronic wavefunction, but only a 500-femtosecond test run has been reported so far (Hartke and Carter, 1992). Ab initio quantum electronic structure methods for simulations would benefit if mathematical scientists improved the computer algorithms or advanced current theory.

Atomic-scale theories have proved to be very valuable in elucidating the properties of all sorts of materials. Electronic structure calculations have been essential in understanding electronic, optical, and transport properties, including elastic constants, conductivities, magnetic properties, and many more. Molecular dynamics is an explanatory mechanism and contributes to determining structural and mechanical properties of complex materials. It should be borne in mind, however, that atomic-scale theories are limited to length scales of a maximum of a few hundred angstroms. Most properties of complex materials, however, are determined by their collective microstructure (grain boundaries, precipitates, inclusions, microvoids, and so on) where the length scale is measured in microns and beyond (Baskes et al., 1992; Pantelides, 1992). Similarly, time scales of atomic simulations are measured in picoseconds or nanoseconds, whereas many diffusive and slip phenomena that underlie plasticity and other processes occur over time scales of microseconds, milliseconds, and beyond. It is therefore necessary to develop theories relating results obtained on atomic scales to desired material properties on more macroscopic length and time scales. A wide-open frontier for new mathematical sciences research is that of building connecting links between materials science theories developed for different length scales.

# 3

# MACROMOLECULAR STRUCTURES

## INTRODUCTION

Polymers are substances composed of many simple molecules that are repeating structural units, called monomers. A single polymer molecule may consist of hundreds to a million monomers and may have a linear, branched, or network structure. Copolymers are polymers composed of two or more different types of monomers.

The complexity of polymer properties is directly related to the complexity of their microscopic structure, and associated with this is a complexity in the theoretical description of their behavior. An adequate description of many polymeric material properties awaits the development of suitable mathematical and statistical tools.

Polymer science is an interdisciplinary field involving the mathematical sciences, physics, chemistry, biology, and engineering. It is an area with a wide range of theoretical and experimental investigations. Polymer science has provided us with a diverse host of new materials, thereby enhancing technological advancement. Meanwhile, the theoretical description of the properties of these materials has involved the use of a wide range of mathematical sciences techniques, which are illustrated below through the use of several examples. References are selective rather than comprehensive.

Polymeric materials are usually shaped in the liquid state, either in the melt or in solution, followed by a solidification process. Typical liquid-state shaping operations include extrusion, injection molding, fiber drawing, and film blowing. The macromolecules orient as a result of the deformations during processing. The properties (mechanical, optical, and so forth) of the solidified object depend in part on the stress and orientation fields developed during processing and solidification, as well as on morphological features of the crystalline phase in semi-crystalline polymers, in addition to the chemical structure and molecular weight of the polymer. (Polyethylene, a high-molecular-weight analog of paraffin wax, is used both for grocery bags and for prosthetic implants.) The strength of an injection-molded part, for example, depends critically on the placement of the ports through which the molten polymer is introduced. Frequently a polymer must flow through tiny channels and surround small and delicate parts. Finally, flow during processing plays a major role in determining multiphase systems' morphological features, such as incompatible blends, block copolymers, and so on.

From the point of view of materials processing, the goal is to take information about the molecular structure and to use computer-aided design methods to predict the structural and stress state, hence the properties, of the solid shaped object. Such a process simulation requires solution of the continuum mass, momentum, and energy balances through all steps of the process, including solidification, as well as solution of molecular-level equations relating macroscopic quantities and structure. The momentum equation requires a relation (a constitutive equation) between the stress and the deformation. A state-of-the-art overview of process simulation can be found in a chapter of an encyclopedia (Denn, 1988), where monograph and textbook references are given.

The first section below on single-chain conformations addresses the case of individual polymers in solution or in interaction with confining surfaces. Many basic concepts of polymer science have arisen in the study of these single-and few-chain systems, and dilute solution experiments are still essential in characterizing the properties of the polymers, so that polymeric materials can be made reproducibly and theories of polymer properties can be tested against carefully controlled experiments. The next section considers protein properties and scientific questions relevant to applications in biotechnology that are associated with predicting the conformation, folding, and long-time dynamics of proteins.

Subsequent sections discuss the flow and equilibrium properties of polymers in the liquid state, the state from which many polymeric materials are fabricated by extrusion, molding, and so forth. Descriptions of the viscoelastic properties of molten polymers often rely on ad hoc phenomenological models. Although these display remarkable agreement with a wide range of experiments, a firm theoretical underpinning for these models is lacking. Mathematical issues arise from this viscoelasticity because the responses typically associated with viscous liquids and elastic solids are combined; the stress at any position depends on the entire deformation history of the material element located at that position. The formulation of viscoelastic constitutive equations that accurately portray material behavior remains a subject of research. Fundamental issues of existence, uniqueness, and qualitative behavior have not been adequately addressed. Computational schemes for flows in complex geometries often fail to converge under conditions of processing interest. Instabilities occur that are absent in low-molecular-weight liquids. Many of the issues discussed here have been reviewed previously (Denn, 1990).

Many theoretical and mathematical sciences issues are involved in the construction of and solutions to models of polymer fluids, which are being developed along three distinct lines. One of the oldest involves the use of an underlying lattice to greatly simplify the mathematics at some concomitant expense in representation of reality. Recent developments in polymer theory build on successes made over the past few decades in the theory of simple molecular fluids, especially in integral equations and density functional methods. Density functional methods are discussed in this chapter in relation to studies of interfaces in polymer systems, followed by a description of problems in block copolymers and in stiff polymers and liquid crystals, as well as mention of other areas; see also Chapter 8.

Problems in polymer science are almost as diverse as those of all of materials science, and are associated with issues of fracture, thermal stability, ageing, transport, adhesion, and so on. Polymers may be used as organic conductors and nonlinear optical materials. Some of the issues are addressed in other chapters in this report. The omission of specific areas is indicative merely of the limited nature of this report.

## SINGLE-CHAIN CONFORMATIONS

Very interesting mathematics arises naturally in the study of polymeric materials. The most basic model in this discipline is the Wiener path model of single polymer chains. This picture represents the shapes of polymer chains as being much like the dynamical trajectories swept out by particles undergoing Brownian motion. At the next level of study,

the self-interactions and mutual interactions between polymer chains are incorporated into the Wiener path construction, where constraints are added to the family of paths describing the polymers. A wide range of phase transitions are encountered in this generalization. Adsorption of polymers onto surfaces, the helix-coil transition, polymer collapse, protein folding, and phase separation of polymeric fluids are examples. Important areas of research are concerned with polymers at interfaces (Douglas et al., 1986a, b) and the dilute solution properties of polymers dissolved in small-molecule solvents (Douglas et al., 1990). Of particular interest is how the topological structure of the polymer is reflected in the bulk properties of polymer solutions. Polymers can be formed in ring shapes, stars, and combs and also in very irregularly branched structures. The properties of interest in characterizing these specialized polymeric fluids include the radius of gyration, hydrodynamic radius, intrinsic viscosity, and virial coefficients. The theoretical description of these different topological classes of interacting polymers relies on the renormalization group (RG) method (see Chapter 8). This nonrigorous mathematical method is closely related to Borel resummation and Euler transform methods for resummation of asymptotic series and allows practical and useful statements to be drawn from rather meager (but messy) perturbative calculations (Freed, 1987). While great success has been achieved in describing the equilibrium properties of dilute and semidilute polymer solutions (Freed, 1987), the dynamical RG theories are in a more primitive state. The convergence of RG expansions appears to be significantly poorer than in the equilibrium case, and dynamics in semidilute solutions are poorly understood. Major questions also remain in problems such as polymer collapse, where several interactions with different critical dimensionalities become important. Although a majority of polymer scientists consider theories of single-chain properties to be in good shape, serious conceptual and mathematical questions abound. Considering that theories of protein structure and dynamics, of molten polymer flow properties, of rubber elasticity and gel swelling, and of many more polymer phenomena have their conceptual underpinnings in single-chain models, further advances in many of these significant single-chain problems will reverberate through polymer science.

The case of a polymer interacting with a surface provides a good example for a study of the RG method from a purely mathematical sciences standpoint, since exact solutions are possible in this instance. Recently, the Wiener integral formulation of interacting polymers has been recast in terms of an equivalent integral equation formulation (Douglas, 1989a). The surface adsorption phase transition can be understood mathematically in terms of the Fredholm alternative, and the RG method can be interpreted naturally in terms of classical integral equation mathematical machinery. The integral equations describing the surface interacting polymers are fractional differential operators, where the order of the fractional differential operators is related to the Hausdorff dimension of the "local time" intersections of the polymer path with the interface. Recent work has involved treating polymers in the proximity of fractal surfaces, and this work is based in large part on rigorous results provided by mathematicians (Douglas, 1989b). Quite recently, the partition function of a polymer near a rough surface ("fractal") has been formulated in terms of renewal theory (Feller, 1971), and results the same as those obtained in heuristic calculations (Douglas, 1989a) are rigorously obtained as a corollary of Feller's theory of recurrent events and some established results of probabilistic potential theory (Hawkes, 1971; Taylor and Wenderl, 1966). This

nicely illustrates the application of ideas from probabilistic geometry to polymer science.

No discussion of polymer conformations would be complete without a brief mention of the rotational isomeric model, which represents the polymer as a discrete chain with fixed discrete values permitted for dihedral angles (Flory, 1969). This model is mathematically isomorphic to a one-dimensional Ising model, but chain conformational properties are represented in three-dimensional space. The model is, in principle, exactly solvable, and considerable ingenuity has been necessary to evaluate numerically the desired chain conformational properties. While it is possible to anticipate several useful applications of this model to describing properties of stiff and helical polymers, it does not appear that additional mathematical advances are necessary in treating the model.

Polymer solutions are routinely employed to separate proteins. Such processes lead to a consideration of the mutual interaction between polymers and particles of dissimilar shape (folded proteins, vesicles, viruses, and so on). Some consideration of the mathematics involved in describing these mutual interactions reveals a connection with the exterior Dirichlet problem (Spitzer, 1964; Kac, 1974). That work is not phrased in terms of polymer science language, but these calculations nonetheless have important practical applications to understanding the stability of suspensions in the presence of dissolved polymers. There is also a need for studies of capacities associated with stable random processes in this connection. Efficient means of calculating the capacity and other shape functionals (Schiffer, 1954; torsional rigidity, fundamental frequency of drums) are needed for general shaped bodies. Another application (Hubbard and Douglas, 1993) relates the friction coefficient of an arbitrary shaped body undergoing Brownian motion to the electrostatic capacity of that body. The "intrinsic viscosity" is another "shape functional" that very badly needs further study. Mathematically this problem is related to determining the polarization of that body (Schiffer and Szego, 1949). Interesting mathematical problems arise in the solution of the interior and exterior Dirichlet problems when the boundary is a "fractal" such as a random walk shaped polymer coil, an irregular (non-differentiable) surface, or a diffuse aggregate. Other "random" polymer problems are associated with the description of random copolymer or controlled sequences of several monomers (see also Maddox, 1993). Random copolymers are of considerable commercial importance, while proteins may be viewed as examples of how controlled monomer sequences can yield diverse and specialized materials.

A potentially very fruitful area of work is concerned with random surfaces, polymers of sheetlike connectivity. These mathematical objects are important in solid-state physics, biology, and high-energy physics and offer great promise in synthetic polymer applications (Abraham and Nelson, 1990). However, very little has been done to extend the multidimensional time generalizations of Brownian motion to describe these sheetlike polymers (Yoder, 1975). This mathematical sciences area, which is rather mature but is largely unknown to physicists and material scientists, provides a tremendous opportunity for applications of the mathematical sciences to practical materials science problems.

In summary, there are not only many opportunities for the practical applications of the mathematical sciences to questions arising in treating the properties of single-chain polymers, but there are also many new mathematical and statistical questions that are naturally posed in describing these physical systems and that lie at the frontier of available mathematics and statistics. There are mutual benefits to be gained for the mathematical

sciences and materials science communities through serious involvement of mathematicians and statisticians in this field.

## MODELING PROTEIN STRUCTURE AND DYNAMICS

Proteins, which are composed of 20 naturally occurring amino acids, provide a special class of linear polymers. Nineteen of these 20 amino acids have a definite "handedness"; that is, they are not equivalent to their mirror images. The specific sequence of amino acid monomers along the protein backbone controls the manner in which that specific molecule prefers to "fold" into a compact three-dimensional shape, and the folded shape is intimately connected with the biological task discharged by the protein. Point mutations (genetic changes of amino acid species at one location along the protein backbone) occasionally have little effect on folding pattern and biological activity; often they have disastrous effects that halt biological activity and prove fatal to the host organism. "The second half of the genetic code," as Sir Francis Crick has stressed, requires understanding precisely how the amino acid sequence determines folded structure; it is still largely an open problem (Gierasch and King, 1990; Chan and Dill, 1993; National Research Council, 1994) but obviously has major consequences for the management of genetic diseases and for aspects of biotechnology.

The protein folding problem suggests several potentially useful roles for mathematical sciences activity. The first keys on the nonlinear optimization character of folding: in most cases the biologically active folded form of a protein corresponds to the global minimum of a sequence-dependent potential energy function; see Chapter 8; also Berg (1993). Because of the flexibility of the protein molecule, the optimization typically involves $10^3$ to $10^5$ variables and a huge number of local minima, perhaps of the order of $10^{1000}$ (Chan and Dill, 1991a, b). Principles of chemical structure and bonding provide strong constraints on folding possibilities, and so specially designed search algorithms are likely to be advantageous.

Folded structures are now experimentally known for several hundred proteins. Attempts to infer general principles of folding from this database (comprising a very small fraction of all proteins) have been only very modestly successful. Consequently, theoretical modeling takes on an enhanced importance. Simplified protein models have included both lattice models (Bryngelson and Wolynes, 1990) and continuum versions and have permitted extensive computer simulations. But the problem is still largely an open one that would benefit from innovative mathematical and statistical insight. Very little is yet known concerning the collapsed state of ordinary polymers, and work in this, perhaps simpler, area should have an impact on our understanding of globular proteins.

It should be mentioned in passing that neural networks (Sasai and Wolynes, 1990) have been applied to the protein folding problem, but so far only with modest success. However, the universes of neural network architectures and of representations of the proteins remain largely unexplored and can likely be strongly improved.

Computer packages, selling for on the order of $100,000, are being used by pharmaceutical and chemical companies in attempts to screen potential drugs before synthesis of the most likely candidates. The protein structure packages are mostly concerned with finding the equilibrium (lowest-energy) configuration of a protein molecule with

thousands of atoms that interact through a complicated set of empirical potential functions. This process involves a huge multidimensional optimization process with many local minima. The sizes of systems considered are limited partly by the efficiency of algorithms for these minimizations. While many computations ignore solvent molecules, an accurate representation requires their inclusion, thereby enormously increasing the number of atoms to be considered and hence the dimensionality of the space in which the optimization is performed; for instance, see Boehncke et al. (1991) and references therein. Advanced optimization schemes will immediately be utilized by the package purveyors. The presence of charged groups in proteins leads to complexities in the computation of electrostatic forces and energies (Harvey, 1989; Schaefer and Froemmel, 1990). Additional advances with protein structure modeling require improvements in the empirical potential functions, especially in describing the influence of the aqueous solvent. One desired approach involves quantum mechanical treatment of the forces within a small region, with empirical force fields used only for interactions with more distant atoms. However, any successful implementation of such a scheme would greatly increase the computational labor, and so the generation of highly efficient algorithms and massively parallel computational schemes becomes a prime necessity.

Some approaches perceive the folding process to be a dynamical event, so that an understanding of protein folding can be obtained only by recourse to theories of the dynamics of proteins in the cellular environment. If protein folding proceeds with the aid of chaperone molecules (Angier, 1992), the complexity of the theoretical description increases significantly because of the requirement to treat the protein, the chaperone, the solvent, and their mutual interactions. Nevertheless, the theoretical and computational challenges are rather similar to those posed by a description of the unassisted protein folding that is discussed here. Thus, an important emerging area of study involves the description of protein dynamics (McCammon and Harvey, 1989). Studies of protein dynamics resort to the use either of simplifying models (Bryngelson and Wolynes, 1990; Sasai and Wolynes, 1990) or of complicated realistic molecular potential functions. Simplified models sacrifice many protein-specific details in order to provide understanding of generic properties of protein dynamics, whereas the potential functions are so complicated and computationally expensive that their use is limited to following the dynamics of rather simple proteins for rather short times. However, many facets of protein dynamics are specific to sequence and structure and occur on time scales that are long compared to those accessible from molecular dynamics simulations. Thus, there is a need for developing new theoretical concepts and methods to enable the treatment of long-time protein dynamics using the most realistic available molecular potential functions (Karplus and McCammon, 1983). By long-time dynamics is meant molecular dynamics calculations involving time scales much longer than current computational facilities allow.

Even if molecular dynamics computations could follow the individual atom (or group) dynamics of a large aqueous protein over long time scales, the amount of information gathered staggers the imagination. This presents us with the classic statistical mechanical problem of having vastly too much information and of needing some reduced description with suitable accuracy (Mori, 1965; Zwanzig, 1961). However, any such theory must be thoroughly tested, and this requires the performance of long-time molecular dynamics

calculations for suitable, nontrivial test cases. Such a process has recently been begun (Hu et al., 1991) for a six-amino-acid fragment of the ACTH protein in 945 water molecules; experimental data on this system are available for fluorescent depolarization of the tryptophan emission (Chen et al., 1987). However, simulation with a Cray-optimized program (not commercially available) generates 4.3 ps of trajectory in 1 hour of Cray-YMP time, while the experimental correlation time is 250 ps. Hence, simulations of a single trajectory for 1 nsec require about 10 days of Cray-YMP time, but this pales in comparison with the times of roughly 23 Cray-YMP years required for a comparable simulation of the whole ACTH protein with only 39 amino acids. Thus, the severe limitations on molecular dynamics simulations of protein dynamics and the need for reduced descriptions immediately become evident.

Apart from the use of realistic molecular potentials, such as those provided by CHARM23 (Karplus and McCammon, 1983), another useful goal is to develop a reduced theory that requires as inputs only equilibrium information and friction coefficients (Hu et al., 1991). The former is to come from computer simulations, while the latter comes from experimental data or simple models. Thus, once the necessary theory has been developed and has passed all the stringent tests, efficient methods will need to be devised for "clever" Monte Carlo simulations (see Chapter 8) to obtain requisite equilibrium information.

Initial efforts at developing a reduced theory of long-time peptide dynamics (Hu et al., 1990, 1991) begin by decoupling the solvent motion by use of a hydrodynamic model for the solvent. Thus, the influence of solvent enters through the use of friction coefficients for individual residues or groups of atoms, depending on the model used. In effect, the dynamical equations follow from a formalism in which the memory functions are neglected. The "relevant" variables are chosen as bond vectors for flexible portions of the protein and ones sufficient to specify the orientation of aromatic groups. Given these choices, the general principles of statistical mechanics dictate the appropriate dynamical Langevin equations governing the protein dynamics (Hu et al., 1990, 1991). The theory specifies the required equilibrium input information, and the dynamical equations are numerically integrated to solve for the orientational correlation functions. However, as described above, very long simulations are required to check the theoretical predictions for these correlation functions (see Chapter 8).

The following three limitations on the current theory will require further testing and theoretical justification:

1. The use of a hydrodynamic model for solvent motion,
2. The use of a limited set of "relevant" variables, and
3. The neglect of memory functions.

Limitation 1 is not expected to be important for longer-time dynamics, but improved models are necessary for group friction coefficients (Pastor and Karplus, 1988; Venable and Pastor, 1988). The all-bond model used suffices, but further reduction in the number of "relevant" variables is desirable in order to treat larger protein systems. Limitation 3 is more severe, and it will be necessary to develop a theory of the memory functions that adequately describes the influence of local conformational transitions and that likewise uses only input

equilibrium information (Perico et al., 1993). Benchmark molecular dynamics calculations and further formal theory will be useful in developing adequate descriptions of memory functions. It should be noted that the theoretical and conceptual problems associated with constructing a reduced theory of long-time protein dynamics are also important in studies concerning the local dynamics of polymers, a subject of relevance to understanding mechanical and dielectric loss properties of polymers and undoubtedly similar phenomena in biological materials; for example, see Travis (1993) and Nanavati and Fernandez (1993). Thus, useful insights can come from cross fertilization between the polymer and protein dynamics areas.

Of interest in the theoretical modeling of biopolymers (polymeric substances formed in a biological system), the above description represents a microcosm of the mathematical sciences research opportunities present in other areas of polymer science (cf., for example, Maddox, 1993). Enormous progress has been made in materials science as a result of computer simulations. It is, however, particularly difficult to simulate polymer systems, because, as is illustrated above, many important properties are associated with the molecules being large and the associated time scales being long. However, the molecules do have a smaller-scale structure with associated shorter time processes, and it is these processes that set the scale for numerical trajectory integration. What is needed is a way to overcome this problem with better integration techniques (perhaps with parallel processors) or with better approximation schemes that jump over the short time scale (such as is done with stiff differential equations). The example given for protein dynamics provides a description of one attempt at developing better approximation schemes, while the modeling of entangled polymer systems is still beset with enormous computational difficulties.

## ENTANGLEMENTS, REPTATION, AND ELASTICITY

The flow properties of polymers are quite different from those of small-molecule systems. An understanding of these flow properties, the viscoelasticity of high-polymer liquids, is essential to the design of many technologically important polymer-processing operations in which molten polymers are forced through dies or into molds in order to control the shape and orientation of the product. The most coherent modeling thus far is of flow in viscoelastic liquids, and that setting is what this section mainly considers.

### Constitutive Equations

Constitutive equations, which relate the local stress and conformational state to the deformation history and flow, are the focus of the field of rheology. Major journals in this field include the *Journal of Rheology*, *Rheologica Acta*, and the *Journal of Non-Newtonian Fluid Mechanics*, as well as the proceedings of the quadrennial International Congress of Rheology. General introductions can be found in the texts; for example, see Larson (1988) and Bird et al. (1987a); also, see Bird (1987) for a summary of some mathematical successes. The development of constitutive equations has followed two parallel routes, one based on

general principles of continuum mechanics and one based on kinetic theory and molecular models. The former leads either to integral models, in which the dependence of the stress on the deformation history is expressed in terms of one or several integrals, or to differential models, where the stress and velocity gradients are coupled through a set of differential equations. The formalism is well understood. Coupling with the momentum equation thus leads to complicated sets of highly nonlinear differential or integrodifferential equations. Incorporation of energetics, which is essential in the analysis of polymer-processing flows, requires consideration of the temperature history in the constitutive equation as well.

Molecular approaches usually model the polymer molecule as a mechanical object, for example, a sequence of springs (simulating the entropic elasticity of "flexible" chains, which admit many conformations), rigid rods, and so on (see Chapter 8). The physical model is completed by specifying the way in which a polymer molecule interacts with the surrounding medium, both through thermodynamic potentials (which might induce a transition to a liquid crystalline phase, for example) and dynamically. The primary dynamical interactions are friction and topological constraints. The polymer molecules in these systems are intertwined, and the resulting geometrical relationship between the molecules acts as a constraint (called "entanglements") on their motions. From a topological point of view the fact that the molecules can be "disentangled" means that they are not truly entangled. This makes it very difficult to characterize the process mathematically. No microscopic treatment of entanglements in polymer systems has been possible because a complete statistical mechanical treatment requires imposition of the topological constraints introduced by the entanglements; this is something that may benefit from the emerging theory of knots (Delbruck, 1962; Korsaris and Muthukumar, 1991; Jones, 1985; Thirumalai, 1992). The result is a reliance on a phenomenological description and the construction of idealized simple models (Doi and Edwards, 1986; Bird et al., 1987b), picturing the molecules as being effectively confined within a tube so that their primary mode of motion involves moving along the tube, a motion called reptation (de Gennes, 1979). Hence, the many-chain problem is reduced to that of a single chain in a postulated mean field. The theories do not really explain the nature of entanglements and how they arise.

While these phenomenological models are extremely successful in explaining and predicting a wide variety of nontrivial aspects of the nonlinear viscoelasticity of high-polymer liquids, there are several severe limitations (Lodge et al., 1990): "The main weaknesses of reptation and reptation-based models are three. First, the reptation hypothesis is just that, and has no real justification in molecular theory. Second, reptation assumes the phenomena of entanglement, and therefore offers little insight into what entanglements are, or under what molecular conditions they become effective. The description of entanglements in polymer systems may benefit from theories of knots or from topological field theories (Birmingham et al., 1991; Kholodenko, 1989). Third, as a single-chain-in-a-mean-field postulate, it is difficult to begin with reptation and build in the effects of many-chain interactions in anything but an arbitrary fashion, no matter how plausibly it may be done." Much remains to be accomplished in developing a molecular theory for the dynamics and viscoelastic properties of high polymer liquids. A molecular theory must contend with the problem's cooperative many-chain nature and thereby quantitatively describe entanglements and their influence on the polymer motion. Reptation-like or alternative models must

emerge as a self-consistent approximation, with a mechanism available for delineating the limitations of the models and for incorporating corrections and superior models in a systematic fashion. Mathematical scientists' assistance is desired for this nontrivial, highly complicated, technologically important problem.

The entanglement problem runs considerably deeper. Rubbery materials exhibit their elastic properties because each molecule in them is attached to other molecules, with the whole forming a network. These connections prevent certain relaxations of the molecules when they are stretched. Descriptions of this source for rubber elasticity have been available for a long time, but again they are based on phenomenological single chain type models. The presence in the network of crosslinks between polymer molecules makes it possible for true topological entanglement (knotting) to occur. However, predicting the manner in which entanglements contribute to rubber elasticity is still a distant, important goal, and polymer elasticity theory for gel swelling is far from satisfactory.

### Existence, Well-Posedness

The solution of boundary value problems for the flow of viscoelastic liquids in complex geometries has been exceedingly difficult in the strongly nonlinear regime. Numerical issues are addressed subsequently. Some investigators believe that the inability to obtain solutions in regions of processing interest is a consequence of problem formulation through inappropriate constitutive equations. Only in the past 15 years have fundamental analytical questions of existence, uniqueness, and qualitative behavior of solutions been addressed in a systematic manner. A summary of progress in this area, up to roughly 1987, has appeared (Renardy et al., 1987).

Existence results for initial value problems generally fall into two categories. First, there are results on local time existence, and second, there are results on global time existence and asymptotic stability for small perturbations of the rest state. There are now numerous results of both types for differential as well as integral constitutive models, and there are also some recent results on kinetic theory models. A far more difficult question is whether solutions exist globally in time for large data. For one thing, this depends on the type of the equations. Some constitutive equations are hyperbolic, and when coupled with the momentum equation the system can change type within the flow field (Joseph, 1990; Luskin, 1984). Problems with change of type are very difficult, and few rigorous mathematical results of a general nature are known, even in the simpler situation of gas dynamics (see Chapter 3). Equations of hyperbolic type do not have globally smooth solutions due to shock formation. Viscosity terms or singular memory functions can preclude shock formation. Under suitable hypotheses, there are some global existence results for such models in one-dimensional problems.

It has been shown that many constitutive models admit Hadamard instabilities in certain flows. Even models that are well posed for smooth solutions could become ill posed in discretized versions that step into forbidden regions of stress.

Rigorous mathematical existence theorems have been developed for flows that perturb a state of rest or uniform flow. Both differential and integral models have been

investigated. There are no global existence results such as are known for the Navier-Stokes equations, and there is even reason to think that such results may not hold.

An interesting question emerges in problems with inflow and outflow boundaries, which may arise from the truncation of the flow domain for numerical purposes. The memory of the fluid manifests itself in the need for prescribing boundary conditions at the inflow boundary, in addition to the ones needed in the Newtonian case. For differential constitutive models, some sets of inflow conditions leading to well-posed problems have been identified, but a characterization of all admissible inflow conditions is but a distant vision.

### Numerical Methods and Singularities

Numerical simulation of non-Newtonian flow is a flourishing area of research, with frequent international workshops. The field has been surveyed (Keunings, 1989), and more recent papers, including refereed workshop proceedings, are published regularly in the *Journal of Non-Newtonian Fluid Mechanics*. A convergence problem known as the High Weissenberg Number Problem still limits many calculations to flow regimes that are uninteresting from the point of view of materials processing. The nature of the problem is understood: large-stress boundary layers, which occur for many viscoelastic constitutive equations near corners and stagnation points, are too sharp to be resolved by usual finite-element and finite-difference techniques, and the resulting errors contaminate the solutions. The cause of the problem is not understood, however. Some investigators believe the problem is one of numerical resolution of large-stress gradients, and have emphasized construction of new algorithms—special finite-element techniques, for example. Others believe the cause is associated with the formulation and question whether integrable solutions to the stresses (that is, finite forces) even exist for the constitutive equations in common use.

The velocity and stress field in the neighborhood of a corner is a fully solved problem for a Newtonian fluid, where the stress exhibits a power-law singularity and is integrable. The solution is unknown for all but the most trivial viscoelastic constitutive equations, but nonexistence of a power law is easily established in a number of cases of interest. Solution of the corner singularity for elementary viscoelastic fluids would be a major advance, since it would establish whether the predicted behavior near corners and in other boundary condition changes is physically sound, and it would provide the opportunity for construction of elements for numerical simulations that incorporate properties of the singularity.

There is some experimental evidence that the no-slip boundary condition (in which the fluid takes on the velocity of a solid boundary at the interface) commonly used for low-molecular-weight fluids breaks down for polymeric liquids in regions of high stress. This observation is discussed below in the context of extrusion instabilities. Wall slip would alleviate the stresses near a corner. From the perspective of micromechanical models of polymer solutions, singularities are an artifact of using too coarse grained a description of fluid rheology and boundary conditions. For example, all commonly used constitutive theories assume local homogeneity of the kinematics that lead to polymer deformation. Some recent theories (El-Kareh and Leal, 1989; Bhave et al., 1991) include the physics of

local nonhomogeneity and predict very local effects, such as stress-induced polymer migration, depletion near solid surfaces, and a macroscopic wall-slip coefficient. In one case, existence has been established by introduction of a reasonable but ad hoc physical assumption (El-Kareh and Leal, 1989). These effects may be extremely important for mitigating singular behavior, but the length scales are too small to allow direct simulation in complex flows with current methodologies.

A large part of the computational problem may be that there is little qualitative "feel" for the spatial and temporal structure of solutions under highly elastic conditions, hence little a priori guidance for optimal discretization, and so forth. Few analytical results exist for confined flows. An illustration of the type of intuition that is needed may be found in a boundary-layer theory for elastic liquids near stagnation points (Harlen et al., 1990), which followed from simulations of flow past a sphere showing highly stressed fluid emanating from the rear stagnation point and complementary experimental observations using birefringence.

### Sharkskin and Spurt Flow

Polymer extrusion operations are limited in throughput by one or more instabilities that produce a distorted surface on the extrudate. Overcoming this limitation is of major commercial importance, and considerable research has been carried out on the introduction of "flow modifiers" to extend the range of stable extrusion. Empirically, extrudate distortions occur beyond a critical die-wall stress, which for nearly all molten polymers is approximately 0.1 MPa. The general rule of thumb is that the critical stress is slightly greater than the shear modulus of the viscoelastic melt or concentrated solution. Similar extrudate distortions are observed in metal and paste extrusion; whether there is any mechanistic connection is unknown.

There are three well-defined regions of unstable extrusion for some melts, including polyethylene. Other polymers may not show the same range of behaviors; see the overviews in Petrie and Denn (1976), Denn (1990), and Larson (1992). The first onset is a high-frequency, small-amplitude surface distortion known as "sharkskin." This is followed at higher throughputs by "spurt," or "stick-slip" flow, where there are alternating regions of "sharkskinned" and relatively smooth extrudate and a discontinuity in the flow rate/pressure drop curve that is reminiscent of an ignition-extinction phenomenon. Finally, there is a transition to "wavy" or "gross melt fracture," in which the extrudate is grossly distorted.

Early attempts at analyzing extrudate instabilities used classical linear stability theory. Instability to infinitesimal disturbances could never be shown, and that line of investigation has generally been abandoned. The possibility that sharkskin may be a physical manifestation of a Hadamard instability arising from the real polymer constitutive equation has been suggested, as has a mechanism based on the propagation of shear discontinuities in a nonlinear material. Two lines of thought are receiving current attention.

Experimental reports that the onset of sharkskin can be delayed by changing the material of construction of the extrusion die and measurements of the inception of apparent wall slip at the onset of sharkskin have motivated theories and experiments based on the notion of adhesive failure between the polymer melt and the die at high stresses. Several

mutually exclusive theoretical formulations (which nevertheless arrive at similar analytical expressions) have been successful in capturing the observed phenomena, both the onset of the instability and the (average) measured slip velocities, including the effect of upstream pressure. This line of thinking (reviewed in Denn, 1992) suggests that progress in understanding extrusion instabilities will be made by pursuing concepts more commonly used in areas like adhesion and dynamic fracture. While it is possible to construct physical scenarios of chain response that could lead to oscillatory phenomena like those observed experimentally, dynamical interactions between the nonlinear field equations and the nonlinear slip boundary conditions have not been explored except in the simplest (linear) cases, where only steady solutions have been observed.

Another approach is based on the concept of a "constitutive" instability. Many constitutive models based on molecular concepts exhibit a nonmonotonic shear stress/shear rate curve, hence the breakdown of steady shear flow at a critical rate. In some cases there are two extrema, leading to a series of investigations dating to 1966 that suggest that the multivalued stress curve is the source of spurt flow. Recent studies have explored the dynamics of shear flow of fluids with non-monotonic flow curves, which result in well-posed initial and boundary value problems (for example, Malkus et al., 1991). Analysis and numerical simulations show that the system changes state in a thin layer near the wall, giving the appearance of a slip layer and showing spurt in pressure-driven flow and persistent oscillations in piston-driven flow. A singular perturbation formulation yields a one-parameter family of quadratic, planar dynamical systems having a rich structure.

## Flow Instabilities

Polymeric liquids are known to exhibit flow instabilities under conditions where the flow of Newtonian fluids would be stable, and in some cases these conditions correspond to the practical regime for processing or property measurement. Taylor-Couette instabilities can occur even in the absence of inertia, for example, and torsional shear flow (which is widely used in rheometry) shows a rich range of unstable behavior; see Petrie and Denn (1976) and Larson (1992) for general reviews. From the point of view of an analyst, one of the major challenges is the rigorous justification of the traditional techniques of studying stability and bifurcation. While the stability (linear and nonlinear) of the rest state has been studied extensively, there are few rigorous results on the far more interesting question of stability of other flows. The issues to be studied are whether linear stability is indeed determined by spectral properties, whether linear stability implies nonlinear stability for small disturbances, and whether the usual reduction procedures of bifurcation theory (for example, center manifolds) can be rigorously applied. Although these issues are well understood for Newtonian fluids, the proofs available in the literature do not extend to the equations governing viscoelastic fluids.

### Micromechanics

Computational and theoretical issues dealing with micromechanics are discussed in Chapter 8 of this report, but they should be mentioned briefly in the context of polymeric materials. There is obvious interest in attacking viscoelastic flow problems for particles in fluids directly at the microscopic level by solving the micromechanical equations together with those describing the motion; insofar as one is interested in materials that match the microscopic description, micromechanical models contain more information than continuum models. In addition to purely macroscopic variables, there is at least a statistical description of the microstructural state. Furthermore, microstructural simulation of extremely simplified flows shows chain behavior that can differ from the dynamics imbedded in continuum formulations (see, for example, Rallison and Hinch, 1988).

Relevant mathematical sciences issues do not seem to have been considered: (1) Given the equations that describe the microdynamics, what can be said about the general types of behavior (that is, the nature of solutions) that are possible? For example, if the motion is unsteady, for what class of motions does the microstructure exhibit globally attracting trajectories in orientation space? (2) How can the micromechanical model equations for nontrivial flow problems be efficiently solved? Consider, for example, a suspension of rodlike particles. Even if the problem of describing rod interactions is ignored and only noninteracting rods are considered, the exact problem solution not only requires the usual continuum velocity, pressure, and stress fields, but also requires keeping track of the statistical distribution of orientations for each material point. This yields a high-dimensional problem at each material point, coupled with a complex macroscopic problem. Can computationally reasonable schemes be developed to solve such problems, and especially can techniques suitable for massively parallel computing be developed? Can approximation schemes be developed for the full problem (which generally involves hierarchies of moment equations or something equivalent, but is bedeviled by closure problems in the approximation scheme)? What particle behaviors may be lost in such schemes?

## THEORY OF THE LIQUID STATE OF POLYMERS

One of the earliest and still widely used models for polymer systems is a lattice model in which the polymers are represented as mutually and self-avoiding random walks on a regular lattice. Each lattice site may be occupied by a monomer or a solvent molecule, or it may be vacant. A species-dependent energy $\boldsymbol{\varepsilon}_{ij}$ is assigned to all pairs of monomers and solvent molecules that occupy neighboring lattice sites. The partition function for the system is defined as the sum of the number of possible configurations for the system, as weighted by the Boltzmann factor $\exp(-\beta E)$, where $E$ is the total interaction energy for the configuration and $\beta$ is the inverse of the thermal energy.

The standard lattice model has led to the development of a variety of counting methods to enumerate approximately the huge number of possible configurations allowed to the system. Work in the 1940s (Flory, 1941, 1942, 1953; Huggins, 1941, 1942;

Guggenheim, 1944) proceeded by considering the probability that a neighboring site (bond) is vacant for placing a subsequent monomer (bonded pair of monomers) on the lattice. This probability, however, is evaluated by ignoring all correlations present in the system. While the theory has several notable successes and while Flory-Huggins theory is perhaps the most widely used theory in polymer science, there are many glaring deficiencies of these approximate theories and the standard lattice model upon which it is based.

Recent work has developed a Mayer-like cluster expansion of the partition function for this lattice model in which Flory-Huggins theory emerges as the zeroth order approximation (Freed and Bawendi, 1989; Dudowicz and Freed, 1991a). The theory proceeds as a double expansion in $z^{-1}$, the inverse of the lattice coordination number (effectively an expansion in $d^{-1}$, the inverse dimensionality of the system), and in a high-temperature expansion in powers of $b\varepsilon_{ij}$. The expansion introduces corrections to Flory-Huggins theory that arise from the presence of local packing and interaction-induced correlations in the system. The $d^{-1}$ expansion is clearly asymptotic at low-volume fractions of polymers (Nemirovsky et al., 1992b). Convergence improves at higher-volume fractions (Dudowicz et al., 1990), but nothing is known mathematically about the nature of the series in this case. The development of a low-temperature expansion for $B\varepsilon_{ij} > 1$ has to date been elusive. The dilute polymer $d^{-1}$ expansion has been performed to fifth order using exact counting methods, but the more general many-chain case has only been carried to second order based on analytical computations using a Mayer-like diagrammatic representation of the series expansion (Freed and Bawendi, 1989; Dudowicz and Freed, 1991a). Further computations will benefit from improved computer-assisted enumeration methods and symbolic mathematical packages. Such computer assistance will be necessary, for instance, to account for the fact that the different submonomer units generally have distinct group interaction energies $\varepsilon_{ij}$.

The cluster expansion method has been accompanied by an extension of the standard lattice model to permit monomers (and solvent molecules) to occupy several lattice sites (Freed and Bawendi, 1989; Nemirovsky et al., 1987). The method can thus more realistically describe the actual monomer chemical structures, and the fact that different monomers (and solvent molecules) have rather different sizes and shapes and cannot be placed on identical lattice sites. Computations to date with this extended lattice model have already explained a wide variety of puzzling experimental data and have predicted several novel phenomena (Dudowicz and Freed, 1991b, 1992a, c; Freed and Dudowicz, 1992; Nemirovsky et al., 1992a), such as re-entrant microphase separation in block copolymers and the pressure dependence of microphase separation. Further generalizations of the lattice model will require significant advances in the mathematical sciences, for instance, to account for the semiflexibility of polymers and to include the presence of rigid, extended units in the polymer. The former generalization is relevant to the study of polymer glasses, while the latter is important for treating liquid crystalline polymers.

Lattice models are known to suffer from inherent deficiencies because the excess free volume is represented by the presence of unoccupied lattice sites (voids) with equal volumes. Although the generalized lattice model assumes that the voids all have the volume of a lattice cell that is smaller than a monomer size, a more realistic description would have voids with an exponential distribution of volumes. The continuum limit of the generalized lattice

model and the relation of this limit to off-lattice theories of polymer systems are interesting issues.

One promising, more recent approach to describing the properties of polymers in the liquid state involves developing generalizations of successful theories for small-molecule fluids. Equilibrium microscopic statistical mechanical theories are being constructed for the conformation, structure, thermodynamic properties (for example, equation of state), and phase transitions of both bulk polymeric materials and inhomogeneous systems, such as polymers near a surface or interface and in confined spaces. The primary theoretical tools are liquid-state molecular integral equation methods, thermodynamic density functional theory, and Monte Carlo computer simulation (see Chapter 8).

The "integral equation" theories require solving coupled nonlinear integral equations of an unusual form (Hansen and McDonald, 1986) for atomic and small-molecule fluids. Efficient numerical algorithms have been developed over the past 25 years (Hansen and McDonald, 1986; Chandler, 1982). Certain types of approximation approaches ("closure") and simple polymer models provide existing algorithms that are adequate for polymers (Schweizer and Curro, 1990). However, many situations of interest involve mathematical difficulties that are significantly enhanced due primarily to two factors: (1) For a chemically realistic description of molecular structure (which is necessary for quantitative materials science applications) and/or multicomponent polymer mixtures, the number of coupled nonlinear equations for structural correlation becomes relatively large (Curro and Schweizer, 1987). Numerical solution using existing methods, such as Picard iteration, Newton-Raphson techniques, and so on, is very slow (even on powerful state-of-the-art workstations) and very sensitive to initial guesses and the "mixing of old and new solutions" (Yethiraj and Schweizer, 1992). (2) The problem becomes increasing difficult as the polymer molecules increase in size because of the enormous growth in the real space length scales over which numerical solutions to the equations must be found, length scales far beyond those considered previously with small-molecule fluid theory. This difficulty gets even worse as a phase transition (critical point) is approached (Hansen and McDonald, 1986). A phase transition greatly complicates the numerical determination of phase diagrams of polymer mixtures. The phase transition problem is particularly important in materials science, and existing iterative solution methods based on a specified grid size and fast Fourier transforms can become impractical or unreliable.

Given the above numerical difficulties, the ability to obtain even approximate analytic solutions would be extremely valuable. Unfortunately, rigorous analytic solution of the nonlinear integral equations is generally only possible for simple atomic fluids (Hansen and McDonald, 1986). However, analytic progress may be possible for more simplified models of polymer molecular structure (Schweizer and Curro, 1990), and a serious mathematical study of this problem would be of great interest.

Opportunities exist in the nonequilibrium area for generalizing and applying nonperturbative statistical dynamical methods that have been developed for simple atomic fluids (mode-mode-coupling theory; see Chapter 9 in Hansen and McDonald, 1986) to the complex problem of describing diffusional and viscoelastic properties of entangled polymer fluids (Schweizer, 1989). The challenge for the mathematical sciences is that a very large number of first-order coupled stochastic differential equations must be solved for the

effective dynamics of a polymer molecule in a dense liquid. In general, the differential equations involve nonlocal kernels ("memory functions") in both the time and spatial variables, and the stochastic "noise" is not "white" but correlated (often called "colored noise"). In order to obtain the physical predictions from such equations, it has been necessary to employ an oversimplified molecular model of the polymer. This allows a reduction of the coupled differential equations to a linear form that can then be solved via normal mode diagonalization methods. Although this scheme does represent a good first approximation for many "universal" dynamical questions of materials science interest, it has serious limitations with regard to the level of chemical realism that can be incorporated (and hence the range of time and spatial length scales that can be treated). For example, early-time "glassy" polymer dynamics cannot be reliably studied. For many materials-specific mechanical and transport properties, the appropriate stochastic differential equations are nonlinear, and new mathematical methods to handle such problems would be valuable.

## INTERFACES IN POLYMER SYSTEMS

Scientific and engineering studies of the dynamics or surface properties of macroscopic systems often require a knowledge of the interface—the boundary region—separating bulk phases. In many interesting situations, little is known about even the equilibrium or static characteristics of such interfaces, to say nothing of their dynamical properties. This motivates the development of mathematical and statistical theories and models that can provide even simple qualitative trends about interfacial properties. Such models can be treated using a formalism known as the theory of inhomogeneous liquids, which is derived from modern statistical mechanics. This theory provides information about the equilibrium (static) properties of matter but also has implications for theories of interfacial dynamics. The chain-like structure of polymer molecules distinguishes polymeric systems from those composed of small molecules and leads to a variety of novel characteristics of polymeric materials. Nevertheless, polymer and small-molecule systems do share certain basic features. Hence, theories of simple liquids and glasses often provide a point of departure for analysis of polymer systems. Modifications of small-molecule theories are then required to describe the chain connectivity, flexibility, and long-range correlations that are present in polymer systems. The properties of phase-separated systems and, in particular, properties of interfaces are one area that displays both the strong similarities between polymers and small molecules and the differences that are imparted by polymer structure. For these reasons, this section begins with general considerations of theories of interfacial properties before turning to the specific challenges posed by theories of polymer interfaces.

Density functional theory focuses on the behavior of distribution functions or probability densities in media (liquids or gases near surfaces, two-phase regions, periodic solids, and so forth) the properties of which vary in space (see Chapters 2 and 8). Of particular interest is the singlet probability distribution function, usually called the density, which gives the probability of observing a particle at a point in space. At equilibrium, this quantity does not depend on time, and variational principles exist for approximately

determining its functional form. This approach to elucidating the thermodynamics of inhomogeneous fluids is often called density functional theory.

The variational condition for the density functional enables theorists to derive integral equations for the density or to obtain more qualitative information through an algebraic minimization of some functional with respect to an approximate, parametrized density. With the exception of certain one-dimensional problems and the dilute, ideal gas limit in which interactions between atoms do not affect the thermodynamics, approximations must be made for the kernels appearing in the integral equations. Obtaining an accurate approximation for the kernels themselves generally requires as much effort as solving for the density, and so theorists normally assume some simple, approximate form for the kernels and use the resulting integral equation or variational condition to solve for the density. Unfortunately, little is understood about the way such approximations affect the predictions of theory, although approximate density functionals often provide reasonable results for a broad range of approximation schemes without any ostensible justification (Evans, 1979). Some researchers have questioned the true practicality of the entire density functional methodology (Lovett, 1988). While formal considerations indicate a unique solution to the exact equation, approximate equations may possess multiple solutions. Methods are necessary for determining which solutions are relevant and which may correspond to interesting metastable states. There are various other fundamental mathematical questions concerning density functional theory; see, for example, Lovett and Stillinger (1991).

From a formal mathematical point of view, density functional theory remains poorly understood though broadly used. The additional insight offered by trained mathematical researchers, capable of carefully studying the effects of approximations within the density functional theories, could have a profound effect on materials research. It is hoped that such investigations will (1) lead to an understanding of the stability of the methodology, (2) suggest classes of approximation schemes most likely to faithfully predict the behavior of particular models, (3) lead to new models of many-body systems, and (4) provide guidance to the solution of the integral equations that commonly occur in this field.

While the theory of atomic systems or models with spherically symmetric potentials has advanced rapidly during the past few decades (Evans, 1979), much work remains before an understanding of molecular systems is achieved. Molecular systems involve several (as for $CO_2$ or $N_2$) or many (as for polymers) atoms covalently bonded together to form complicated geometrical objects that often frustrate theories primarily designed to treat the atomic case. Important progress in developing new approaches to molecular models has been achieved recently (Wertheim, 1988) by using conventional graph theory specifically tailored to describe the molecular case. It is hoped that future progress in this area will lead to new and more accurate descriptions of molecular fluids and solids. However, relatively few mathematical researchers with the skills necessary to achieve such goals are currently working in this area.

With every improvement in the theory of equilibrium interfaces comes a compelling urge to advance the theory of interfacial dynamics (Gunton et al., 1983). Present theories of interfacial dynamics are phenomenological and based on order parameters (very often Fourier modes of the density) and fluctuation-dissipation theorems. Even at this level, theories seldom allow for the coupling of more than two order parameters because of the

intractability of the resulting nonlinear partial differential equations. Mathematical researchers could make a grand contribution to this field by developing new computational or other algorithms for solving such equations. Better still, new formulations based on first principles instead of phenomenological considerations would enhance the field.

An increasing number of new composite materials are being fabricated from phase-separated polymers, where the strengths of the materials are often determined by the interfacial strength and morphology. A significant amount of experimental investigation (Anastasiadis et al., 1988, 1990; Bates et al., 1984) and theoretical research (Scheutjens and Fleer, 1979, 1985; Helfand et al., 1989; Hong and Noolandi, 1983; Joanny and Leibler, 1978; Binder and Frisch, 1984; de Gennes, 1980) has focused on interfaces in binary blends. Recent developments of density functional theory have been associated with extensions to polymer systems (Roe, 1986; Broseta et al., 1990; McMullen and Freed, 1990a, b; Tang and Freed, 1991a), where the complexity of polymers compounds the above-described difficulties. However, many opportunities exist for using density functional theory to aid in understanding currently used approximations and in developing useful extensions for polymer systems. Theories for interfacial properties of polymer systems have been developed that are most useful in two limiting situations. Self-consistent field approaches (Helfand et al., 1989; Binder and Frisch, 1984) are generally applied in the strong segregation limit, while the density functional methods (Joanny and Leibler, 1978; McMullen, 1991) are most suitable in the weak segregation limit. Several predictions of the two limiting theories coincide, indicating close interrelations between the apparently extremely different methods. Fundamental studies of the relation between both types of theories could be useful in order to devise better theories for treating the important intermediate segregation regime.

Density functional theories of interfacial widths and tensions in phase-separated binary polymer blends are predicated on a number of simplifying assumptions as follows (Helfand et al., 1989; Joanny and Leibler, 1978; Binder and Frisch, 1984; de Gennes, 1980): (1) the homogeneous component of the free-energy functional is taken as having a Flory-Huggins form; (2) the interaction parameter $\chi$ is assumed to be composition-independent; (3) the inhomogeneous portion of the free-energy functional is truncated at the square gradient term (Roe, 1986; Broseta et al., 1990); (4) different numerical coefficients of the square gradient term are employed for the weak (Joanny and Leibler, 1978) and strong (de Gennes, 1980) segregation limits, and the square gradient coefficient is made composition-independent, an ad hoc assumption lying outside the underlying, original Cahn-Hilliard formulation (Roe, 1986; Broseta et al., 1990; see, however, Akcasu and Sanchez, 1988); (5) comparisons with experiment often take the $\chi$ parameter from data for the corresponding block copolymer system; and (6) the system is assumed to be incompressible. While there is some agreement between theory and experiment, the origins of observed discrepancies are unclear (Anastasiadis et al., 1988, 1990; Bates et al., 1984), and it is important to assess the implications of lifting the above theoretical assumptions.

Some studies have begun systematically investigating the validity of the above six assumptions for interfaces in phase-separated binary blends (McMullen and Freed, 1990b; Tang and Freed, 1991a, b, d). Use of rigorous density functional methods has enabled the derivation (Tang and Freed, 1991d) of the de Gennes composition-dependent square gradient coefficient (Joanny and Leibler, 1978; Binder and Frisch, 1984) for the weak

segregation limit and when nonlocal connectivity considerations arise, as they do in self-consistent field formulations (Tang and Freed, 1991a). The Roe density functional (Roe, 1986) has been shown to be correct only in the limit of infinite molecular weights (Tang and Freed, 1991a), although the finite chain corrections are not necessarily of the generally assumed Flory-Huggins form but are nonetheless important to explain real experiments (Tang and Freed, 1991b). Allowing for simple linear or quadratic dependences of $\chi$ on composition has been shown (Tang and Freed, 1991b) to introduce, especially near spinodals, substantial deviations from the standard theories of interfacial widths and tensions. Lattice cluster theory computations of $\chi$ for diblock copolymers (Dudowicz and Freed, 1992b) indicate that the junction introduces considerable 1/N entropic contributions to $\chi$. Consequently, $\chi$ for the lower-molecular-weight diblock copolymers is predicted to depart, often qualitatively, from $\chi$ for the corresponding binary blend.

Interesting problems abound. First of all, it remains to test the incompressibility assumption and determine the dependence of interfacial properties on the thermodynamic state (called equation-of-state effects). A compressible theory is complicated by the fact that the Euler-Lagrange equations for the interfacial profile now become numerically unstable coupled nonlinear differential equations, and suitable mathematical approximation schemes must be devised. The development of a compressible theory would enable prediction of the pressure dependence of interfacial properties, something of potential technological importance. Other questions are associated with the derivation of an improved density functional for the intermediate segregation regime and for the treatment of segregation phenomena that occur near free or substrate surfaces. The latter are important in thin polymer films. The dynamics of phase separation in blends, microphase separation in block copolymers, spinodal decomposition, and crystallization are fields with many opportunities. Many features parallel similar processes in other areas of materials science, as discussed in Chapter 4. However, the extremely slow diffusive motion of large polymers enormously slows the dynamics to enable observation of the linear domain, which is unobservable in metallurgical applications, as well as the stages of nonlinear coarsening and ripening.

## BLOCK COPOLYMERS

Materials closely related to composites are formed from block copolymers. Individual block copolymer molecules contain long sequences of one type of unit, followed by a long sequence of another type. When the two types of polymer are incompatible, they attempt to phase separate, but because of the unseverable molecular attachment, the different species cannot get very far from each other. Thus, a microdomain structure is formed that has been considered a regular periodic array with periodicities on the scale of polymer chain dimensions (hundreds to thousands of angstroms) (Bates, 1991; Bates and Frederickson, 1990; Hadziioannou and Skoulious, 1982; Almdal et al., 1990; Bates et al., 1990). Recently, it has been discovered that the arrays in this microphase separation transition may be quite complex geometrically. An example is the double-diamond structure, an array of interpenetrating, continuous phases, each with the symmetry of a diamond lattice. One theory holds that the tendency to form such arrays is related to the drive toward formation

of minimal surfaces between the two materials (Thomas et al., 1988). Considerable experimental (Bates, 1991; Bates and Frederickson, 1990; Hadziioannou and Skoulious, 1982; Almdal et al., 1990; Bates et al., 1990) and theoretical (Leibler, 1980; Ohta and Kawasaki, 1986; Melenkevitz and Muthukumar, 1991; de la Cruz and Sanchez, 1986) efforts have been devoted to elucidating the morphology of microphase separation in block copolymers, partly because of their technological importance but also because of the deep conceptual scientific questions associated with describing phenomena in these fascinating inhomogeneous systems. Other interests in block copolymers arise from their use in the stabilization of blends and their ability to form micelles and other self-assembling structures.

Theories of block copolymer systems (Leibler, 1980; Ohta and Kawasaki, 1986; Melenkevitz and Muthukumar, 1991; de la Cruz and Sanchez, 1986; Frederickson and Helfand, 1987) are replete with either untested or clearly oversimplifying assumptions. The list of largely untested simplifying assumptions includes all those made in theories of interfacial properties in phase-separated polymer blends and many more. For instance, Customary approximations include the neglect of compressibility, the use of a composition-and molecular-weight-independent effective interaction parameter $\chi_{eff}$, the interchangeability of $\chi_{eff}$ between block copolymer melts and the corresponding binary blends, and the use of the incompressible random phase approximation. A dependence of $\chi_{eff}$ on pressure and composition, in addition to the assumed dependence on temperature, implies that $\chi_{eff}$ is a function of the thermodynamic state of the block copolymer system, or equivalently, that $\chi_{eff}$ depends on compressibility or equation-of-state effects. Because of the rather small differences in computed free energies for different morphologies, it is unclear which of these myriad assumptions is responsible for the current lack of a theoretical explanation, for instance, of the circumstances under which the double diamond and other more intricate structures are to be observed.

Other interesting questions involve (1) describing the pressure dependence of the morphology for microphase-separated block copolymer systems, (2) understanding the implications of possible fluctuating ordered domains at temperatures above the microphase separation transition (Hadziioannou and Skoulious, 1982; Almdal et al., 1990; Bates et al., 1990; Fried and Binder, 1991; Hasegawa et al., 1987; Herman et al., 1987; Rosedale and Bates, 1990), and (3) explaining the observed nonuniversality of the phase diagram (Tang and Freed, 1992), a result that, at fixed molecular weight, conflicts with theoretical predictions (Leihler, 1980; Ohta and Kawasaki, 1986; Melenkevitz and Muthukumar, 1991; de Ia Cruz and Sanchez, 1986; Frederickson and Helfand, 1987). The first question requires the development of a theory for compressible systems, which presents many of the mathematical complexities associated with the treatment of interfacial properties for phase-separated binary blends. Lattice cluster theory computations of the microphase separation transition temperature predict a substantial pressure dependence (Dudowicz and Freed, 1992b), a phenomenon that has to our knowledge not been observed but that would be of technological interest. Monte Carlo simulations (Fried and Binder, 1991) and a scaling theory (Tang and Freed, 1992) suggest that resolution of the second and third questions resides in a nonperturbative treatment of the fluctuating domains, something for which mathematical tools are currently unavailable. A possible resolution of the third question emerges from a consideration of a quadratic composition-dependent $\chi$ in the Leibler theory

of block copolymer microphase separation. This simple modification (Tang and Freed, 1991c) leads to the emergence of five different phase diagrams, two of which coincide with the Leibler and the fluctuation theory phase diagrams. Another two of the new phase diagrams agree with experimental observations. This provides one example in which physically significant deviations appear from standard theories when complexities present in realistic systems are taken into consideration. Lifting the customary assumptions sometimes leads to severe mathematical difficulties, and describing the dynamics of microphase separation poses a number of conceptual and mathematical challenges.

## STIFF POLYMERS AND LIQUID CRYSTALS

Polymers that are liquid crystalline in the fluid state, such as Dupont's Kevlar® and Hoechst-Celanese's Vectra®, have found use in high-performance applications, and the versatility of possible polymer morphologies and compositions provides the promise for additional novel liquid crystalline polymers in the future. There are many theoretical problems associated with describing the various liquid crystalline phases possible in polymers. Liquid crystalline polymers are discussed in Chapter 5 in the general context of liquid crystals. One basic problem is associated with the description of semiflexible chains that lie intermediate between fully flexible chains and rigid rods. The Kratky-Porod wormlike chain model provides a venerable solution to this problem, but in a form that is much too cumbersome for simple use in theories of liquid crystalline behavior. Thus, many efforts have been devoted to obtaining analytically more tractable models. A recent advancement in this area uses an analogy between the path integral descriptions of polymers and Dirac fermions (Kholodenko, 1992). The new model correctly reproduces the mean square end-to-end distance of the wormlike chain model, and low-order computations provide results that tend toward the Flory-Huggins and Onsager limits for fully flexible chains and rigid rods, respectively. Applications to liquid crystalline polymers would be welcomed. Many interesting experiments involve polymers with both flexible portions and liquid crystal mesogens on the same chain, and thorough theoretical descriptions are lacking.

The presence of topological constraints has been argued to introduce effective stiffness to chains (Kholodenko, 1991), and this effect may influence the viscoelastic properties of concentrated polymer solutions. Another consideration of chain stiffness enters into descriptions of semiflexible elastomers (Warner and Wang, 1992).

The dynamical theory of liquid crystalline polymers is discussed in the Chapter 5 section on liquid crystals. It suffices to note here that solution of the dynamical equations for structural models is particularly delicate in the case of rigid-backbone polymers that form a nematic liquid-crystalline phase. Here, uniform shear can become unstable at very low shear rates because of the tumbling nature of the nematic phase. As a consequence, the system becomes "structured" in space (polydomain) in the sense that the characteristic orientation of the nematic phase changes spatially, passing through lines of orientational discontinuities (defects or disclinations; Marrucci and Maffetone, 1990). Defect theory has become heavily dependent on differential geometry. There are many outstanding problems, and this general question is addressed further in Chapter 5.

## OTHER PROBLEMS

Polymer science presents an enormous array of other problems for which progress may benefit from improved mathematical approaches. The above discussions are illustrative of some of the ways in which mathematicians can contribute to polymer science. There are many more; see, for example, Kroschwitz (1990). Although these cannot all be discussed in detail here, it is perhaps worthwhile to give several examples.

Most of the polymeric materials ubiquitous around us are actually not pure, but rather are combinations of different types of molecules. For example, the reason that polymeric glasses do not shatter is that they are impact modified. That means that they are blended with rubbery materials. The phases do not truly mix, but rather form an intimate composite of small rubbery domains within the glassy matrix. Many other examples of polymeric composites exist, and frequently polymeric materials contain a large fraction of solid filler material. An important problem is to characterize the path of a fracture, and how the rubbery inclusions in a glass cause the fracture to branch and be terminated (Kausch, 1978; Brostow and Corneliussen, 1986). It is also important to be able to predict the properties of composites, particularly what type of averaging is necessary to describe effective properties (for example, effective viscosity, dielectric constant, or elastic constant). These subjects are discussed in Chapters 5 and 6.

The glassy state of matter is a form in which many polymers find use. There appear to he numerous mathematical issues to be sorted out in the development of a theory for this type of material (see Chapter 6). Many of these problems parallel ones associated with the description of protein dynamics and folding. Descriptions of relaxation phenomena in glasses require the solutions of multidimensional integro-(partial-) differential equations with a wide range of relevant time scales. Methods must be developed for isolating the subset of "relevant" degrees of freedom and for extracting the difficult-to-compute, long-time relaxation dynamics.

# 4

# EVOLUTION OF MICROSTRUCTURES

## INTRODUCTION

This chapter surveys some issues involved in phase-separation kinetics and the dynamics of interfaces. This is a natural subject for collaboration between the mathematical and materials sciences: on the one hand, although the physics is mostly understood, the processes are often quite complicated and of importance for the practicing materials scientist; on the other hand, the new models of the processes are of mathematical interest, and modern machinery in partial differential equations is helpful in studying them.

Energy reduction (involving chemical, elastic, or magnetic energy, or for surface energy) is the driving force. Transport issues (heat and chemical diffusion, surface diffusion, interface kinetics) help determine the resulting dynamics. For shape-memory alloys and magnetic materials, the important questions concern domain structure. For these materials, it is therefore crucial to understand how microstructures arise and change with changes of temperature, stress, and fields.

## SPINODAL DECOMPOSITION AND NUCLEATION

Phase-separation kinetics at the coarse-grained microscopic level involves a continuum description down to a scale slightly greater than atomic dimensions. One is not attempting to study details at the atomic scale but is searching for universal behavior in the fluctuations on larger scales.

Several lines of attack have been used. (1) Forward integration in time from a high-temperature initial condition to a temperature substantially below the phase-separation critical point leads to phase ordering, spinodal decomposition, or nucleation depending on the particular transition. Spinodal decomposition happens without an energy barrier for nucleation (second-order phase transition often modeled by the Cahn-Hilliard equation; Cahn and Hilliard, 1958); otherwise, there is a barrier to nucleation of regions of the new phases determined by competition between an increase in surface energy and a reduction in bulk energy. Nucleation is often studied using statistical mechanics on lattice models. The aim, frequently, is to study the systematic behavior of the growth of domains. Domain growth presents interesting nonequilibrium problems without nearby steady states, and is relevant to metallurgy, polymer processing, and other areas in materials research. Significant opportunities exist for mathematical sciences research; for example, there are still unsolved aspects of the Cahn-Hilliard equation in one dimension! (2) Beginning from the coarse-grained Ginzburg-Landau description (see Chapter 8), the related macroscopic equations and boundary conditions have been derived using matched asymptotics thanks to the mathematical contributions of a number of researchers; see, for instance, Cahn and Hilliard (1958) and Pego (1989). Generally the mathematical and physics challenges involve connecting descriptions involving different scales, and gaining analytical understanding of the

evolution of growth patterns into the nonlinear regime. (3) If a substrate is present, nucleation will often occur on it since the energy harrier height for heterogeneous nucleation is usually much lower than that for homogeneous nucleation. From the coarse-grained viewpoint and taking into consideration surface energy and elastic energy, the energy barrier height is a function of orientations of the interface, substrate, and nucleating crystal. The barrier height is one factor involved in determining the orientation of crystals deposited on substrates in the preparation of thin films. By reducing the context to a competition between volume energies and surface energies, the orientations with lowest barrier height can he determined geometrically (Cahn and Taylor, 1988), although elastic considerations usually dominate when the substrate is itself a crystal; see the review and many references cited in Grinfeld (1993); also, see especially Srolovitz (1989).

## GRAIN GROWTH AND OTHER INTERFACE MOTION CONTROLLED BY INTERFACE KINETICS

The progression toward equilibrium of a system of spatially distinct domains, produced, for instance, by phase nucleation, proceeds by the motion of the domain interfaces. Examples include the growth of a new phase into an old one, domain growth in spinodal decomposition, or in an ordering system, grain growth, and solid-state or liquid-phase sintering. Driving forces for the motion are bulk or surface energy reduction, and the response is governed by diffusion or interface control. Either the surface energy or the mobility can be anisotropic (that is, can vary depending on the normal directions of the interface). Diffusion may appear to occur extremely rapidly, or it may appear that nothing is present to diffuse, so that interface kinetics control the rate of interface motion. Such diffusionless evolutions are discussed in this section; evolutions involving diffusion are discussed later in this chapter.

In grain growth, there is no bulk energy reduction since (it is assumed that) crystals of a variety of orientations grow until they fill space. Further growth occurs only to reduce surface energy. When the surface energy is assumed to be isotropic, the result is motion by mean curvature, with many junctions where multiple grains meet. "Soliton" self-similar solutions and a growth-shrinkage theorem for network cells were investigated quite early (Mullins, 1956). The first major mathematical consideration of motion by mean curvature treated this multiple-grain case in a highly abstract setting (Brakke, 1978). A flurry of mathematical effort was set off by a study of curves in the plane moving by curvature (Gage and Hamilton, 1986), and many of the techniques developed there apply more generally to interface-kinetics-controlled motion.

Collaboration between materials scientists and mathematical scientists have led to understanding of the general classes of equations to which such interface problems belong as well as to understanding of the properties of such equations, the different methods for finding solutions, and the conditions under which each method becomes the preferred one to use. Recent mathematical advances have been surveyed for the situations in which diffusion does not limit the rate of surface motion (Taylor et al., 1992). The methods include mapping of a fixed manifold (such as a circle or line in 2-space, or a sphere or plane

in 3-space), Brakke's varifold formulation, Taylor's crystalline method, least-time method, method of characteristics, regularization by addition of a smooth (nonphysical) term to the evolution equation, viscosity solutions of a Hamilton-Jacobi partial differential equation, phase-field methods for an order parameter, and order-disorder transformation via Monte Carlo simulations with a Q-state Potts model on a lattice. There are both theoretical and computational versions of most of these methods, although many computational methods are fully developed only for one-dimensional interfaces in 2-space. An extensive list of references and open problems, including that of the convergence of solutions for these diffusionless formulations to those for formulations with diffusion, has been recently compiled (Taylor et al., 1992). Still more recent is the development of a variational method (Almgren et al., 1993) and two applications (Almgren and Taylor, 1992; Roosen, 1993).

Many issues remain open in the case of surfaces with facets. In fact, the relative importance of facet formation to the motion of interfaces is currently a hotly debated topic in materials science. Here growth occurs most easily by the spreading of existing layers of atoms (from places where the surface is locally not the boundary of a convex region of crystal or from ledges emanating from where screw dislocations emerge to the surface) and otherwise by the nucleation of new layers. If surface energy is not directly included in the equations, this situation can be handled by anisotropic mobility (Frank, 1972; Cahn et al., 1991). Surface energy is invoked to determine the barrier height to nucleating new layers; it is possible to incorporate surface energy into the equations by defining an analog of weighted mean curvature (Taylor, 1992) for faceted surfaces. However, the relationship between surface energy and dynamics is not as clear. For example, a recent Ising model computation indicates that the most probable path to nucleating a new layer does not yield a nucleus of the minimum energy barrier height.

Overall, a major mathematical challenge is to produce a comprehensive and practical theory of surfaces and their evolution. A considerable part of the work done during the past 30 years on questions in the geometric calculus of variations arose in modeling physical phenomena in interfaces. In this work, the configuration of interfaces is not specified in advance but emerges as part of the calculated solution. Some earlier work studied the structure of energy-minimizing surfaces and interfaces. More recent work has been on evolution issues and on developing algorithms for computing both static and dynamic solutions (Roosen and Taylor, 1992; also, Computer Algorithms subsection, below).

Interfaces between immiscible liquids of different densities inside a jar, grain boundaries in polycrystalline materials, and a soap bubble froth are examples of physical surfaces that arise when a combination of interface and bulk energies must be minimized subject to constraints. The regularity of solutions of elliptic variational problems is well understood; regularity almost everywhere of solutions to elliptic variational problems with constraints has been studied in Almgren (1976), and a theory of quasi-minimizing functions is being developed. Modeling their time-evolution under changing conditions is a challenge on which some progress is beginning to be made (see Computer Algorithms, below). Models of crystal growth from a melt, with differing heat capacities or heat conductivities, present challenging research opportunities in the evolution of geometric configurations and dendritic features (Almgren and Wang, 1992).

Given a question concerning a surface, one would like to be able to put the boundary conditions, forces, and constraints for a situation into an algorithm and have the answer pop out, much as one can do now in linear programming contexts. But surfaces are nonlinear, and such a "black box" solver is still quite elusive. There already are many existence and regularity theorems, but these theorems do not deal with all circumstances and do not always help in solving particular problems. The general algorithms available are computer models, all of which have severe limitations. Even when analytic representations of surfaces are known to exist, such as the Weierstrass representation for minimal surfaces, finding that actual representation is usually impossible as a practical matter. Being able to analyze an arbitrary surface will take truly outstanding mathematical breakthroughs.

Some easily stated questions exemplify how far off a good practical theory of surfaces and their evolution lies:

- Given a wire, what is the shape of the soap film it bounds? Analytically, there may exist a Weierstrass representation, but in practice it may not be findable. For something as simple as the soap film on a cubical wire frame, the equations of the surfaces are not known. However, a good computational tool is now available (Brakke, 1992a, b), and a proof exists that the surface produced by this tool is near a true area-minimizing surface (Underwood, 1993). Soap films are often used as models for grain boundaries, assuming that the grain boundaries have isotropic surface energy; in the cubical frame case, the soap film would separate six appropriately chosen grains. The lack of known solutions in such simple contexts illustrates the difficulty of seeking analytical solutions in general.
- How many different soap films can a particular wire bound? This is connected to the question of how many different grain-boundary configurations there can be under various circumstances. Even for the case of an octahedral frame, one does not know how many different soap films can form (five are known), or which has the least total area.
- What is the best way to partition space into regions of volume 1 with the least interface area? Lord Kelvin conjectured a solution a century ago, and nobody since has been able to prove it or improve upon it. In grain boundaries, Kelvin's solution is not observed, but that is probably because there are many local minima with sizable energy barriers between them for the context. Nevertheless, it would be interesting to know whether or not Kelvin's solution is indeed the "ground state."
- A more general version of this question is, When seeking a minimal surface can one prove that a given local minimum is (or is not) a global minimum? Techniques such as calibrations are useful when they work; see, for example, Morgan (1988). One can perhaps prove that the minimum has a calibration, but how can it be obtained in a particular case?
- Finally, in an annealing metal (modeled by a surface with 3-fold and 4-fold grain junctions, moving by mean curvature), do the grains that shrink and disappear reach a limiting stable shape before they disappear, and what can such shapes be? This question has been studied in the materials science literature for some time, but the confusion between motion by mean curvature and the type of motion that soap films undergo (involving diffusion of gas and instantaneous rearrangement to a locally area-minimizing configuration) seems to have clouded the issue. The complete mathematical solution is not known.

There are also fundamental questions about why there are surfaces and regular arrays of atoms in crystals. Even how regular arrays form is an open issue, and the existence of stable quasicrystals (Shechtman et al., 1984; Cahn and Gratias, 1987; Senechal and Taylor, 1990) indicates that it is of more than abstract interest. Quasicrystals are alloys whose electron diffraction patterns exhibit a clear and sharp symmetry (typically icosahedral) that is impossible for a periodic translation lattice to have. A quasicrystal "tiles" space non-periodically, with the simplest case possessing "prohibited" (by classical crystallography theory) 5-fold symmetry with respect to some axis (that is, possessing invariance with respect to two-fifths $\pi$ of a rotation about some axis). A clear and unmistakable diffraction pattern of any sort is evidence of long-range order, since the diffraction pattern is a picture of a Fourier transform. In spite of the surprise of crystallographers at the existence of these alloys, there is in fact no contradiction with any physical or mathematical theory, since it has never been proved that the stable energy state of matter must be a periodic array of atoms, and mathematicians have long known that almost-periodic functions have Fourier transforms that are atomic measures. Number theorists have pointed out the relevance of Pisot numbers and other number theoretic concepts to understanding quasicrystals, and mathematicians involved in tilings and Fourier analysis have made contributions to quasicrystal theory and likewise have had their own mathematical fields enriched by the discovery of this class of alloys.

### Computer Algorithms

In developing algorithms and computer programs for solving geometric optimization and evolution problems, the creation of new mathematical ideas and approaches has often been indispensable. Some programs serve primarily mathematical purposes. Some aim to simulate crystal growth and are based on new mathematical approaches such as those mentioned above. Other programs, such as Surface Evolver (Brakke, 1992a, b), are also being used by others for purposes beyond those for which they were initially designed. For example, Surface Evolver now has scores of users:

- A Martin-Marietta engineer is using it to simulate liquid fuel shape in weightlessness for a space shuttle small fuel tank (Tegart, 1991).
- Scientists at MIT have used it in analysis of liquid-solid geometries that occur in soldered connections (Racz and Szekely, 1993a, b, c; Racz et al., 1993; Abbott et al., 1993).
- Scientists at the National Institute of Standards and Technology are using it in studies of sintering processes. A NIST metallurgist has said of it, "I found new materials science problems to solve after seeing the ideal tool to tackle them with."

## SHAPE EVOLUTION CONTROLLED BY SURFACE DIFFUSION

Surface shape evolution due to surface diffusion leads to an equation in which the normal velocity is proportional to the surface Laplacian of the mean curvature (in the

isotropic case). This is a fourth-order (instead of a second-order) equation. In general, features of such equations are not well established. Solutions are known (Mullins, 1963) for the linearized equation corresponding to nearly flat surfaces; some of these are shape preserving. Recent work on thin films and small-scale sintering (for example, of ceramic powders) has revived interest in the solutions and properties of the surface evolution equation.

Simple cases described by the above surface evolution equation are the smoothing of an initially undulating surface (Mullins, 1959), the evolution of a general closed body toward a sphere or the blunting of a cone (Nichols, 1965) (for example, field emitter tip). A further example is the development of a groove where a grain boundary meets an external surface (Mullins, 1957) or an internal void. A case described by related equations for materials whose surface energy is sufficiently anisotropic is the faceting of an initially planar surface.

Examples of important practical situations modeled in part by the isotropic surface evolution equation described above are sintering, grain growth in thin films, the breakup of thin films into an island structure, and texture development in thin-film growth from vapor. These situations arise in such materials science processes as molecular beam or liquid-phase epitaxy, and deposition by ion beam or sputtering or chemical vapor. Such issues are important in, for instance, the production of artificially structured materials for such applications as semiconductors, insulators, and new combinations of metals. In sintering, the total surface energy is reduced as the initial set of voids among an aggregate of particles is ultimately eliminated by diffusion of matter into them from the grain boundaries and the concomitant reduction of interparticle distances. In thin-film grain growth, migrating grain boundaries are inhibited by drag exerted by the surface grooves, which can completely trap them. If the deepening grooves reach the substrate, the film breaks up into an island structure. Finally, in polycrystalline thin-film growth from vapor, the migration of grain-boundary groove systems can determine which grains encroach on their neighbors and hence which orientations survive.

In cases involving grain boundaries, as in grooving or sintering, the only known solutions to the surface evolution equation are those for a static planar grain boundary perpendicular to the initial surface plane and those for a few simple translating groove-boundary systems (Mullins, 1958). The general solution for such systems, central to some of the processes described above, has not been studied. Given a simple rule of grain-boundary motion (for example, the mean curvature rule), the situation can be described as two coupled free-boundary problems; see Chapter 8.

## MORPHOLOGICAL STABILITY

The interplay between mathematical sciences concepts and the materials science issue of microstructure formation during solidification deserves emphasis. During solidification of a typical alloy, the rate-limiting step of the crystal formation process is the diffusion of impurities and/or heat. Thirty years ago, it was demonstrated that diffusively controlled growth would be unstable to the "complexification" of the advancing crystal-liquid phase

boundary (Mullins and Sekerka, 1963, 1964); this can, depending on geometry, materials, and so on, lead to cellular solidification, lamellar eutectics, or dendritic growth of fractal structures. Since the resultant microstructure is directly traceable to the growth process, one must come to grips with these inherently nonlinear, nonlocal, and nonequilibrium dynamics.

Mathematics in the broadest sense is crucial for making real progress in this field of materials science. Simulation techniques are essential in the study of any nonequilibrium system. All successful methods for simulating free-boundary problems require sophisticated mathematics. In this regard, work on boundary-integral methods (for steady growth), variational formulations (for nonsteady growth) and phase-field considerations is proceeding apace (Taylor et al., 1992; Taylor, 1993). Mathematicians are not just pursuing existence theorems; they are actually computing real growth patterns.

In certain moving-boundary situations, ranging from viscous fingering to solidification, self-similar growth patterns develop following a morphological instability. These have been studied using methods based on boundary integrals that range from large-scale numerical simulation to qualitative approaches based on renormalization group ideas developed in studies of critical phenomena (see Chapter 8). The mathematical challenges are to overcome computational limitations, extract asymptotic behavior from the relevant integral equations, and take into account that one envisions a statistical process (such as an ensemble of initial conditions).

### Phase Transformations and Pattern Formation

An area where there has been considerable mathematical effort, with and without collaboration with materials scientists, is in solidification. One example involving strong interaction between materials scientists, mathematicians, and numerical analysts concerns a new theory and method of calculation for pattern formation during alloy solidification (Wheeler et al., 1992; see also Chapter 8). A method has been developed that predicts the growth patterns of solids (crystals) forming from a melt during alloy solidification. It has come to be known as the "phase-field model." The phase field model is a set of phase field equations. These are time-dependent partial differential equations (usually parabolic) describing the phase transition in which the interface is determined by level sets of a function (called the phase or order parameter); the transition from one phase to another is gradual. In extreme limits, the interface thickness shrinks to zero, and the sharp interface is referred to as the free boundary separating the two phases. This method treats the system as a whole using a continuous field variable to describe the state (liquid or solid) of the various regions of the system. The interfacial region is modeled as a diffuse layer. This phase-field model approach involves solving a system of nonlinear coupled parabolic partial differential equations, and incorporates a wide variety of physical phenomena such as nonequilibrium kinetics and capillarity. Previously developed for pure materials (Wheeler et al., 1992), this method has been extended to the more useful case of binary alloys. Growth-pattern and associated Oswald-ripening calculations that yield the composition segregation pattern in final solid alloy products can now be done. These segregation patterns are responsible for defects that limit the mechanical and corrosion properties of

many alloys. Understanding such defects is one of the basic issues of metallurgy and materials science to which mathematical sciences research can contribute. See Caginalp (1989) and Kobayashi (1992) for further discussion and sources.

While these equations present an elegant formulation of alloy solidification, many mathematical challenges arise in their solution. The equations are "stiff"; that is, they involve small parameters multiplying the highest-order derivatives. Simple finite-difference methods with implicit time stepping currently in use are not sufficiently accurate. New solution procedures are necessary to obtain results that will provide realistic microstructure predictions of use to materials scientists. Significant questions remain about the stability of the solution with respect to mesh size, orientation, numerical noise, and time step.

Computer modeling of solidification of alloys from a melt is an active area of materials research; see, for example, Hurle and Jakeman (1981) and Brown (1988). It is also important for materials processing (see Chapter 7). In some cases it is desirable to prevent inhomogeneous regions in a crystal (as is the case for semiconductors), while in other cases the presence of such inhomogeneities is desirable because it improves the mechanical strength of the solid. Trial-and-error procedures are often used to try to determine optimal processing conditions. For large-scale processing operations, trial and error can be quite costly. It would be advantageous to have a computer model of a crystal furnace that can be used in a fashion analogous to the "numerical wind tunnels" provided by computational aerodynamics, which allow significant savings over design validation using conventional wind tunnels.

While a crystal furnace computer model is a laudable goal, practical difficulties make computational simulation of crystal furnaces unattainable with current resources. Convection occurs in the melt and the description of crystal growth requires the solution of the Navier-Stokes equations with both heat and solute transport. The observed flow is often unsteady and three dimensional; turbulent flow conditions are not uncommon. In addition, the solidification process is a free-boundary problem, of which the classical Stefan problem is a simple example. On the latter, see, for instance, Rubinstein (1971) and Meirmanov (1992); also see Crank (1975) and Caginalp (1989). The geometry can be quite complicated: dendritic growth with secondary and tertiary sidearm formation, inclusions in the crystal, and so on (see Chapter 8). In attempts to control the process better, the systems are often subjected to various types of external forcing, including bulk rotation of the sample, vibration of the sample, and imposition of magnetic or electric fields. Realistic computational simulation of actual processes under these conditions is currently infeasible.

Piecemeal progress is possible under various simplifications, which, in light of the above discussion, may omit important physical processes. A natural approach is to consider simplified geometries, for example, near-planar growth, in which the complications associated with the free-boundary nature of the process are limited. One then has recourse to classical approaches such as linear stability, perturbation theory, and conventional numerical computations. Even in this setting, the difficulties are formidable: the length scales of transport phenomena, flow fields, and crystal-melt interface shapes in real materials can differ by orders of magnitude, ranging from tens of microns for microstructure associated with interfacial instabilities to centimeter-sized flow patterns on the scale of the container size. This variety of length scales makes a brute-force approach by large-scale computing

unrealistic even in idealized geometries.

One approach to this difficulty might be to use analytical means to reformulate parts of the problem. For example, one could conceivably make use of the different length scales in a systematic asymptotic expansion, as is done in homogenization approaches for multiphase flow. To date, little work has been performed along these lines.

Another possibility is to make use of numerical algorithms more sophisticated than those used to date. By and large, work thus far has used conventional finite-difference, finite-element, and boundary integral methods to model solidification. The amount of research addressing the unsteady and three-dimensional situations has been small, and the questions of mesh generation for complicated time-dependent geometries that may produce changes in topology, are formidable. Recent algorithmic developments that offer advances in these directions include fast multipole methods (Greengard and Rokhlin, 1987), efficient time-dependent boundary integral methods (Sethian and Strain, 1991; Brattkus and Meiron, 1992), Hamilton-Jacobi formulations of interface motion (Osher and Sethian, 1988), and implementations of phase field models (Fife, 1988).

Crystal growth from the melt illustrates that successful mathematical modeling in materials science requires an interdisciplinary effort in which applied mathematicians play an important role. Under extreme processing conditions, how to derive the appropriate governing equations and boundary conditions is often an open question, one that requires mathematical as well as physical insight. Guidance is required from both ends of the research spectrum.

## Dendritic Growth

Consider the example of the single dendritic crystal. Much work has been devoted to demonstrating that the shape and growth rate of a single dendrite can be calculated via a novel "solvability" mechanism arising due to non-perturbative effects in the surface energy. See, for example, Segur et al. (1992), Brener and Mel'nikov (1991), Kessler et al. (1988), Pelce (1988), and Langer (1987). This mechanism consists in adding (anisotropic) surface energy to the consideration in a way that fundamentally alters the mathematics of the diffusive growth equation and leads to the formation of distinctive patterns. The theory (especially in the real three-dimensional case) remains somewhat controversial within the materials community. It has helped create the entirely new applied mathematics concept of asymptotics beyond all orders (Segur et al., 1992). Citing this example does not imply advocating the theory (or the "asymptotics beyond all orders" concept, which does not contribute to the real case); it is offered only to point out that this issue is likely to be resolved by the combined efforts of materials scientists and mathematical scientists. The mathematical sciences will be enrichened in the process.

Some years ago, the Institute for Theoretical Physics (ITP) in Santa Barbara hosted a program concerned with understanding dendritic crystal growth in a quantitative way. The focus was on predicting the properties of dendrites, including growth speed, dimensions, and side-branching behavior. Dendritic growth is the generic growth mode under diffusion-controlled conditions, and progress in understanding dendrites will lead to an ability

to predict and control in a scientific manner the microstructures of metals, including alloys, and other materials. Although this context had previously attracted the attention of materials scientists and mathematicians, the ITP program approached the questions afresh, using physical principles to construct simplified (two-dimensional) models of the process that were amenable to numerical methods and some analytic work. It was discovered that the existing formulation was physically inadequate—it ignored the role of crystal anisotropy, which was shown by the research of the program to be crucial. Once the correct physics had been identified, it was necessary to solve the resulting mathematical models. This turned out to be a subtle issue in singular perturbation theory, which involved asymptotics beyond all orders. M. Kruskal and H. Segur, who were visitors to ITP that year, worked out the general mathematical framework for this difficult situation (Segur et al., 1992), and their contribution formed the basis for subsequent calculations by physicists in the field.

## MUSHY ZONES

So-called mushy zones present an interesting challenge to mathematical scientists. These layers between the liquid and solid phases, which consist of tiny parallel needles separated by fluid regions, have been the subject of intensive research in recent years (Huppert, 1990). Currently, it is not fully understood why they form, but there has been success in describing the evolution of the microstructured layer, viewed as a continuum: there is structure that emerges at several levels. The needles themselves have stable side branches but, on a larger scale, organize themselves into uniform regions populated by chimneys. Here, a challenge is to provide a better understanding of how macroscopic equations are related to transport processes near the needles, while accounting for the complex forest of needles. The types of mushy regions best understood by mathematical scientists are those arising in pure material that is being melted under volumetric heating (Atthey, 1974). In this setting the mushy zone has no structure, but what is possible in the distribution of crystal size has been considered (Lacey and Taylor, 1983).

## PRECIPITATION AND COARSENING

Many of the properties of multiphase materials depend strongly on the morphology and spatial distribution of minority precipitate phases within a majority matrix phase. The morphologies and spatial distribution of these precipitates are in many cases governed by the dynamics of a phase transformation process. For example, cooling a single-phase alloy to a lower temperature can result in the formation of small nuclei within the high-temperature phase that then proceed to grow. It is this growth and the subsequent coarsening process that frequently determine the morphology and spatial distribution of the particles. In many systems, ranging from transformation-toughened ceramics to high-temperature superalloys, the minority-phase particles possesses a density that differs from the density of the matrix phase. This difference in density engenders elastic stress fields in both the matrix and the particles that can strongly influence the nature of the transformation

process and the morphology of the particles.

Describing the dynamics of diffusional growth and of the coarsening of second-phase particles in the presence of elastic stress has all of the complications of the classical Stefan free-boundary problem augmented by the fact that the boundary conditions at the particle-matrix interface are a function of the local curvature (through the interfacial energy) and a function of the entire shape of the particle and the distribution of the other particles in the system (Voorhees, 1992). The presence of a long-range elastic stress field gives rise to strong spatial correlations between particles during coarsening and to diffusional migration of particles in solids. Although some solutions in this context have been found, much of the mathematical structure of these elastochemical free-boundary problems remains unexplored.

An example of the effect of stresses on the evolution of a two-component system is the later stages of a phase transformation. In this phase, particles usually coarsen (decrease in number and increase in size while maintaining a nearly constant total volume). In several technologically interesting cases, however, this coarsening ceases and the particles begin to split. The stresses that are presumed to give rise to these phenomena are caused by compositional inhomogeneity, external loads, or particle misfit strains.

The elastic stresses manifest themselves in the diffusional and mechanical field equations and in the boundary conditions for diffusion. The long-range elastic fields render the diffusion equation a function of the composition field, the size and spatial distribution of the "second-phase" particles, and the system geometry. There have been many attempts to generalize the Lifshitz-Slyozov theory of grain growth and coarsening (Lifshitz and Slyozov, 1961) during the last thirty years. By modeling a collection of spherical particles under a number of simplifying assumptions, including interface isotropy and equal molar volumes as a homogeneous (single-phase) system in which the particles are replaced by multipole sources and sinks of strengths determined by solution of Poisson's equation, particle growth and migration rates can be determined by computer simulations (Abinandanan and Johnson, 1992). The approach is limited by the inability to solve for strongly coupled elastic and diffusion fields. It also suffers from the inability to treat particle shape changes; compare with Boettinger et al. (1993) and Roosen (1993), which do allow for shape changes.

The simplest models of coarsening omit any influence of stress or texture. These models apply to solid-fluid systems and to solid-solid systems in which there is a negligible misfit strain. Theoretical treatments of these models by the Lifshitz-Slyozov method (Lifshitz and Slyozov, 1961) and its generalizations show that the distribution of particle sizes divided by the (increasing) average particle size becomes asymptotically time invariant. When the Lifshitz-Slyozov model is assumed, the system becomes self-similar in a statistical sense (as defined, for example, in Mullins and Vinals, 1989). The same property is observed in grain-growth models that treat all boundaries as being the same. There is no general mathematical theory that details the conditions under which an evolving system will develop a statistically self-similar structure.

### Evolution of Microstructures; Stress and Current Effects

Stress affects both the (final) equilibrium state of crystalline solids and the evolution of a solid not originally in equilibrium. The local state of the material is typically characterized by a displacement gradient and several scalar parameters such as composition and temperature. In the equilibrium setting, one seeks the state that minimizes a particular integral (total energy) over the volume of the material, given the temperature, overall composition, other parameters, and boundary conditions (displacements, applied tractions, and so on). Surfaces of discontinuities can exist within this volume, and their existence and shape are usually part of the question. Ever since Gibbs's famous chapter on solids in contact with fluids (Gibbs, 1876, 1878), the first step in obtaining solutions has been derivation of coupled partial differential and algebraic equations that must be solved at an extremum (Larché and Cahn, 1978). The evolution situation is often formulated as a set of nonlinear partial differential equations with boundary conditions on moving boundaries; see Larché and Cahn (1992) for a simple example. The theory combines classical elasticity, thermodynamic effects on solutions (as a notoriously nonlinear ingredient in the energy of the solid), and the interfaces (that usually involve stronger conditions than simple contact) between parts of solids with different orientations or different properties.

Some open questions in this field are the following: (1) How can a line of discontinuity, such as a dislocation, he incorporated into the energy minimization approach of the example mentioned above (Larché and Cahn, 1978)? (2) What are the necessary conditions for a minimum? (3) What are the general properties of the solutions? (4) When elastic effects are present, a modification of the shape of the regions containing different phases changes the energy of the system (Cahn and Larché, 1984). One can then ask: What geometric arrangement in space produces a minimum in the appropriate energy (including surface energy)? How sensitive is the evolution of such a system to initial conditions? Corollary: What can really he predicted? (5) The presence of a displacement gradient as a local variable to describe the state of a solid often introduces nonlocal effects in the partial differential equations describing the evolution of the system (Larché and Cahn, 1992). What are the general properties of the solutions of these equations?

Stress-induced diffusion often causes voids to grow. Similarly, current-induced diffusion (electromigration) leads to void growth, extrusions, and other microstructural changes. These problems are particularly severe in the microelectronics industry, where they occur in metal interconnects on chips. The theoretical and mathematical models of induced diffusion are currently quite elementary. More comprehensive formulations are needed.

## MARTENSITE AND SHAPE-MEMORY MATERIALS

Martensite transformations are phase transformations that produce a change of shape and a change of crystal symmetry. Shape-memory materials are materials that are extremely malleable in the martensite phase below a transformation temperature, but that return to a "remembered" original shape when heated above the transformation temperature. In this orderly change of phase, nearest neighbors of atoms are maintained. One can picture a

cubic lattice, for example, that deforms by elongating along one of the cube edges. Since the three cube edges are crystallographically equivalent, there are three different ways the cubic crystal can deform; these are the variants of martensite. After transformation, the variants arrange themselves in complex patterns characteristic of the material. The goal of mathematical theories of martensitic transformations is to predict these patterns of microstructure, to understand why certain materials exhibit certain patterns, and to explain the macroscopic properties of these materials. One of the most intriguing, yet-to-be-understood aspects of shape-memory materials is that they occur for special compositions (Liu, 1992; Otsuka and Shimizu, 1989).

Coherent phase transitions of crystalline solids lead to mixtures of distinct phases or phase variants with characteristic fine-scale structures. Such transitions can be modeled using continuum elasticity (see Chapter 8). Microstructures arise due to elastic energy minimization. This topic is closely linked to the study of structural optimization and to the identification of extremal composites (see Chapter 6).

The materials science literature in this area is extensive. For martensite, research is dominated by the phenomenological "crystallographic theory" (Christian, 1975). There is also the work of Khachaturyan (1983), Roitburd (1978), and others based on geometrically linear elasticity. Most work oriented toward understanding the shape of coherent precipitates has dealt with isolated inclusions and has taken as a starting point the work of Eshelby (1975).

Recent mathematical work has introduced new ideas and opened new doors. One important development is the modeling of microstructure based on geometrically nonlinear elasticity (Ball and James, 1987). In geometrically linear theory, free energy depends only on linear elastic strain and is therefore invariant only under infinitesimal rotations. In the geometrically nonlinear theory, the free energy depends on the nonlinear Cauchy-Green elastic strain, since it is invariant under all rigid body rotations. This amounts to a marriage of the "crystallographic theory of martensite," which is nonlinear but strictly phenomenological, and the earlier work of Khachaturyan and Roitburd, which uses energy minimization but is geometrically linear. This new approach has suggested specific quantitative predictions of energy minimization (Ball and James, 1992) and new criteria for the design of shape-memory materials (Bhattacharya, 1991, 1993); see also Chapter 8.

Another development is the impact of surface energy as a selection mechanism. It is widely appreciated in the materials literature that the length scale of microstructure is determined by the interaction of bulk-energy and surface-energy effects. A recent attempt to make the theory in this area rigorous led to an entirely unexpected prediction of twin branching in martensite (Kohn and Muller, 1992).

Much remains to be done. In practice there are at least two small parameters: surface energy and geometrical nonlinearity. How they interact and how they together serve to select between otherwise equivalent microstructures are not understood. Combining the strengths of geometrically linear and geometrically nonlinear approaches would he a worthwhile development. The recent progress on extremal microstructures in linear elasticity has yet to be exploited in the setting of coherent precipitates. All important is the modeling of local minima and dynamical effects, a topic that has received current attention (Ball et al., 1991a; Semenovskaya and Khachaturyan, 1992) but that is far from well understood.

On the dynamic side, there are outstanding challenges for mathematical scientists.

One involves a marriage between microstructure and kinetics. It is known that the microstructure of domains is history dependent. Minimizing the energy does give the right kind of microstructure qualitatively, but many key questions involve the dynamics of microstructure. Among the family of minimizing sequences of domain patterns for a given boundary condition, which one will be chosen (see Chapter 8)? Given the one that is chosen for time zero and given a deformation as a function of time, what will the deformation be later in time? We need a theory of parallel transport, of dynamics, on the space of minimizing sequences. Perhaps this will prove impossible: some domain patterns may not be able to change smoothly after sufficiently large deformations.

These dynamic and kinetic considerations may be crucial to the understanding of hysteresis in martensitic materials. Among different martensitic materials, there is a huge variation in the size of hysteresis loops—the transition temperatures on heating and cooling can vary by as little as 1°C and as much as 100°C. The dynamics and kinetics of martensitic materials can also be understood in terms of metastability. In this regard, the current understanding of relative minimizers of energy is inadequate. Recently, this has become an active area of research, with many ideas and models put forth about the origins of hysteresis. Mathematical work that improves the models, suggests new approaches, and discovers underlying connections between the current models is needed.

The computation of the microstructure of materials is important in the development of many emerging technologies such as shape-memory materials (Collins and Luskin, 1989; Collins et al., 1993) and magnetostrictive materials (Luskin and Ma, 1992). The role of computation is both to facilitate the development of theory and to aid in the design of materials that are important for technological applications. The challenge of computing complex material microstructures has brought these concerns to the forefront of modern numerical analysis.

Three-dimensional equilibrium computations for crystalline microstructure constitute a relatively recent phenomenon. This setting is not unlike that of the protein folding problem (see Chapter 3) in there being extreme nonlinearity and huge numbers of relative minima. Here, there is a twist: some (but clearly not all) of these relative minima may be important for the understanding of metastability. The first such computations proved that the deformation of macroscopic crystals could be modeled with effective continuum theory and advanced computational methods (Collins and Luskin, 1989). New techniques have been introduced to give a rigorous error analysis for the numerical approximation of microstructure (Collins and Luskin, 1991; Collins et al., 1991). Future challenges for the mathematical sciences are to create more efficient algorithms that will make possible the computation of more complex microstructures, and to extend error analysis to multidimensional contexts where there is not a unique solution.

Even more challenging is the computation of the dynamics of crystalline microstructure. It remains a fact that, in many branches of the study of phase transformations, the kinetics of transformation is often fit by an essentially empirical relation. A major challenge is to develop kinetic models that relate directly to material parameters. This will not be possible without the ability to account accurately for the full complexity of evolving microstructures. Progress in this area is in its infancy but is encouraging. Recently, dynamical solutions have been computed for the development of microstructure in

three-dimensional martensitic crystals and for the movement of the interface separating martensitic and austenitic phases (Kloucek and Luskin, 1993).

## MAGNETIC MATERIALS

Magnetic materials offer promising opportunities for interactions among materials scientists, applied physicists, and mathematical scientists. Important issues include the prediction of complex domain structures, the sizes and shapes of hysteresis loops, the quantitative effects of defects, and understanding the fascinating properties of thin-film and nanocomposite magnetic materials.

Micromagnetics deals with the prediction of magnetic domains at the micron level. This theory (Brown, 1963) has been influenced strongly by Landau and Lifshitz (1969) and has experienced both remarkable success and spectacular failure. On the successful side, it gave a quantitative prediction of the behavior of small magnetic particles and provided the basis for the design of the strongest magnets, which are obtained by sintering these particles in a way that avoids exchange interactions. It was less successful in dealing with large magnets. Its failure (by a factor of 5000) to predict the size of the hysteresis loop of single crystals of iron came to be known as the coercivity paradox. This was resolved by a series of careful experiments that revealed the huge influence of defects, both scratches on the surface and internal defects. The validity of the theory of micromagnetics was confirmed by growing defect-free iron whiskers, the hysteresis loops of which closely agreed with the micromagnetic predictions. However, except for studies of a single domain or a single defect, a workable form of micromagnetics for defective crystals remains a challenge. Some methods have emerged for coping with complex microstructure (James and Kinderlehrer, 1990), and there has been recent progress on establishing a relation between micromagnetics and phase theory (De Simone, 1993), but these methods fall short of comprehensively treating defective crystals.

Magnetostriction is the phenomenon whereby magnetization produces deformation and, conversely, deformation produces magnetization. Of particular interest because of its comparatively large magnetostriction is the iron/rare-earth alloy Terfenol-D, the magnetostriction of which under the influence of even an extremely small field can be as much as 1 part in 1000. It has a complicated microstructure whose role in magnetostrictive properties is yet to be clarified. In conjunction with experimental work, a theory has been developed that is being applied to this material (James and Kinderlehrer, 1993). There is also a related computer model. Many open issues remain, especially issues related to the mechanism of magnetostriction and possible hindering mechanisms.

Terfenol-D is one of a family of materials that in recent years have been called "smart materials"; see, for example, Gandhi and Thompson (1992), Rogers (1989), Travis (1993), and Nanavati and Fernandez (1993). These materials can be used in sensors and actuators. They can be used in sensors to understand the behavior of small volumes of material, which can differ quite markedly from the behavior of large volumes. One trend is the application of smart materials to micromachines, that is, tiny mechanical machines.

Although there has been interesting progress in the ability to compute configurations,

computational issues continue to present great difficulties. These are not mere technical obstacles but fundamental obstacles connected with the nature of nonconvex optimization (see Chapter 8). They are most readily resolved in collaborations between materials scientists and analysts. For example, anisotropy of the computational grid and anisotropy of the material can compete to give poor results, especially when many potential wells are separated by low barriers. Such mismatches can be avoided by increased cross-disciplinary understanding.

The basic model in present use for dynamic situations is the Landau-Lifshitz-Gilbert equation. This time-dependent partial differential equation for the magnetization vector is a gradient flow for the micromagnetic energy. Much remains to be learned about the properties and applicability of this equation. The equation exhibits nonuniqueness, and it is likely that with certain applied fields and geometry a smooth solution develops increasingly fine oscillations (see Blue and Scheinfein, 1991; Hoffend, 1993; James and Kinderlehrer, 1990; also see Visintin, 1985, and the references given therein).

## SUPERCONDUCTIVITY

Discovery of high-$T_c$ superconducting materials has revitalized the study of all superconducting materials and has focused attention on applications of superconductivity at a level not seen since the 1960s. The modeling of both the macroscopic and microscopic properties of superconducting materials and of the processes for preparing them provides important scientific opportunities for the mathematics community, opportunities that affect both fundamental and applied aspects of the subject. These opportunities involve both conventional metal-based materials and the new high-$T_c$ materials that have been found within the last 6 years.

The macroscopic properties of the new superconducting materials are more complicated than those of metallic superconductors due to anisotropy, layered character, short coherence lengths, and high values of the upper critical magnetic field. As a consequence, the macroscopic equations for the superconducting order parameter, namely, the Ginzburg-Landau equations, are different from and more complex than those used to describe metallic materials. These equations are in need of serious study by mathematical scientists (see Chapter 8). Understanding the solutions of these equations is essential for quantitatively modeling the response of superconductors to magnetic fields and currents; see, for example, Bishop et al. (1993). These are fundamental issues that have an impact on the development of applications.

As a consequence of this complexity, the phenomena observed when high-$T_c$ superconductors are subjected to magnetic fields are far richer than those found in metallic type II superconductors. Both kinds of materials exhibit the Meissner effect; that is, they have a flux-excluding state at low fields, and they both have a mixed state at higher magnetic fields characterized by the penetration of field through the presence of Abrikosov vortices. Because of the anisotropy and layered nature of high-$T_c$ materials, vortices in these materials are more complicated than those in conventional metallicsuperconductors. High-$T_c$ a materials can exhibit, with increasing temperature or magnetic field, either vortex lattice

melting (in ordered materials) or vortex glass melting (in disordered systems and thin films). Although the precise physics of the transitions from a lattice or a glass to a fluid of vortices is currently a subject of physical investigation and is not resolved, any of the proposed models that may ultimately describe these transitions represent significant opportunities for mathematical scientists.

Modeling the dynamical properties of superconducting vortices in the presence of transport currents and magnetic fields is a key to producing materials and configurations in which transport is dissipationless and critical currents are high, features that are required in many applications. The key to building stable systems for high-power applications such as magnets will be determining how vortex dynamics and energy dissipation are related to heat. This is complicated by the fact that ductile conductors may be composite materials, as is the case for metallic superconductors.

On a microscopic level, the details of vortex dynamics depend phenomenologically on the particular nature of pinning sites. The study of the interaction of Abrikosov vortices with structural defects of various types such as point defects, dislocations, grain boundaries (see Chapter 5), and twin planes, all of which can serve as pinning sites, may also be an opportunity for mathematical scientists. The fundamental understanding of this interaction phenomenon has benefited over recent years from the development of various microscopic theories that now permit the quantitative characterization of defects.

A variety of devices incorporating superconductors have been proposed over the years. Development of these devices provides a plethora of research opportunities for mathematical scientists. The most ubiquitous devices are those involving Josephson effects, which have been proposed as computer-processor and computer-memory elements as well as sensors of electromagnetic radiation and magnetic fields. Individual junctions can be modeled as simple dynamical systems or sine-Gordon systems. In physical applications, junctions are perturbed by high-frequency fields or are coupled to other junctions. The detailed modeling of the behavior of Josephson-effect devices, and of diverse geometric arrays of devices subjected to a assortment of purturbing fields, presents additional opportunities for mathematical scientists.

Conventional superconductors can he described microscopically by the Bardeen-Cooper-Schrieffer (BCS) theory (see Chapter 8). The new high-temperature superconductors are likely to be understood using either a modified version of the BCS theory, such as one in which there is nonzero angular momentum paring, or an entirely new theory. The issue at this point has not been resolved by the physics community. Whatever theory comes out of the physical investigations, it will involve new challenges for applied mathematicians.

Another potential application of the mathematical sciences to the study of superconductors is in modeling the materials' synthesis and processing, both in bulk and in thin-film form. Such processing details determine the morphology and chemistry of the materials along with their ultimate physical properties and usefulness. For example, in producing thin films and thin-film devices, it would be invaluable to be able to model film growth and predict the growth mode and such properties as structure, surface smoothness, and chemical composition. This is a research opportunity in surfaces and interfaces that has experimental, analytical, and computational aspects. There are similar issues in controlling

the processing of bulk materials. The solution of synthesis and processing problems for superconductors is key to the development of a competitive superconducting technology.

There has been a recent surge of activity in macroscopic modeling for superconductivity. The mathematical methods involved include the use of asymptotic analysis, free-boundary formulations, variational principles, and finite-element approximations. For comprehensive reviews, see Chapman et al. (1992) and Du et al. (1992).

# 5

# DEFECTS, DEFORMATION, AND INTERFACES

## INTRODUCTION

The mechanical performance of materials is of central importance for many materials applications. Such applications range from the airframes of aircraft and automobile structures to the interconnects of microelectronic circuits. It has been recognized that defects and the response of defects to internal and external fields dictate in many ways the mechanical behavior of materials. Defects are also important for many other properties of materials such as diffusion, dielectric breakdown, chemical durability, and so on. The evolution of microstructures, described in Chapter 4, is microscopically mediated by defects.

To understand the fundamental characteristics of defects—including point defects, dislocations, and interfaces—materials scientists have turned increasingly to atomistic simulations (Chapter 2). The spatial extent of defects, however, often encompasses both atomic and mesoscopic length scales, making it necessary to include a large number of atoms in these simulations. Therefore, finding an efficient method to deal with these atomic simulation problems is no less a challenge than the one for purely atomistic simulations addressed in Chapter 2. Moreover, the large local distortions associated with point defects, dislocation cores, and interfaces sometimes make it difficult to apply interatomic potentials that were developed under more restricted conditions (for example, nearly constant volume). Therefore, ab initio calculations are preferred for defect problems. At the mesoscopic length scale, it has been customary to impose a boundary condition specifying that the solution match the continuum solution. Such a procedure, however, has not been fully justified and may require more attention in view of the sensitivity of solutions to boundary conditions. Lastly, although the determination of forces and stress tensors from atomic displacement is trivial in these simulations, the inverse problem at both atomic and mesoscopic length scales is ill posed. This ill-posedness, which is common to other applications such as nondestructive testing using scattering waves (described in more detail in Chapter 7), has hindered the application of simulation techniques to these classes of materials problems.

Interfaces viewed as continuum entities with macroscopically defined parameters (for example, free energy per unit area, mobility, and so on) are important in many phenomena treated in other chapters and are discussed in Chapter 3. In the discussion of interfaces in the present chapter, the emphasis is on the way in which geometry, interatomic potentials, and entropy combine to yield the equilibrium ensemble of interface structures under given conditions. The interfaces considered are solid surfaces, grain boundaries, and interfaces in emulsions.

The response of defects to internal and external fields is an important subject in materials science and at the same time one of the most difficult and least understood. Two important examples of point defect aggregation are (1) void formation in grain boundaries in stressed turbine blades at high temperatures and (2) three-and four-grain junctions under electric fields in microelectronic interconnects. The internal field arises from (long-range)

interactions among defects. Such interactions are responsible for defect aggregation. In modeling internal fields, questions arise regarding what is the statistical nature of defect distribution, what (if any) correlations there are between defects, and what length scales are required to take these correlations into consideration. Defects appear to have many intermediate configurations that may be near local minima of the energy. In response to internal and external fields, defect configurations evolve in time in a complex manner. For example, the way that dislocations arrange and rearrange into network, cell, and subgrain boundaries and eventually into grain boundaries during deformation is not yet understood. The evolution of defects is highly dynamic in nature and presents significant challenges to materials scientists and mathematical scientists. Currently, it is simply not known whether there exists a unique minimum or multiple local minima for groups of dislocations.

The modeling of the evolution of defects is important in materials science because, in many cases, defects directly control microstructural evolution, and knowledge of microstructural evolution is a basis for designing thermomechanical treatments in industry. Defects determine the mechanical constitutive equations in nearly all cases: plastic deformation, fatigue, and creep. Constitutive equations are usually formulated at the continuum length scale and omit the details at the mesoscopic scale. Many (but not all) deformation and fracture problems of interest to materials scientists and structural engineers are well defined. Applied mathematicians, known as applied mechanicians, have for years had a tremendous impact in this domain in analyzing deformation and fracture problems (elasticity, plasticity, fracture mechanics, and micromechanics). Standard mathematical methods, such as partial differential equations, singularity analysis, finite-element methods, and so on have been intensely utilized and further developed in this area. Applied mathematicians have contributed to creating materials with improved mechanical performance that provide greater margins of safety in structural engineering applications.

In many materials, especially brittle materials, eventual failure is attributed mostly to inherent flaws in the materials. Often, the most severe flaws control the probability of failure of the material. This situation is not unique to mechanical failure; it is also encountered in other types of failure such as dielectric breakdown and failure in superconducting networks. Treatment of such problems demands statistical methods. In recent years, however, materials scientists have also resorted to discrete modeling to treat such problems at a scale traditionally appropriate for continuum mechanics.

In the following sections, additional problem areas are presented, including modeling methodology, mechanics of defects and interfaces, plasticity and fracture, large local fields and instability in random systems, dynamic fracture, liquid crystals, and a few topics concerning the structure of interfaces on the atomistic level and the macroscopic properties that result. They provide a glimpse into some of the current activities in the areas of defects, deformations, and interfaces and point out some issues that may interest mathematical scientists. These problem areas are representative but not exhaustive, and the reader is encouraged to refer to the large current literature of applied mechanics (for example, appearing in the *Journal of Applied Mechanics*) and materials science (for example, appearing in the *Journal of Materials Research*, the *Journal of the American Ceramics Society* , and so on) for further exploration of this field.

## DEVELOPMENT OF MESOSCALE STATISTICAL MECHANICS OF SOLIDS

Many of the important problems in the science of solids, especially metals and semiconductors, involve predicting defects—such as clusters of impurities and point defects, dislocations, grain boundaries, and interfaces—in the solid lattice. These phenomena are modeled in macroscopic continuum theories using constitutive models and rate expressions for which the coefficients come from either experiments or more macroscopic theories. Direct simulation by ab initio methods and even atomistic calculations using empirical interatomic potentials are in many cases too expensive to be of practical utility for complex systems (see Chapter 8).

Mathematical analysis aimed at combining direct simulation of local behavior with a mean-field theory is needed to develop descriptions of nonhomogeneous solid phases. Thermodynamic density functional approaches, as developed for description of liquid/gas and solid/liquid interfaces, are a first step toward the development of such a mean field theory. Density functional theories have proven successful for relatively simple problems, for example, describing interfaces in systems governed by simple intermolecular potentials such as hard spheres and Lennard-Jones potentials, but have not been extended to a general framework that will allow input from more complicated interatomic descriptions or from ab initio calculations. These extensions will require the input of mathematical analysis, numerical analysis, and statistical physics.

## MECHANICS OF DEFECTS AND INTERFACES

The description of point defects, defect clusters, dislocations, and interfaces using classical elasticity, nonlinear elasticity, and atomistic theory is a major field of micromechanics research that bridges physics and engineering (Hirth and Lothe, 1982; Mura, 1982). The issue is to describe the configurations of dislocations, voids, precipitates, twins, interfaces between phases, vacancies, and clusters, to describe the interaction in these configurations, and to understand how these configurations give rise to macroscopic phenomena such as plasticity, magnetic hysteresis, and transformation kinetics. Much of the past work has been on equilibrium configurations of defects—see, for example, Mura and Nakasone (1989), Qin et al. (1991), Fan et al. (1991), Venkataraman et al. (1991), and Mura (1987). Mathematical models of dislocation distributions were developed in Head et al. (1987), and free-boundary methods were used to study such models in Caffarelli and Friedman (1988) and Howison (1990). There is now a need to understand the evolution of defects during deformation and crack initiation under cyclic loading. The use of nonlinear elasticity, atomistic interaction potentials, and, occasionally, the Schrödinger equation is often called for in these problems as in problems of crack nucleation, defect clusters, and other aspects of material inhomogeneity and deformation heterogeneity (Morinaga et al., 1987, 1988; Sato et al., 1988; Watanabe et al., 1989). In many cases, such as the inversion of residual stresses and plastic deformation from surface displacements, and the prediction from pull-out test data of sliding and debonding of fiber from matrix, the problems are inverse problems. Such ill-posed problems can be solved under certain circumstances (Gao

and Mura, 1989; Mura and Gao, 1989, 1992). Similar problems exist in nondestructive evaluation of material defects (described in Chapter 7).

A general approach to the description of defects that relies on topological classification is discussed in Mermin (1979) and Kléman (1983). In this theory, defects are classified by homotopy: all defects in the same class are homotopic, that is, can be obtained one from the other by continuous deformation. While this provides an elegant way to classify many different kinds of defects and provides an interesting application of topology to materials science, it remains to forge a stronger link between the topological type of a defect and its actual behavior as described by differential equations that connect external forces and defect motions.

## PLASTICITY AND FRACTURE

Understanding the theory of plasticity is fundamental to understanding a large variety of behaviors of materials in processing and performance, including metal forming, injection molding, instability, fatigue, fracture, friction, wear, and penetration (Drucker and Prager, 1952). The simplest governing equations of plasticity undergo a change of type from elliptic to hyperbolic as a material's capacity to harden with strain is lost (that is, in the perfectly plastic limit). These simplest theories of plasticity have received a fair amount of attention from mathematicians. There are three fundamental issues here that need attention: plastic deformations are intrinsically time-dependent, the deformations are generally large, and there are significant microstructural effects. Although there have been important attempts to model these effects—see, for example, Simo and Ortiz (1985) and Wallace (1985)—most materials scientists believe that the effects remain to be modeled accurately. There are subtle issues associated with boundary conditions, which, in metal-forming problems, must respect frictional constraints.

There are important challenges in numerically solving the equations of plasticity. As a material's plasticity is increased, the governing elliptic equations become very stiff, and the hyperbolic limits of these elliptic equations cannot easily be solved by numerical procedures. Hyperbolic equations describe perfectly plastic materials, but the uniqueness of their solutions is not guaranteed. To obtain a solution for plastic materials, different solutions for perfectly plastic materials can be obtained and the ones that match low-hardness solutions selected as the corresponding perfect-plastic solutions. Alternatively, unique and well-defined plasticity solutions may be sought by incorporating elasticity. Finite-element methods are especially useful for this latter type of problem.

A different approach to plasticity is the theory of continuous distributions of dislocations. A single dislocation can be seen at a distance from its center from local deformations of the crystal geometry. Thus if a circuit enclosing the defect is made through the lattice, and each lattice bond angle is assumed to be that of a perfect crystal, the sum of the angles on the circuit will not total 360 degrees; the difference between the total and 360 degrees is the torsion of the circuit. The Burger's vector is that vector needed to close the loop. In the continuous theory, these vectors are given a continuous density distribution. This theory links the failure of Burger's circuits to close when dislocations are present to the

fact that the tensor field describing local deformation is not integrable. The nonvanishing torsion of this tensor field is associated with the presence of dislocations. An additional theory, mostly kinematic and with close ties to differential geometry, is developed for this torsion. This theory, like the topological theory of defects, has provided a useful conceptional framework, but classical treatments of it, for example, Kröner (1958) and Nabarro (1967), have not come to grips with forces and energies. More recently, a related theory with possibilities for development beyond kinematics has appeared (Davini, 1986; Davini and Parry, 1993).

The onset of plastic deformation, or yield, is often assumed to be insensitive to pressure. This is usually a good assumption for metals and many polymers under many conditions, although it does break down under large tensile stress as experienced at the crack tip due to void formation. In more brittle materials, the extent of intrinsic plasticity is usually small, and various damage mechanisms, including friction, microfracturing, and cavitation, often contribute significantly to the apparent plastic strains. Since these mechanisms are all pressure-dependent, the resultant plasticity is also pressure-dependent. Another type of pressure-sensitive plasticity occurs in phase transformation, as in steels and zirconia. In both cases, the transformation can be triggered by deformation or stress and the volume increases during phase transformation. By taking advantage of this capability, ceramists have invented toughened ceramics using zirconia in which fracture energy is increased by a factor of nearly 50 (McMeeking and Evans, 1982; Budiansky et al., 1983; Chen and Morel, 1986; Chen, 1992).

Coulomb's yield criterion, which considers a linear combination of effective shear stress and pressure to be yield-inducing, has been adopted to investigate crack-tip fields in pressure-sensitive dilatant materials. The use of Coulomb's yield criterion is justified by experimental results for polymers and zirconia. In the last few years, a systematic study has begun on fracture mechanics under such a yield criterion. Although plane-strain and plane-stress crack-tip fields can be obtained by both asymptotic analyses and finite-element methods (Li and Pan, 1990a, b; Dong and Pan, 1991), anomalous behavior is found beyond a certain range of dilatancy. (Large dilatancy corresponds to strong pressure sensitivity.) This is due to two causes. First, for plane strain, the stress ahead of the crack is purely hydrostatic for large pressure sensitivity. This purely hydrostatic stress is located at the vertex of the yield surface in the stress space where the plastic flow cannot be uniquely determined according to rate-independent plasticity theory. Second, for extremely large pressure sensitivity, the dilatational strain at the crack tip, and especially at the crack faces, may cause material interference. As the material hardening decreases and the perfectly plastic regime is entered, the plastic zone ahead of the crack tip collapses into a thin line at a critical pressure sensitivity. Such a zone collapse, which is not predicted by classical fracture mechanics, has actually been observed in ceria-stabilized zirconia (Yu and Shetty, 1989) and rubber-toughened epoxy.

It is likely that many novel features in fracture mechanics remain to be discovered as the scope of constitutive behavior is broadened beyond the classical types of plastic flow. Such explorations could further extend the enormous success of conventional fracture mechanics in engineering and materials science applications. Solution of these problems will probably require considerable use of the finite-element method, but a more rigorous and

formal mathematical approach that seeks to classify governing equations and to outline the basic types of their solutions near crack-like discontinuities should prove fruitful. The classifications should be based on the parameters in the constitutive equation and the magnitude of strains or stresses. Rigorous theorems of existence and uniqueness typically are lacking.

## LARGE LOCAL FIELD-INDUCED INSTABILITY IN RANDOM SYSTEMS

Although mechanical failure has been intensively studied, it is difficult to model microstructures from which failure can be reliably predicted (Herrmann and Roux, 1990). These microstructures may be quasi-homogeneous and continuous, as in most real materials, or they can be discrete assemblages such as a single bundle or bundles of cables. Many advanced composites in use and under investigation have microstructures between these two extremes. Many methods have been developed to analyze these problems. Continuum theory is usually a good starting point to handle failure in the first type of microstructure, while discrete statistics or probability theory has been more commonly adopted to describe failure in the second type. Neither approach is complete or adequate, even under the best of circumstances, and a combined approach is probably necessary but may not be sufficient for more general problems.

Material heterogeneity has a strong influence on the strength of quasi-homogeneous materials. However, there is no general prescription for finding bounds for the strength of materials in the same way that there is for finding bounds for effective elastic moduli (Li and Duxbury, 1989; Duxbury and Kim, 1991). The reason no such general bounds currently exist is that, due to the size effect that occurs in most statistical models of materials strength, bounds depend partly on volume and volume may depend on microstructure. Which aspects of the microstructure are of importance is still open to debate. The slow convergence to asymptotic behavior typical in the area of materials strength makes the need for analytical input more acute.

The statistics of strength of quasi-homogeneous materials are also anomalous, as is well known from experiment and by weak-link arguments (that is, arguments using spatial variability in local strength). Phenomenological distributions, such as the Weibull distribution, have been adequate to fit experimental data, but it is a challenge to determine the relationship between the parameters in the phenomenological distributions and the microstructure of the materials. Moreover, weak-link arguments do not usually take into account the inhomogeneous strain field inside a material; in this sense, fracture mechanics and fracture statistics are incompatible.

Mechanical failure is merely one example of a large class of instability properties of quasi-homogeneous materials that do not yield in a straightforward manner to solution by the homogenization procedures that have been so successful for modeling effective transport properties and elastic moduli. These and similar instability problems, for example, dielectric breakdown (Duxbury et al., 1990) and resistance problems (Duxbury et al., 1987, 1991; Li and Duxbury, 1987), have received less rigorous attention than effective elastic and transport property problems.

Many attempts have been made to predict the strength of composites using regular arrays of inclusions, the mechanics of which is studied in enormous detail using finite-element methods. These approaches fail because statistical variability, so important in strength problems, is absent from the analysis. At the other extreme, the physics community has recently introduced random network models that treat the statistics in some detail, but the mechanics in less detail. Mathematical analysis is needed to find a balance between the mechanics and statistical variability that can lead to effective prediction of strength and of instability problems.

Statistical modeling of material strength and mechanical failure is closely related to percolation theory. The material is usually modeled as a network or lattice of elements, each of which may be present or absent with a certain probability. These elements have randomly distributed strength or fail in time according to a distribution that is a function of the load history. Monte Carlo simulations using such models yield information on asymptotic distributions for strength and lifetime, scaling phenomena, critical points and transitions, fractal behavior, localization, universality, renormalization, fracture toughness, and interface effects among elements. Although many of the phenomena observed in Monte Carlo simulations can be explained in the context of mathematical statistics, some of them are still not understood.

## DYNAMIC FRACTURE

One of the outstanding open problems in fracture mechanics is that of dynamic fracture. In principle, dynamic fracture occurs in its simplest form in brittle materials, such as ceramics, where elasticity is presumably obeyed. However, even here there are many unsolved problems. These include both one-dimensional and two-dimensional crack propagation problems as well as the more difficult, but more commonly encountered, three-dimensional problems. There now exists a large body of observations on dynamic fracture that are used empirically for failure analysis. A more rigorous interpretation of these observations using dynamic fracture mechanics (Freund, 1990) is a challenge for mechanicians and mathematicians.

At the simplest level, many interesting problems can be posed in the context of one-dimensional models. Even these simple models are most often nonlinear and difficult to solve. It would be very useful to find explicit steady-state solutions of these models. Steady-state solutions of these models can be found for a monoatomic square lattice in two dimensions, but what about other lattices, including diatomic ones? What is the effect of adding disorder to these models, either in the form of spatially random bond strengths or in the form of external perturbations? Solution of these mathematical challenges could provide insight into experimental observations.

One of the major problems in the field of fracture dynamics in two dimensions has already been solved completely. This problem is the problem of finding the stress fields produced on the basis of linear elasticity by a crack moving in a straight line in an infinite two-dimensional plate. More difficult two-dimensional problems that are still unsolved include the linear stability of the crack solutions (linear stability has been checked only with

respect to certain limited perturbations) and problems in plates that have boundaries (the motion of a crack in a strip is understood thoroughly only in the limit in which its acceleration is infinitesimally small). Our ability to tackle three-dimensional problems is even less adequate. The problem of general motion of crack fronts seems so difficult that it is always approached with many simplifications, such as reduction to linear motion in two dimensions. In most practical cases, failure is a three-dimensional phenomenon. Even in a two-dimensional plate, dynamic crack growth usually becomes three-dimensional in nature if the plate is not flat. Patterns and topography of crack propagation and bifurcation, which are of central importance for failure analysis, can be understood only if three-dimensional characteristics are considered. This is not possible at the present time.

Additional problems result from considering the types of nonlinearity present in real materials. From the continuum viewpoint, one can imagine changing the constitutive relations of the material in which the crack moves to include plastic flow or dependence on strain-rate. Effects of dilatancy and even adiabatic heating, which could result in structural changes, may also be important in some materials, for example, polymers. The problems of heterogeneity and residual stresses, typically encountered in real materials, require attention. Finally, as noted in Chapter 3, fracture dynamics may be connected with the "sharkskin" and "spurt" instabilities encountered in polymer melt extrusion.

## LIQUID CRYSTALS

Liquid crystals are "meso-phases" or "meso-states" of matter intermediate between ordered crystals and disordered liquids. On a continuum scale, the material is anisotropic with sufficient disorder in at least one spatial direction to permit flow but with a high degree of order in at least one other direction. The molecules of a liquid crystal are either rod-or disk-like. A liquid crystalline state can be achieved either in a solution (lyotropic liquid crystal) by increasing the concentration of the mesogen (that is, the mesophase-forming substance), or from a melt (thermotropic liquid crystal) by passing through a thermal transition; see, for example, Doi and Edwards (1986). Liquid crystalline materials are commonly described in terms of a director field. When the director is correlated in a single spatial direction, the meso-phase is called nematic; the simplest conceptual picture of a nematic phase is aligned rod-like molecules. Cholesteric liquid crystals are nematic-like structures in which the director has a helical twist. When there is two-dimensional correlation in the fluid phase with periodicity in one of these dimensions, the meso-phase is called smectic; smectic phases, of which there are many, differ according to point group-symmetries.

Liquid crystals are found among both low-and high-molar-mass organic compounds. Low-molar-mass liquid crystals are typically responsive to applied fields and may be optically active; they are used in electronics applications, including displays. Liquid crystal nonlinear optics (NLO) devices are being investigated with respect to possible applications for eye or sensor protection from laser radiation. Optical wave mixing and parametric conversion in liquid crystals have also been demonstrated in the infrared spectral domain, a context in which few other NLO materials exhibit these properties. Polymeric liquid crystals are of two

types: in one, the mesogenic unit is in the backbone of the macromolecule; in the other, it is a pendant side chain. Main-chain liquid crystalline polymers have been shaped into fibers that have specific moduli and tensile strengths superior to steel, high use temperatures, and excellent chemical resistance. They are also under study for possible applications to nonlinear optics (see Chapter 7). Applications in structural materials have been limited by an inability to control microstructure (and hence macroscopic properties). Potential applications for side-chain liquid crystalline polymers are analogous to those for low-molar-mass liquid crystals, except that structural considerations for such side-chain types are incorporated through the polymer backbone.

An equilibrium theory for low-molar-mass nematic liquid crystals developed by Oseen, Frank, and Ericksen describes static configurations in these materials rather well, including configurations that occur under the competing influences of external magnetic and electric fields and solid surfaces to control alignment in these transversely isotropic liquids; see de Gennes (1974) and Ericksen (1976) for references. Quantitative predictions of the theory have been used successfully to optimize performance in sophisticated display devices; see, for example, the articles by Raynes, Needham, Schaefer, and Berreman in Hilsum and Raynes (1983). The lack of a correspondingly successful model for smectic liquid crystals has proved to be a serious obstacle to progress in understanding these more complex thermotropic systems. The close connection between the theory for nematics (in the limit of equal elastic coefficients for all modes of elastic strain) and harmonic mappings from three-dimensional space onto the sphere has received considerable mathematical attention, for example, in Coron et al. (1991).

As recently as the 1960s, non-Newtonian flow of a nematic liquid crystal was ascribed to variations in the degree of orientational ordering induced by flow. However, the dynamic continuum theory for these anisotropic liquids developed by Ericksen and Leslie (Leslie 1979; de Gennes, 1974), which successfully predicted the novel scaling exhibited in shear and Poiseuille flow, clearly demonstrated that non-Newtonian flow effects stem from competition between flow and solid boundaries to control alignment. The study of shear flow instabilities for liquid crystal flow is far more complex than that for fluids modeled by the Navier-Stokes equations (Luskin and Pan, 1992). Analyses based on the Leslie-Ericksen continuum theory explain many flow phenomena, including a number of instabilities in the presence of flow, electric and magnetic fields, and temperature gradients (Manneville, 1990). Indeed, this theory led to the experimental discovery that one can, in certain circumstances, induce Bénard convection in a nematic by heating from above!

There are three main mathematical challenges in this area: (1) development of models that capture the correct asymptotic behavior of the original equations for non-Newtonian flow of nematic liquid crystal; (2) development of better tools to study the bifurcation diagram of spatially extended systems in which the symmetries of the various states are not necessarily known a priori; and (3) development of numerical algorithms to study the evolution following instabilities, the existence of time-dependent a periodic states, and chaotic flow. The so-called amplitude equations used to study the slow, long-distance behavior of non-Newtonian flow in nematic liquid crystals are inadequate to study the evolution between the various structures or the ways in which these structures compete. For example, recent experiments on convection in non-Boussinesq fluids show that the front that

separates a region of hexagonal symmetry propagating into the conduction background is not simple but rather is itself composed of parallel convective rolls.

The formation and motion of orientation defects, both "disinclinations" (singularities in the director field) and "walls" (orientation boundary layers), are of considerable importance. The rheology of nematics often appears to be dominated by the dynamics of defects. Very little is known about defect dynamics, including conditions under which a grain-like multidomain morphology will develop. Developing the theory for defect dynamics remains a rich lode of problems for nonlinear mathematics; see, for example, Coron et al. (1991) and several chapters in Lam and Prost (1991). The nature of nematic order in the neighborhood of a defect and the need to incorporate imperfections of local alignment in a consistent way have been of particular recent interest for both low-and high-molar-mass liquid crystals. For low-molar-mass liquid crystals, these topics have recently been discussed in Pismen and Rubinstein (1992).

Liquid crystalline polymers were introduced in Chapter 3. The properties of nematic main-chain liquid crystalline polymers and the current understanding of their rheology have been reviewed in Ciferri (1991). Morphology has been addressed in detail in Donald and Windle (1992). Thermotropic systems are typically random copolymers, which would not normally be expected to form regular crystals in the solid state. Crystal-like patterns are observed in x-ray diffraction, however, and attempts to explain these patterns in systems with random molecular ordering have required new thinking about the solid phase formation.

A fundamental issue from the point of view of applications of liquid crystalline polymers to structural materials is control of orientation (that is, the director field) in complex processing flows such as those that would be experienced in molding. The outstanding mechanical properties achieved in fibers, which result from the ease of alignment of the nematic director in the flow utilized for fiber drawing—and hence from the covalent bonds of the rigid polymer backbone—cannot be achieved in the more complex flow fields experienced in an injection or compression mold. Liquid crystalline polymer films tend to have excellent mechanical properties in one direction but very poor properties in a direction transverse to that one. The Leslie-Ericksen theory is inadequate for liquid crystalline polymer macromolecules, but a generalization due to Doi (Doi and Edwards, 1986) has had some success. The macromolecular dynamics are dominated experimentally by a multidomain texture that is not explained by existing theory. It is known that, at a critical shear rate, the director field in shear flow undergoes a transition from "aligned" to "tumbling." Both limited experimental observations and scaling arguments based on molecular size considerations suggest that director singularities must be "soft"; that is, the elastic coefficients must depend on the distance to a singularity's core. Thermotropic liquid crystalline polymers of possible commercial interest are multiphasic in the melt. They have a nematic liquid phase and low-melting crystal-like structures that grow on time scales of experimental interest; see, for example, Kalika et al. (1990) and Amundson et al. (1991).

Molded parts of thermotropic liquid crystalline polymers typically show a complex "skin-core" morphology reminiscent of that seen in fiber-filled polymer composites. In the absence of an adequate continuum theory, it has been difficult to address velocity and structure development in complex flows by computation. Simple models of processing flows using the Leslie-Ericksen theory show the possibility of a variety of bifurcations within the

flow field (Rey, 1991), but even these do not consider the multidomain structure of the fluid. Continuum theories for fiber-filled systems, which lack the elastic stresses resulting from the nematic potential, show qualitative changes in flow field structure at even very low fiber loadings (Lipscomb et al., 1988).

## EQUILIBRIUM AND NONEQUILIBRIUM SURFACE STRUCTURE

Experimentalists have benefited from a large body of mathematical and theoretical development in surface structure. The evolution of this work has occurred over a long period of time during which there was little experimental capability to conduct serious tests of the theory. In the last 10 years, a remarkable confluence of theoretical, computational, and experimental capabilities has occurred. The breakthroughs in all three areas described in the following two paragraphs could not have been predicted, and yet the current fruitful synergy of theory, computation, and experiment could not have occurred without the many years of effort that preceded them. The history of how this synergy developed is briefly reviewed here.

The crucial underpinnings of the theory of the equilibrium properties of solid surfaces were established by Gibbs (1876, 1878, 1961) and developed extensively during the first half of the twentieth century, culminating in some beautiful work in the 1950s (Herring, 1951, 1953). Fundamental issues in nonequilibrium crystal growth were investigated in the 1950s (Burton et al., 1951). This early work set the language and framework for interpretation of all contemporary and subsequent experimental work in the field. It was not, however, until the pioneering work of Mullins (Gruber and Mullins, 1967), followed in the 1970s and early 1980s by extensive progress in the understanding of critical phenomena (Nozieres, 1991; Wortis, 1988), that the language and formalism necessary for describing the finite temperature properties of surfaces were developed. While crystal growth is one of the most important problems in surface science, the mathematical and theoretical language necessary for describing growth processes that are not in the steady-state setting of Burton, Cabrera, and Frank (Burton et al., 1951) has advanced only recently and still remains far from complete; see Villain (1991), Villain et al. (1992), and Venables (1992) as well as Chapter 4 and the references therein for additional information about mathematical models for crystal growth.

The 1980s saw breakthroughs in experimental techniques for studying structural properties, most notably scanning tunneling microscopy (Binnig and Rohrer, 1987). These new experimental capabilities now allow direct observations that require recent theoretical formalisms for interpretation and that allow detailed predictions of theories to be tested (Metois and Heyraud, 1987; Eaglesham et al., 1990; Williams and Bartelt, 1991; Alfonso et al., 1992). Great advances in computer power now allow sophisticated theoretical tools, such as Monte Carlo and molecular dynamics simulations, fractal and scaling analysis, and transfer matrix and free fermion calculations, to be applied routinely to data interpretation. In principle, the computing power now available allows experimentalists to present and interpret their results at a level that challenges further theoretical development.

## DEVELOPMENT OF A LATTICE MODEL OF MICROEMULSIONS

A microemulsion is a homogeneous solution of water and a hydrocarbon oil, rendered mutually soluble by a third component that is amphiphilic, that is, that has both a water-soluble (hydrophilic) part and an oil-soluble (hydrophobic) part. The earliest and simplest lattice model of microemulsions was developed in the 1960s (Wheeler and Widom, 1968) and applied in the analysis of experimental results. Although there are now many alternative and more elaborate lattice microemulsion models, as well as a large succeeding and closely related literature on complex fluids, vesicles, microemulsions, biomembranes, and so on, the Wheeler-Widom model is presented in some detail here to illustrate the basic ideas of microemulsion models and to convey a sense of the analysis done in this context.

The Wheeler-Widom microemulsion model envisions three species of molecules in the mixture: AA (oil), BB (water), and AB (amphiphile), with strong repulsions between AAs and BBs. The amphiphile solubilizes the AA in BB by creating micelles (submicroscopic aggregations of molecules; see Figure 5.1): An oil molecule AA is surrounded by amphiphiles, the A ends of which point inward toward the AA and the B ends of which point outward. Since B-B contacts are allowed, such a micellar complex is then readily accommodated in a phase that is primarily BB. The amphiphile has shielded the As from direct contact with the Bs. With roles in the picture reversed, one has BB dissolved in AA.

In this early version of the model, the molecules AA, BB, and AB were imagined to occupy the bonds of a lattice, with only A ends or only B ends allowed to meet at a common lattice site, never both As and Bs. Infinitely strong repulsion between As and Bs was imposed. At the same time, each lattice site became unambiguously identifiable as an A site or a B site, and the model thus became equivalent to an Ising spin model, where, at each site, there is one of two spin states. All the properties of the AA, BB, AB mixture model

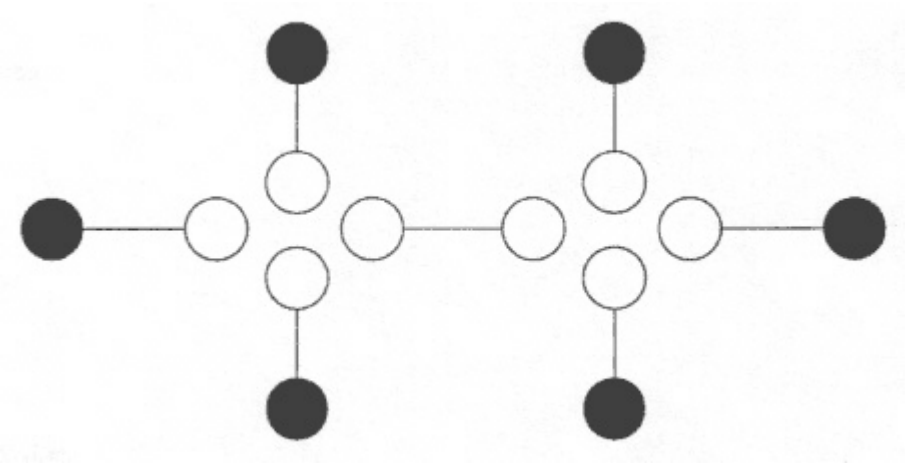

Figure 5.1 Model of microemulsion. The A ends of the amphiphiles are unshaded, and the B ends are shaded. The center A-A structure is an oil molecule that has been solubilized in water.

could then be directly mapped, or transcribed, from those of the thoroughly studied Ising model. That theme is discernible in all of the later models as well.

After the publication of the paper (Wheeler and Widom, 1968) in which the model was first introduced and the analysis begun, much of the analysis was done by B. Widom, K. A. Dawson, and M. D. Lipkin; see, for example, Widom et al. (1988). Lipkin found and classified the many complex ground states (zero-temperature states) of the model (Lipkin, 1988), and Dawson generalized the model in several ways and introduced more sophisticated methods of approximation and analysis for deriving its properties, including low-temperature series expansions, renormalization-group methods, and Monte Carlo computer simulation (Dawson, 1987).

Among the experimentally observed properties of microemulsions for which a model should account is the peak at wave vector between about 0.02 and 0.05 $Å^{-1}$ in small-angle x-ray or neutron scattering. This peak implies an incipient periodicity in an otherwise isotropic solution, which prefigures the liquid crystalline phases that are so prominent a part of the phase diagrams of real water-oil-amphiphile solutions. The scattering functions implied by the model were found by several methods, including a mean-field theory based on the local-mean-field approximation that had already been applied to sketch the phase diagram, and computer simulation. The model gave a convincing account of the origin of the experimentally observed scattering peak. The lattice models later proposed by other theorists have been similarly, and in some cases even more, successful in accounting for the observed scattering.

Such lattice models are now dominant in the theoretical literature on microemulsions. They are notable for the great range and extraordinary subtlety of the phenomena that they are capable of illuminating and for requiring the full battery of techniques of statistical mechanics—analytical and computational—for their application.

## GRAIN BOUNDARIES

Grain boundaries are planer crystal defects that possess complex structures and engage in highly complex behavior. In most cases to date, only primitive models have been developed in efforts to cope with this complexity. There are many areas where more powerful approaches based on more sophisticated mathematical concepts and techniques would be fruitful. A discussion of some of these concepts and techniques is presented in this section. See Chapter 4 for discussion of the dynamics of grain-boundary motion.

### Statistical Issues

An important current issue is how to predict the macroscopic properties of a polycrystal consisting of many different types of boundaries (with different individual properties) distributed throughout the material in different ways (Watanabe, 1992). Two of the many phenomena of interest are intergranular fracture and penetration by boundary short-circuit diffusion. Another issue is how to extract information about the boundaries

present in a polycrystal from a technique such as texture analysis. Further advances in statistical approaches to these questions are required in order to advance the recent concept of "grain boundary engineering." that is, tailoring the boundary structure in order to improve the overall properties (Raj and Sass, 1988).

### Statistical Mechanics Models

Relatively little is known about the fundamentals of how grain boundary structure depends upon temperature. Some primitive models have been developed (Kikuchi and Cahn, 1980). More realistic statistical mechanical models involving new mathematical approaches would be useful. See also two Chapter 8 sections, Microscopic Scale and Potentially Applicable Mathematical Sciences Developments.

### Computer Simulation

Computer simulation has made an enormous contribution to the complex study of grain boundaries; see, for example, Alber et al. (1992). There is a great need for increasing our capacity to work with atomistic simulation models of increasing size using more realistic (that is, more complicated) interatomic force laws (Vitek and Srolovitz, 1989). Mathematicians can be of assistance in developing more efficient ways of minimizing N-dimensional functions and in creating faster and more robust algorithms for the calculations. Effective computer simulation of three-dimensional grain growth in the continuum remains a challenge.

# 6

# AGGREGATES AND DISORDERED MATERIAL

## INTRODUCTION

Many materials are made up of aggregates with characteristic length scales ranging from 0.1 to 10 $\mu$m. These disordered materials can have properties that are not achievable with a homogeneous phase. For example, polymers can exhibit high impact strength by dispersion of a rubbery phase in a glassy matrix. Ceramic parts are fabricated by molding of concentrated suspensions of colloidal particles in an organic carrier fluid followed by removal or reaction of the liquid phase. A fundamental problem is the prediction of bulk properties from the properties and distributions of the individual phases and interphase interactions.

Glasses and other amorphous materials are another class of disordered materials. In contrast to the aggregates just mentioned, they appear to be uniform down to a length scale of nanometers. Many preparation techniques, including melt quenching, vigorous mechanical working, vapor deposition, and reactive component interdiffusion, are available to produce these materials and to frustrate the tendency toward crystallization. Properties depend on the technique selected in a manner that has thus far eluded deep understanding.

## COLLOIDAL SUSPENSIONS

Fluids containing aggregates with complex microstructures arise in a variety of materials applications. Typical microstructures are formed from colloidal and noncolloidal dispersions or through the self-assembly of amphiphilic macromolecules. Examples of materials processed from submicron particles or macromolecular aggregates dispersed in a liquid at concentrations ranging from dilute to closely packed include advanced ceramics, water-based automotive and architectural coatings, polymeric composites synthesized via emulsion copolymerization and from block copolymers, electrorheogical fluids, and nanostructured materials. Noncolloidal systems include structural composites composed of dispersed particles in a polymer matrix. The important properties usually depend on interactions among the particles or dispersed domains through a variety of physico-chemical, hydrodynamic, and Brownian forces (Russel et al., 1990). Free polymer in the liquid phase often moderates the direct interactions. The theory requires accurate predictions of the various interparticle forces via low Reynolds number fluid mechanics, quantum mechanics classical electrostatics, and polymer statistical mechanics. The resulting structure is predicted by equilibrium and nonequilibrium statistical mechanics and computer simulations.

The potential for advances in materials applications lies in constructing robust structure and properties in the multidimensional parameter space characteristic of complex fluids. For example, the end use and application requirements for coatings are numerous and conflicting. Consequently, formulations involve multiple components, with each affecting most of the properties. For relatively simple thermodynamic properties, such as solvent

volatility and viscosity, the theoretical basis has been constructed (Wu, 1987); for nonequilibrium behavior of the fluid phase, such as rheology, and the optical and mechanical properties of the final solid, the basic theory is only partially in place.

A second example currently receiving considerable attention is the formulation and application of electrorheological fluids, which consist of polar particles in a nonpolar fluid. These are normally low-viscosity fluids, but a strong electric field induces dipoles in the particles and creates a volume-filling, particulate network with an elastic or pseudoplastic response to an applied stress. Here the issue is how to control or optimize the magnitude and dynamics of the response (Gast and Zukoski, 1990). The physical phenomena are reasonably well defined, but many-body interactions dominate and the behavior is highly nonlinear.

The fabrication of ceramics by colloidal processing aims for dense packing without large-scale inhomogeneities (Lange, 1989). Consolidation via centrifugation or filtration permits application of forces strong enough to overcome the short-range attractions inevitable between dense particles of 0.1-to 10.0-micron diameter in water or an organic liquid. Given accurate constitutive relations for the permeability and the stress supported by the particulate network, continuum theory describes the evolution of density profiles during the consolidation process (Buscall and White, 1987; Auzerais et al., 1990). The mathematical problem is to solve the highly nonlinear set of equations accurately enough to capture the propagation of several nearly discontinuous transitions in a one-, two-, or three-dimensional spatial domain.

For composite materials, the challenge is to relate the spatial structure and properties of the individual phases to macroscopic mechanical, optical, and electronic properties. Prediction of equilibrium structure via statistical mechanics is being developed for some classes of systems (Bates and Frederickson, 1990; Monovoukas and Gast, 1989). Considerable progress has been made in predicting linear responses through variational and bounding techniques (Torquato, 1990). However, nonlinear behaviors of considerable interest, such as yielding, fracture, and nonlinear optical properties, are still largely untouched.

One might define the challenge for mathematical theory as developing techniques for accurately handling strong many-body interactions. This challenge is complementary to the challenge to physics of describing interparticle forces, equilibrium phase behavior, and polymer thermodynamics. Many aspects of the subject have advanced to the point that sophisticated mathematical analysis and numerical solution procedures are needed to provide the quantitative predictions necessary to keep up with the physics and experimental investigations in this area. As is pointed out in Chapter 8, this is the case not just for this area but also in many other areas of materials science.

One can identify a number of relatively advanced approaches to this class of problems:

### Stokesian Dynamics

For colloidal problems, significant movement occurs only after many thermal

fluctuations. This permits analytical integration of the equations of motion on the diffusion time scale and produces equations for the displacement of particles due to random Brownian events and deterministic translation under interparticle and external forces. The difficulty is that hydrodynamic interactions essentially couple all particles within a simulation cell. These effects have been captured with a methodology known as Stokesian dynamics at the expense of very large matrix inversions (Brady and Bossis, 1988). An efficient code that runs on a workstation now enables simulations in three dimensions with a reasonable number of particles.

### Computational Microhydrodynamics

The equations of motion in the absence of inertia (the usual case for materials applications) are fully linear and can be recast as contraction mappings and iterations to a fixed-point solution. The hydrodynamic force is shape dependent, and so the basic problem for a particle suspension is a three-dimensional boundary value problem with complex and evolving geometry. Lorentz formulated the problem more than 100 years ago as a two-dimensional boundary-integral equation; the result is a Fredholm integral equation of the first kind. For the complex geometries of interest, the ill-posed nature of the problem manifests itself as ill-conditioning, and convergence to the numerical solution cannot be obtained merely by refining the discretization.

The existence of a velocity representation that yields a Fredholm equation of the second kind has been established (Power and Miranda, 1987), and a solution methodology, the completed double layer boundary integral method, has been developed (Kim and Karrila, 1991). The iterative strategies map naturally to emerging high-performance parallel computer architectures (Fuentes and Kim, 1992). Work is in progress, for example, to simulate a system with 1 million particles using 80 million boundary elements on the CM5 parallel supercomputer.

### Nonequilibrium Statistical Mechanics

Approaches developed for molecular fluids have been applied rather superficially to colloidal problems, generally ignoring hydrodynamic interactions and simply adopting conventional approximations for dynamical couplings (Hess and Klein, 1983). Recent alternative closures, analogous to well-established equilibrium closures, convert the Smoluchoski equation to an integrodifferential equation for the nonequilibrium structure. Dynamical properties follow from the structure via straightforward integration of the appropriate forces or fluxes (Russel, 1992). Work is under way to test the accuracy of this approach against simulations and experimental data for model systems. If the approximations prove accurate, then mathematical analysis and efficient numerical solution of these coupled integrodifferential equations become important.

### Variational Techniques

For materials with static structures partially characterized by statistical measures, mechanical and electromagnetic properties satisfying linear field equations can be bounded rather accurately by variational techniques (Torquato, 1990; Milton and Kohn, 1988). As with the preceding nonequilibrium statistical mechanics case, testing against computer simulations is usually important, but the results here have the potential of greater generality.

### Self-Consistent Field Theories

Approaches formulated for polymer statistics by Edwards, Helfand, and de Gennes in the 1970s have been applied with considerable success to a broad range of interesting problems, including the prediction of microphase separation in diblock melts. With the discovery of the strong stretching approximation, apparently by Semenov, the subject has exploded mathematically. A range of classical techniques, involving asymptotic expansions and conformal mappings complemented by computational solutions, have yielded elegant and relatively simple predictions of phase behavior (Ball et al., 1991b; Kawasaki and Kawakatsu, 1990). Many interesting problems remain, such as the incorporation of nanometer-sized particles into these melts to produce nanocomposites with controlled structure.

## EQUILIBRIUM STRUCTURE

The thermodynamic equilibrium of a system is described by specifying the number, composition, elastic state, and spatial configuration of the phases present. Equilibrium not only defines the end-state of an evolving system, but is also useful in trying to describe local features of the system during evolution, such as interface intersection angles, bulk compositions at interfaces, and particle shapes. Two examples of challenging equilibrium problems are mentioned in what follows, as well as the problem of inferring three-dimensional configurations from a two-dimensional cross-section.

The characteristics of phase diagrams are qualitatively altered by elastic stresses. Effects include radical alterations in the phase rule and in the construction of phase diagrams, restricted validity of the common tangent construction, and the presence of multiple stable equilibrium solutions for a given set of experimental parameters. It can be shown (Johnson and Muller, 1991) that the long-range elastic forces arising from differences in lattice parameters between phases or from an externally applied load permit several stable equilibrium states that depend on the mechanical boundary conditions and system geometry. A catalogue of possible features, similar to what is known for fluid or unstressed systems, is not known. A geometrical description of such possible phase diagram constructions would be most helpful.

In the absence of stress, the equilibrium morphology of a particle in a matrix is simply a minimal surface problem. In contrast, in the presence of elastic stress, the equilibrium

shape is found by minimizing a certain combination of the interfacial and elastic energy of the system. Very few solutions to this variational problem have been found wherein the particle morphologies are not constrained to be of a certain class of geometric shapes. Recently, solutions have been obtained wherein the particle shapes have not been so constrained but have been limited to a numerical determination of the particle morphologies in two dimensions (Johnson and Voorhees, 1988). Much work remains to be done in this area.

It is often not possible to perform structural measurements directly on 3-D microstructures. They are performed on a 2-D section of the specimen and then are reconstructed for 3-D by a set of rules known as stereology. Thus, for cellular structures it is possible to reconstruct (roughly) a 3-D cell size distribution by the size distribution in a 2-D section. The usual assumptions are that the cell shape is close to spherical and the cells are randomly distributed in space (Underwood, 1970; Exner and Hougardy, 1988). Both assumptions fail for densely packed structures. Moreover, for such structures the topological aspects of packing are of interest. There is, at present, no "topological stereology" to reconstruct 3-D topological structures from those of 2-D sections. Even for the case of Voronoi mosaics, the problem is open; see Hermann and Lorz (1992) and the references therein. The typical questions are the following: What are the average numbers of faces, edges, and vertices per cell? What are the distributions of the number of faces, edges, and vertices per cell? The problem of topological classification of 3-D cells is also important (Weaire and Rivier, 1984; Rivier, 1985; Fortes and Ferro, 1985).

## EFFECTIVE MODULI OF COMPOSITES

Composite materials are interesting precisely because their overall properties are not just a simple average of the properties of the components. Indeed a composite can sometimes exhibit properties completely unlike those of its constituent materials. For example, transparent glass containing a suspension of spherical gold particles is not gold in color, but rather red. In fact, a well-known approximation formula for calculating the optical properties of such suspensions (known as the Maxwell-Garnet formula) led to an understanding of how the Venetians achieved the colors in their glasses; see Landauer (1978), which contains a good historical survey of the field.

Sometimes a composite can combine desired properties of one phase with other attributes of a second phase. The simplest example of this is a laminate of conducting sheets of metal alternating with insulating layers of rubber. The composite combines the conductivity of the metal in directions parallel to the layers with the insulating properties of the rubber in directions perpendicular to the layers. Formulas abound in the literature for calculating effective properties—such as the effective conductivity, elasticity, and piezoelectric and thermoelastic tensors—of simple laminates. But most of these formulas are derived under restrictive assumptions about the isotropy of the phases or their orientation relative to the direction of slicing. It is interesting, and perhaps illustrative of the potential for mathematicians to make significant contributions, that general formulas for calculating the effective properties of simple laminates have been developed only in the past

10 years and that these were developed by mathematicians (Tartar, 1985; Francfort and Murat, 1986); see Chapter 8.

A surprising example of what can be achieved with a careful choice of composite microstructure is elastically isotropic composite materials with negative Poisson's ratios, that is, materials that are easily compressed but that are resistant to shear (Lakes, 1991; Milton, 1992). Contrary to usual experience, such materials get fatter as they are stretched. They are constructed from a stiff phase and a compliant phase and combine the resistance to shear of the rigid phase with the ease of compression of the compliant phase. The existence of such materials had been a subject of debate for nearly a century. The fact that they were discovered only relatively recently points to the need for a systematic approach to finding what sort of effective behavior is possible and to finding microstructures that achieve this behavior. Mathematicians have begun to embark on this program and have achieved considerable success. Not all the structures proposed by mathematicians are realistic: for example, they may involve microstructure on widely separated length scales that would be difficult for an experimentalist to reproduce. But the analysis does provide guidelines for making more realistic structures. One area that needs exploration is the effect of adding surface-area penalizing terms. Once these are introduced, the resultant optimal microstructures are bound to be much more realistic.

In other applications, one is given a specific composite with a microstructure that is partially known and the objective is to estimate its properties. For example, one might want to calculate the fluid permeability of a porous rock, a problem that has obvious applications in the oil industry. Or one might want to calculate the elastic constants and hence the acoustic wavespeeds in a polycrystalline aggregate; this is of interest to geophysicists studying earthquakes (Watt et al., 1976). In this context, one needs to identify appropriate geometric quantities that are strongly correlated with the relevant effective property of interest. Correlation functions provide a natural description of composite geometry, but not all information contained in the correlation functions is relevant to the determination of the effective property. One task for mathematicians is to filter out from the correlation functions relevant information. Many effective moduli, such as effective elasticity and conductivity tensors, are insensitive to the size of the microstructure, so that it is natural to extract from the correlation functions quantities or functions that are insensitive to the size of the microstructure. Examples include geometric parameters that enter series expansions (Milton, 1981; Torquato, 1991) and measures defined on surfaces of spheres that are obtained by Radon transformations (Willis, 1981) or by integration of the usual correlation functions along rays in Fourier space (Avellaneda, 1987a; Tartar, 1990).

Other effective properties can be correlated with the effective property of primary interest. For instance a well-known empirical relation provides a correlation between the electrical conductivity of a porous rock and its permeability. This empirical relation is useful because the electrical conductivity is much easier to measure than the fluid permeability. Some bounding methods provide a means whereby one property can be correlated with another through rigorous inequalities (Cherkaev and Gibiansky, 1992).

Experimentalists and scientists working in other fields have often developed approximation formulas for effective properties based on empirical evidence or a heuristic model. Here mathematicians can help and have helped by placing these approximation

formulas on a rigorous basis by showing either that they correspond to the moduli of certain geometries (Milton, 1985; Avellaneda, 1987b) or that they have the correct asymptotic behavior. Moreover, mathematicians have identified cases where these approximation formulas break down.

There are many other areas of practical importance where mathematicians can make a significant impact. To name a few, we need a better understanding of wave propagation in composites, the effective properties of cracked solids and of multiphase fluids and slurries (where the composite geometry changes with time), and the response of composites that display nonlinear effects such as plasticity or fracture. Not only do these problems have interesting applications; they also have an intrinsic mathematical appeal. The surprising aspect of the subject is the breadth of mathematical techniques that have been introduced to solve current problems, and correspondingly the need for new techniques to address unsolved problems (see Chapter 8).

## Future Directions

There is a long history to the study of composite materials. By the early 1970s, the field was considered rather mature, at least as far as linear materials were concerned (Willis, 1981). Over the past 10 years, however, the field has seen a renaissance. There are basically three reasons: (1) a focus on new types of questions, motivated by applications to structural optimization; (2) the introduction of new analytical methods for bounding effective moduli; and (3) the development of new computational methods for simulating the behavior of random media.

When the diameter of the particles in a composite shrinks to zero, the properties of the limit material can be analyzed by studying the limit of solutions of the partial differential equations associated with the elastic moduli of the two phases of the composite. The limit concept for the composite material is called G-convergence. A related (and more recent) concept is H-convergence (Tartar, 1990), and one of the basic tools used in developing this approach is compensated compactness; it allows one to go to the limit, say $A_nB_n \rightarrow AB$, even though $A_n$ and $B_n$ do not converge to, respectively, $A$ and $B$ in the standard sense.

Some of the recent mathematical work has been devoted to "cleaning up" points of confusion. For example, there was controversy in the physics literature over whether one could discuss composites without a separation of scales (microscopic vs. macroscopic); this has been resolved by the theory of G-convergence (Zhikov et al., 1979). Another important development has been the creation of a rigorous theory of random composites (Papanicoloau and Varadhan, 1982).

Hashin and Strikman (1963) have developed a variational principle that enabled them to derive optimal upper and lower bounds on the elastic moduli in terms of the volume fractions of the two phases of the composite. However, when additional information about the composite is known, such as some geometric features of the second phase, or when the elastic moduli of the two phases differ greatly from each other (that is, the composite is very heterogeneous), the Hashin-Strickman bounds are too crude. Some of the mathematical work has explored connections between bounds for effective moduli and classical questions

in the calculus of variations (Kohn and Strang, 1986).

Of more direct interest to materials science, however, are the new methods for bounding effective moduli introduced by mathematicians and mathematically minded scientists from other fields. They use (1) Lagrangians or lower semicontinuous quadratic forms to derive new variational principles from old ones (Avellaneda et al., 1988; Milton, 1990), (2) methods based on function theory (Milton, 1991), and (3) new applications of the Hashin-Strikman variational principle (Avellaneda, 1987a; Allaire and Kohn, 1992). These techniques have led to many new bounds on effective moduli, often bounds that are in fact optimal. It will take much more work, however, to obtain a full understanding of their power and their limitations.

The new mathematical methods, including G- and H-convergence, compensated compactness, statistical mechanics of distribution functions, percolation theory, and renormalization group methods, have thus far been developed primarily for linear models of material behavior; it is a major challenge for the future to apply them in nonlinear settings as well. Coupled-field problems, for example, piezoelectricity, have only begun to be studied from this viewpoint; further progress in piezoelectricity could lead to the design of better actuators and other practical devices. Most of the recent mathematical activity has been concerned with bounds in terms of volume fractions only and incorporates no further statistical information about the microstructure. This sort of bounding is natural for structural optimization, but there are other situations where statistical information is available and could improve the bound computations. We must learn to incorporate more statistical information into new bounding procedures.

An important direction of research is the development of improved algorithms for calculating the bulk effective properties of composite media, especially in challenging situations such as when the system is nondilute, when the contrast (that is, the ratio of moduli) is very different from the contrasts of situations already considered (Dal Maso and Dell'Antonio, 1991), and when the microstructure is not completely specified, as in disordered media. A new direction of research that has started developing recently is nonlinear properties of composites. One of the most important types of nonlinear behavior in materials is mechanical or electrical failure or breakdown. Failure is often the result of small, macroscopic defects in an otherwise homogeneous material. Such a material can be considered to be a dilute composite. Despite some progress that has been made, there is a pressing need to develop new, effective mathematical methods for studying and calculating the macroscopic nonlinear behavior of such materials. Some of the more recent relevant references are Bensoussan et al. (1986), Duxbury et al. (1987), Lee and Duxbury (1987), Stroud and Hui (1988), Bergman (1991), Blumenfeld and Bergman (1991), Chakrabarti (1991), Weinan (1992), and Evans (1992). There will be many more interesting new developments in this area in the next few years.

Colloidal suspensions are discussed in the Complex Fluids section of this chapter. Homogenization methods have been applied in recent years to colloidal suspensions (Fleury, 1980; Levy, 1983, 1985; Sancez-Palencia, 1985, 1987). It is clear, however, that the models are too simple and that, for more realistic models, new ideas will be needed to derive good estimates of the effective physical parameters.

Microcomposites are interesting nonlinear materials in which local field effects are

important (Stroud and Hui, 1988; Blumenfeld and Bergman, 1991). Since the field inside a particle, which is small compared to the wavelength, is different from the field in the surrounding medium, if the particle is irregularly shaped, the electric field in it is highly nonuniform and concentrated in regions of large curvature. This electric field strongly influences both linear and nonlinear optical properties. In the mathematical description of the problem, a transcendental equation including both linear and nonlinear susceptibility always results. Thus far it has been solved only approximately and only for the most simple shapes. Local fields in irregular disordered nonlinear media should be analyzed further.

## OPTIMAL COMPOSITES

The goal of structural optimization is to choose the shape or composition of a structure so as to optimize some feature of its elastic behavior. A typical goal is to minimize the weight subject to a constraint on the work done by a given load.

This topic has been considered at length in the mechanical engineering community (Pironneau, 1984; Haftka and Grandhi, 1986). There is what might be called a "standard approach": (1) guess an initial design; then (2) discretize the associated elasticity problem; then (3) use sensitivity analysis and front-tracking methods to improve the design incrementally.

An alternative approach emerged in the mathematical literature of the 1970s. The main idea is to admit as design components not only the originally given materials, but also composites that can be made from them. This process, known as relaxation, does not change the essential design problem (Lurie and Cherkaev, 1982; Murat and Tartar, 1985; Kohn and Strang, 1986). The relaxed formulation has several advantages over the more traditional one: it is easier to solve numerically, it tends to have fewer local minima, and there is a satisfactory mathematical existence theory.

Relaxation is now attracting the attention of a growing community of engineers (Bendse and Kikuchi, 1988; Suzuki and Kikuchi, 1991; Bendse and Mota Soares, 1992). For the most part, it is viewed by engineers as a scheme for "topology optimization."

Thus far, most work in optimal composites has been on compliance optimization problems involving a single loading condition. More work (and new methods) will be required to handle design criteria other than compliance and structures subject to multiple loads. The optimal designs obtained this way naturally make use of composite materials, which may be difficult to manufacture. It is therefore natural to seek methods for avoiding the use of composites. Some promising methods have been proposed and explored numerically, although they do not yet have any basis in mathematical theory.

Should this work be viewed as "materials science"? Some might say not, and it is certainly not in the mainstream of conventional materials science. But its basis is an application of a materials science concept, namely, composite materials, especially those with optimal microstructures, to the apparently unrelated area of structural optimization. Also, it has led to the development of new methods for bounding effective moduli (see the subsection Future Directions above) and of connections with the modeling of coherent phase transitions (see the discussion of martensite materials in Chapter 4), both of which are

mainstream topics. The idea that microstructure is important along with shape is by no means new to materials science; see Ashby (1991) for a thoughtful discussion. The essence of the new approach to structural optimization is the recognition that optimizing microstructure and optimizing shape are really the same problem on different length scales.

## GLASSES AND OTHER AMORPHOUS SOLIDS

Solid materials that lack periodic or quasiperiodic order but are homogeneous above the nanometer length scale constitute an important class of substances that offer many technological advantages. These advantages include corrosion resistance, modified magnetic and elastic properties, and ease of fabrication. Glasses are a subset of amorphous solids that are formed by supercooling liquids through their glass transition point, below which flow processes become immeasurably slow. Other disordered solids are produced by mechanical working or strong radiation damage of crystalline materials, by interdiffusion of distinct components, and by vapor-phase deposition. In all cases, the product of these processes is a metastable form of matter. As a result of this metastability, the amorphous material has properties that not only depend on the ambient conditions (temperature and pressure), but also can depend on aspects of the history of the material, such as the conditions of formation and subsequent thermal conditions; for background and more details, see, for example, Angell and Goldstein (1986), Phillips (1982), and O'Reilly and Goldstein (1981).

Computer simulation has begun to play an important role for research in glasses and other disordered solids. Computer simulation is now being used to classify the types of short-range atomic order that appear, in contrast to that of the corresponding crystalline substances. However, these simulations have suffered from a severe time-scale problem: glasses and other amorphous solids exhibit dynamical processes over an extremely wide range of characteristic times. At the short end ($10^{-13}$ to $10^{-12}$ s), atoms vibrate about mechanical equilibrium sites; such motions (possibly quite anharmonic) are well represented by present-day computer simulations. At the other extreme are relaxation processes, apparently involving rearrangements of large numbers of atoms to lower overall energy, that may have characteristic times of days, months, or years. Because the computer simulation processing time scale for molecular dynamics is approximately 1015 slower than "real" time, the observation and description of relaxation processes in glasses via molecular dynamics computer simulation are, unfortunately, far beyond reach at present. Novel conceptual insights are required to accelerate sluggish and rare relaxation processes (Berg, 1993), perhaps by temporarily switching from one potential energy surface to another with suppressed barriers.

It is desirable to develop a rational predictive capability to determine what materials will resist crystal nucleation, supercool easily, and pass into a rigid glassy state at a sharply defined glass transition temperature. Ideally, the only input should be the chemical structure of the substance under consideration. Such predictive capacity is currently lacking.

Empirically, the relaxation of a wide variety of mechanical, thermal, electrical, and spectroscopic properties in glasses can be described by a "stretched exponential" function of time, that is, a negative exponential of time raised to a power between 0 and 1. Some

theoretical models for such stretched exponential behavior have been advanced, but their relation to and possible deduction from atomic-level Hamiltonians continue to remain obscure. Rigorous mathematical analysis of such connections or proving their strict absence would be a valuable contribution.

Mathematicians might be able to supply basic and extremely valuable insights to this field. For example, it would be important to establish or obtain the following results for some nontrivial class of intermolecular potential functions (e.g., pairwise additive spherical interactions):

- Prove that the lowest overall potential energy, in the large system limit, is attained for a periodic spatial arrangement of molecules (a crystal).
- Prove that if periodicity is strongly disallowed in some suitable sense, that amorphous molecular arrangements still exist as relative minima of the potential energy function.
- Develop rigorous bounds on the rise in potential energy that results from imposition of the nonperiodicity constraint in the preceding result.
- Enumerate the inequivalent potential energy minima, at least in the sense of exponential rise rate in the large system limit, or as rigorous bounds on this rise rate.

# 7

# PROCESSING, FABRICATION, AND EVALUATION

## INTRODUCTION

Materials processing and fabrication involve not only large-scale changes to materials associated with manufacturing (for example, solidification, sintering, joining, and mechanical modification) but also the creation of artificially structured advanced materials with properties tailored to meet specific criteria. This chapter presents an assortment (that is far from comprehensive) of materials processing, fabrication, and evaluation topics that involve applications of or offer research opportunities in the mathematical sciences. As mentioned in the first chapter, the committee organized this report's topics by various themes. Two topics, processing of semiconductor chips and nonlinear optical (NLO) materials, involve considerable common ground; since the topic of NLO materials does not quite fit with the themes of the previous chapter, it has been included in this one. For additional processing, fabrication, and evaluation background and topics, and a description of general materials research challenges, see Chapter 4 and Appendix B of National Research Council (1989); see also Friedman et al. (1992a) and Szekely (1993).

## PROCESSING OF SEMICONDUCTOR CHIPS

The first step in the processing of semiconductor chips is the production of crystals. Typically one inserts a seed crystal into a silicon melt and slowly extracts it from the melt. Under appropriate temperature and dynamic conditions, the crystal grows (Czochralski's growth) as it is pulled out. Other methods of growing crystals are the Bridgman and float-zone methods. The mathematical description of the model is based on the Navier-Stokes equation with a free surface, the boundary of the melt. See Langlois (1985) and Jones (1988); see Brown (1988) for an excellent review article on crystal growth processing; also see the section Morphological Stability in Chapter 4.

The crystals used for producing semiconductor chips are cylindrical with a diameter of 8 to 20 cm. Each crystal is sliced into discs or wafers of a few millimeters thickness. On each wafer, many rectangular chips with side lengths between 0.1 mm and 1 cm will be produced. With present technology, there can be up to several million "devices" on each finished chip.

Laying out the devices on the chip consists of several "photolithographic" steps. These include (Friedman et al., 1992a): (1) oxidization of a thin layer of the silicon wafer; (2) coating uniformly with photoresist, a polymeric fluid sensitive to light; (3) covering the wafer by a patterned mask and exposing to light (the photoresist that is exposed to light "develops"; that is, it polymerizes, or hardens); (4) washing away uncovered areas of the photoresist layer, thereby leaving the silicon oxide layer bare; (5) etching out the bare portions of the silicon dioxide layer, down to the silicon substrate, by hydrofluoric-base acid that attacks neither the hardened photoresist nor the silicon; and (6) stripping off the

hardened photoresist. Devices are fabricated by incorporating dopant impurities either by direct diffusion or ion implantation and annealing. During subsequent processing, further diffusion takes place.

Many of the steps described above have been modeled to various degrees of accuracy by partial differential equations that describe the relevant physics. Modeling of diffusion of impurities in a nondeforming single crystal is done today with considerable sophistication that can take into account point defect interactions (Cole et al., 1990; Rorris et al., 1991). The theory of diffusion in a polycrystal, where diffusion occurs mostly along the grain boundaries (Tseng et al., 1992), and in the presence of external stresses, is not, however, adequately developed. Stresses and elastic deformations have long been investigated by applied mathematicians and mechanical engineers. There is a need to combine expertise and develop methods for the cross-coupled problems of diffusion and deformation in complex materials.

Modeling oxidation of silicon (Chin et al., 1983; Peng et al., 1991) poses problems of moving boundaries and the generation of plastic flow by stresses. Stresses are inherent in the process because oxidation yields an oxide that would normally occupy more than twice the volume of the silicon that is consumed. This volume expansion leads to flow and a shape change. In turn, the stresses affect the rate of oxidation, the diffusivity of oxygen, and so on. Self-consistent solutions are needed. Under high stresses and high temperatures, the oxide behaves like an incompressible fluid. To date, there is no completely satisfactory mathematical model for calculating the pressure during incompressible fluid flow. There are, however, promising mathematical developments for simpler models (Tayler and King, 1990; King, 1993).

Other areas of semiconductor processing have been modeled to different degrees of sophistication, but major problems remain to be solved. Examples include the modeling of etching (Kuiken, 1990), of the exposure of photoresist (Gerber, 1988), and of warping caused by titanium silicide growth (Willemsen et al., 1988; Friedman and Hu, 1992).

Overall, modeling of processing steps in microelectronics currently has substantial gaps, especially in the areas of deposition, etching, and lithography. The works referenced above constitute a starting point. Considerable amounts of information are generated by atomic-scale theories, but this knowledge is yet to be folded into a theoretical description at the appropriate mesoscopic length scales of process modeling.

There are various physical processes, not well understood, that contribute to variability of the performance of semiconductors. These include dislocations that develop during doping, diffusion of dopants in polycrystals, and elastic strain created during the various steps of depositions. One highly developed theory that seems relevant to semiconductor performance variability is the theory of dislocations (Hirth and Lothe, 1982; Eshelby, 1975). The analysis of one dislocation loop has been studied numerically (Borucki, 1993) and mathematically (Friedman et al., 1992b). However, nucleation of dislocations and the dynamics of the aggregate of dislocations remain open problems that mathematical sciences research could help to solve.

There has been a surge of mathematical analysis in the modeling of semiconductor devices, with increasing attention to small devices. A few representative recent papers are Poupaud (1993), Schmeiser and Unterreiter (1993), and Ward et al. (1993).

## AMORPHOUS SEMICONDUCTORS

In polysilicon, the silicon grains are arranged in a random polygonal structure. A typical size of a grain is 1,000 to 10,000 Å, whereas the distance between two neighboring silicon atoms is 2 to 3 Å. In amorphous polysilicon, the atoms are typically in groups of 4 to 6 atoms. In order to pacify the dangling bonds, hydrogen is added (about 20%). Thin-film transistors fabricated from hydrogenated amorphous silicon are now used in flat panel displays such as in fax machines. The mathematical model is an extension of the equations for a silicon semiconductor device; it includes diffusion equations for the trapped holes and electrons, which depend on the density-of-states and the occupation functions (Shaw et al., 1991). There are various experimental power laws suggested by simulations (Shaw and Hack, 1988), but rigorous mathematical justification is needed.

## CASTING

The process of producing an object of a desired shape through the injection of fluid into a mold followed by the solidification of the fluid within the mold is called casting. Casting is a phenomenon that involves two phases, solid and liquid, and the transition between them. There are various theories modeling the phase transition. Perhaps the best known is the Stefan problem formulation that describes the transition from solid to liquid by a sharp boundary. This interface is "free" in the sense that its location in space varies in time and it is one of the unknowns of the problem. There is a considerable amount of mathematical literature dealing with Stefan problems (Kinderlehrer and Stampacchia, 1980; Luckhaus, 1990; Friedman, 1992); see also the discussion of dendrites in Chapter 4 and the references therein, and the section Macroscopic Scale in Chapter 8.

Other models consider the boundary between solid and liquid to be a "mushy" region (addressed in the section Mushy Zones in Chapter 4). In order to gain a better understanding of the mushy region where both solid and liquid phases coexist, a molecular theory was developed by J. W. Gibbs; see, for example, Gibbs (1961). In this theory, an order parameter $\varphi$ is used. The temperature $T$, together with $\varphi$, satisfy a nonlinear parabolic system with various unspecified parameters. As these parameters go to certain limits, one formally obtains a version of the Stefan problem with surface tension appearing in one of the free-boundary conditions (Caginalp, 1989). This new problem is under current mathematical investigation (Chen and Reitich, 1990; Luckhaus, 1990), and it yields more realistic results regarding dendritic growth during the casting process. Nonetheless, this approach does not explain more complicated but important phenomena such as second-order dendritic growth; see also the subsection Dendritic Growth in Chapter 4. Further mathematical models and ideas are needed to tackle this problem.

A good review of mathematical modeling for ingot solidification, continuous casting, and rapid solidification is given in Szekely (1990).

## POLYMER PROCESSING

The processing of polymer materials involves mixing, reaction, and flow in the liquid state and shaping in the solid state. Some of these issues are addressed in Chapter 3. Mathematical analysis and computation have played major roles in understanding polymer processing; see references in the Entanglements, Reptation, and Elasticity section of Chapter 3, and the recent reviews in Denn (1988) and Larson (1992). Asymptotic methods are addressed in Pearson (1985), and computational issues are investigated in Pearson and Richardson (1983) and Tucker (1989). The simulation of non-Newtonian fluid flow, heat transfer, and phase-change in a deformation field have received the greatest attention. Outstanding mathematical sciences research issues in these contexts are summarized in Chapter 3.

## OTHER PROCESSING

There are many other materials processing settings where opportunities for mathematical sciences research exist. Optical fiber processing involves several steps that offer challenges: soot deposition (Chen, 1989), sintering (Sherer, 1979), and fiber drawing (Meyers, 1989). In particular, the fiber-drawing step is modeled as a free-boundary problem for a fluid with vorticity. This situation has been recently analyzed for a somewhat idealized flow (Liu, 1993).

Another context presenting mathematical research challenges is electrochemical machining. Here, metal is removed from an anodically polarized workpiece via erosion caused by an electrical discharge that is produced in an electrolytic solution. The process, used for smoothing surfaces and for drilling holes in hard materials, is a focus of ongoing research (McGeough and Rasmussen, 1990). In this setting, the mathematical formulation of the shape of the desired product is a free boundary; see Lacey (1990).

## MIXING

Mixing processes are ubiquitous in materials technology. Mixing can involve two or more fluids, often of very different viscosities, and granular or powdered solids. Mixing processes are often accompanied by a breakup of droplets and other fluid microstructures, aggregation of colloidal particles, and diffusion-controlled reactions in complex flows. The range of mixing practices has been surveyed in a number of texts and monographs, for example, in Harnaby et al. (1985). For centuries, developments in the field of mixing were empirical. Recent developments spurred by results in dynamical systems theory are providing a foundation for various aspects of the subject, particularly for slow flows of the type encountered in blending of viscous liquids; see the overviews and references in Ottino (1989, 1990) and in Ottino et al. (1992).

There are significant differences between standard studies of dynamical systems and issues of concern in mixing. The studies usually focus on long-time or asymptotic behavior,

for example, convergence to attractors in dissipative systems, while the desire for rapid mixing places interest on short-time behavior. It is desirable to have as much chaos as possible, and so perturbations must be large, limiting the usefulness of analytical tools based on small perturbations away from integrability. Finally, global behavior is much more important in mixing than in ordinary studies of dynamical systems.

One of the most important problems in mixing is to devise suitable measures for the intuitive concept of "goodness of mixing." A related issue is to connect mixing measures to the fluid mechanics of the mixing process. Such connections can be investigated using tools inspired by the concepts of scaling and multifractals as well as using the statistics of multiplicative processes with weakly correlated steps.

The obstacles to a purely computational attack on problems involving chaotic flows are well illustrated by the example of mixing of two highly reactive substances. A direct simulation of the coupled mixing-diffusion-reaction process might be impossible even in flows where the velocity field is relatively simple. The interface of reaction becomes nearly impossible to track when the stretching ratio exceeds 105, and if the reactions are diffusion controlled, the important processes are those within the striations (that is, at the smallest scales) and are lost with coarse graining.

## MATHEMATICAL MODELING IN QUANTITATIVE NONDESTRUCTIVE EVALUATION

Nondestructive evaluation (NDE) is just one example from the class of inversion problems, such as those posed by x-ray and neutron diffraction and electron microscopy, arising from characterization or evaluation techniques of tremendous importance in materials science. Over the last decade, one of the most significant advances in NDE has been the evolution of NDE from a conglomeration of empirical techniques to a well-defined field of interdisciplinary science and engineering. NDE is an inverse problem that is generally ill posed. In the course of this development it has become well recognized that NDE should be based on quantitative models of the measurement processes of the various inspection techniques. The principal purpose of a model is to predict the response of the measurement system to specific anomalies in a given material or structure, for example, cracks, voids, distributed damage, corrosion, and deviation in material properties from specifications. A good model includes the configuration of the probe and the component under inspection as well as a description of the generation, propagation, and reception of the interrogating energy. For ultrasonics, this description requires computation of the transducer radiation pattern, refraction of the beam at surfaces, the beam profile, and the propagation characteristics in the host material, including effects of material anisotropy, attenuation, and diffraction losses. Detailed modeling of field-flaw interactions, which generate the response function of the measurement system, must also be included as well as information on conditions that produce statistical noise and add uncertainty to the results. A well-constructed model should be able to predict specific responses of instruments to anomalies in complex materials and structures as well as to "standard" flaws placed in various calibration blocks.

A number of models have been formulated in the past several years for different inspection techniques (Gray et al., 1989). For practical applications, the challenge lies in making approximations that permit the computations to be tractable while retaining sufficient accuracy so that the engineering applications are not compromised.

Numerical results based on a reliable model are very helpful in the design and optimization of efficient testing configurations. A good model is also indispensable in the interpretation of experimental data and the recognition of characteristic signal features. Parametric studies can be carried out with relative ease for models, which facilitates an assessment of the probability of detection of anomalies. A model of the measurement system is a virtual requirement for the development of an inverse technique based on quantitative data. Last but not least, a model, the accuracy of which has been tested by comparison with experimental data, provides a practical way of generating a training set for a neural network or a knowledge base for an expert system.

An essential component of a measurement system model for quantitative ultrasonics is the modeling of the interaction of ultrasound with a defect. Of special interest are crack-like defects. A mathematical crack is a surface in a solid body that cannot transmit surface tractions (that is, surface tension from, for example, adhesive friction). Under the influence of incident ultrasound, a crack becomes a surface of displacement discontinuity. Considerable progress has been achieved in the mathematical formulation and solution of crack-scattering problems (Achenbach, 1992). The direct problem is well understood, but further progress is required in the inverse problem of determining the size, shape, and orientation of a crack from the scattered field.

## FUNCTIONALLY GRADIENT MATERIALS

Functionally gradient materials (FGMs) are nano-composites, alloys, and intermetallics that are macroscopically homogeneous but have continuously varying (rather than constant) microstructure with special thermomechanical properties. FGMs were conceived as "smart" or "intelligent" improvements over layered materials capable of enduring the steep temperature gradients, protracted exposure to high temperatures, and highly oxidizing environments that Earth-to-orbit winged planes face (Gandhi and Thompson, 1992; Rogers, 1989; Travis, 1993; Nanavati and Fernandez, 1993). Skin temperatures on such aerospace planes reach 2000 K, while the temperature just below the skin may be 1000 K cooler (Niino and Maeda, 1990). Layered materials, such as materials with a ceramic coating to protect a metallic substrate or with directly bonded homogeneous layers, have major disadvantages here: high thermal and residual stresses and poor bond strength (Houck, 1988). However, the recently developed technique of intentionally grading the composition of an interfacial region (Kerrihara et al., 1990) or entire coating (Kawasaki and Watanabe, 1990) seems effective in overcoming such disadvantages. Composition grading also improves the fracture toughness, fatigue, and corrosion crack resistance of thermal barrier coatings (Yamanouchi et al., 1990). Continuous graded composition occurs naturally in interfacial regions of many diffusion-bonded materials (Shiau et al., 1988) and occurs in certain deposition techniques such as plating, sputtering, and plasma spray coating

(Houck, 1988).

FGMs are macroscopically modeled as inhomogeneous continua, while microscopically they are two-or three-phase composites with continuously varying composition made up of piecewise homogeneous regions. They can be analyzed as inhomogeneous isotropic (linear or nonlinear) elastic solids with known property distributions, including composite media microstructure specifications of desired thermomechanical properties. Inhomogeneous medium problems in potential theory and continuum solid mechanics can be formulated mathematically as a system of partial differential equations with variable coefficients (Olszak, 1958).

The mathematical opportunities lie in finding sufficiently general methods for solving specific boundary value problems. Even in the simplest cases (for example, one-dimensional wave and diffusion equations, and two-dimensional equations of potential theory), general methods do not exist. To date, the most comprehensive solution method is based on an inverse method whereby the general (two-dimensional) second-order partial differential equation with variable coefficients is reduced to a system of first-order nonlinear Ricatti ordinary differential equations (Varley and Seymour, 1988). A particularly important mathematical challenge is to develop alternatives to the present approach that, in order to achieve analytically tractable solutions, uses a simple function to represent material nonhomogeneity despite this assumption possibly producing results that are not physically meaningful (Kassir and Chauprasert, 1974). However, see Bakirtas (1980) for a modification that yields some meaningful results. Another mathematical challenge is developing homogenization techniques for the estimation of the effective thermomechanical properties of FGMs from given composition profiles and micromechanical parameters.

## NONLINEAR OPTICAL MATERIALS

Nonlinear optics (NLO) emerged as an independent field in the early 1960s after the invention of the solid-state laser (Shimoda, 1986). NLO encompasses a host of phenomena related to the nonlinear interaction of laser radiation with matter as well as applications and technology based on these phenomena (National Research Council, 1992).

Many NLO effects are already understood, but recent advances in both laser technology and materials science offer exciting opportunities for new properties and new devices, which in turn offer new mathematical challenges. Some examples of NLO effects are frequency conversions (such as higher harmonics, generation of sum and difference frequencies, optical parametric oscillations, and stimulated Raman scattering), nonlinear refractive indexes and related self-action effects (such as self-focusing, self-trapping, self-bending, optical bistability, solitons in fibers), nonlinear absorption (in particular, saturable and multiphoton absorption), photorefractivity and related phase-conjugation effects, and diverse multiwave mixings. Most of these effects can be enhanced by resonances between radiation frequencies and quantum transitions in the material. A partial list of current NLO materials applications includes such frequency conversion; control, steering, rectification, and restoration of laser beams; radiation protection and optical limiting; all-optical switching; logic and computer memory operations; general optical signal

processing; and soliton-based optical fiber communications.

The most promising NLO materials are found in the following areas (Auston et al., 1987): (1) bulk materials (mostly semiconductors, glasses and semiconductor-doped glasses), (2) multiple-quantum wells, (3) photorefractive materials, (4) liquid crystals, (5) inorganic frequency-conversion materials, and (6) organic and polymeric materials.

Bulk materials, particularly solid-state crystals, are classic NLO materials for such applications as frequency conversion. In 1965, two mathematicaians discovered the soliton (Zabusky and Kruskal, 1965). Soliton pulses in NLO fibers were first predicted in the early 1970s (Hasegawa and Tappert, 1973) on the basis of soliton solutions of the nonlinear Schrödinger equation that had been discovered a short time earlier (Zakharov and Shabat, 1972). These solutions are some of the finest examples of the contributions of the mathematical sciences to NLO; highly transparent fibers can now propagate soliton pulses for distances exceeding 1000 km. They also exemplify the potential for real-world application of mathematical sciences research in NLO: an undersea trans-Atlantic cable that was recently developed by AT&T Bell Laboratories uses solitons as information carriers. The mathematical sciences can assist in formulating optimal material parameters for fibers used for soliton propagation. The mathematical sciences can provide better theoretical understanding of nonlinear distortions produced by higher-order dispersion and nonlinearity terms and by relaxation (proven to generate the so-called red shift in soliton frequency). A fundamental challenge concerns the "quantum" theory of solitons.

Bulk semiconductors are some of the most universal nonlinear optical materials; under proper conditions they can demonstrate almost any possible nonlinear optical effect and can be used for applications from 0.3-to 12-μm wavelengths with a variety of materials systems. The nonlinear phenomenon in bulk semiconductors that has attracted most of the attention in the last decade is the nonlinear refractive index and related effects. For the next decade, the challenges in bulk semiconductors are to develop better physical understanding of the interplay of different nonlinearity mechanisms (Trillo et al., 1986; Fork et al., 1987) and, in applications, to reduce switching energy and switching time. The latter problem involves the ability to cycle these devices at rates of multigigabits per second. Good mathematical models will be required to describe these processes.

In the 1980s, many quantum-mechanical calculations of semiconductor nonlinear susceptibilities were done, in particular for generation of higher optical harmonics. Some of the recent calculations agree well with experimental data, but all of the calculations are valid only for static situations—they fail to predict the temporal dynamics of the materials. A major mathematical challenge is to develop a dynamic theory of transient processes in NLO semiconductor systems (and in quantum well devices, which are discussed in the next paragraph), especially for nonlinear refractive indexes. Thus far, the nonstationary models that have been developed have been quite simple.

Quantum well structures (QWSs), and multiple QWSs (MQWSs), are semiconductor structures with two-dimensional carrier confinement. They are fundamental to laser sources and have lately received much attention; for example, enhanced QWS exciton resonances led to the development of self-electrooptic effect devices (SEEDs). It has been demonstrated that quantum well structures, and devices based on them, can be used as logic gates and surface emitting lasers. The theory of QWSs and MQWSs involves a great deal

of modeling. It combines many-body electron-hole physics with nonlinear propagation effects, and results in nonlinear coupled partial integrodifferential equations, such as the so-called Maxwell-Semiconductor Bloch equations (MSBEs). The general approach to describing optical properties and many-body processes in such highly excited semiconductors is via nonequilibrium Green's functions and projection operator techniques. Both formalisms yield the relevant set of semiconductor Bloch and Boltzmann equations, which describe the kinetic effects of an excited semiconductor system and its optical response function. The equations are nonlinear integrodifferential equations that have to be solved numerically using advanced techniques of parallel computing. The charge-transfer problem for quantum wave functions should be addressed by simultaneous and self-consistent solution of the Poisson and Schrödinger equations. Thus far, only finite-element numerical methods have been used in computational attempts at such a solution. It is desirable to find at least semianalytical methods for solving and/or analyzing the equations for both MSBE and Poisson-Schrödinger problems. Doing so would yield better insight into the physics of the processes and tools for optimizing materials parameters (see the discussion of interatomic potentials in Chapter 2).

An important feature of many nonlinear optical systems is that their response is intrinsically dynamical; see, for example, the special issue of *Journal of the Optical Society of America, Part B*, "Nonlinear Dynamics of Lasers," Vol. 5, May 1988. There are huge time-scale separations between competing physical processes. For example, one has very fast quasi-particle scattering processes that lead to extremely short dephasing rates, often on the order of a few tens of femtoseconds (1 fs = $10^{-15}$ s). On the other hand, even after complete dephasing, the system is still far out of its equilibrium state. In many instances, a truncated model for dephasing that eliminates the dynamic response of the material exhibits rather trivial dynamics having little in common with experimentally observed processes. The end result is often highly unpredictable weakly turbulent spatio-temporal pulsations. Nonlinear optics offers numerous manifestations of such space-time complexity and chaos in need of fundamental mathematical analysis. See, for example, Winful and Cooperman (1982), Silberberg and Bar-Joseph (1984), and Firth and Paré (1988); for discussions on optical bistability and chaos, see, for example, National Research Council (1992, 1986) and Gibbs (1985); for information concerning QWSs and chaos, see, for instance, Chemla (1993) and Jensen (1991).

There are now quality QWSs and MQWSs based on advanced growth techniques developed in the 1980s, such as molecular beam epitaxy and metallo-organic chemical vapor deposition, and advanced processing techniques such as reactive ion-beam etching and electron-beam lithography. Better theoretical guidance in the simulation of heteroepitaxial growth is sorely needed. Films can grow into fascinating self-similar and fractal structures. Kinetic growth theories based, for example, on random-deposition models and ballistic-deposition models are very attractive from both the physical and the mathematical point of view in that they exhibit dynamic scaling properties governed by simple functions with constant characteristic exponents. However, a great need exists for more sophisticated models able to provide viable tools for predicting properties of the epitaxially grown structures. Another important concern is the mechanical stability of the structures grown, especially when there is a considerable lattice mismatch between neighboring layers; a reliable mathematical theory of this stability would enable researchers to predict mechanical

properties of composite structures and thereby design such structures.

Within the past few years, the notions of two-dimensional QWSs have been extended to one-dimensional structures (quantum wires) and zero-dimensional structures (quantum dots); see, for instance, Heitmann and Kotthaus (1993). Since one can dilute or concentrate the dots essentially at will, placing quantum dots in glass fibers, for example, allows the creation of local nonlinearities, the magnitudes of which can be manipulated. Theoretically, quantum dots are the ultimate laser material. However, the theory of nonlinearity in these structures is far from satisfactory—analytical solutions have been obtained only for very special cases—and presents another case in which the mathematical topic of chaos arises; for example, see Stone and Bruus (1993). Also, existing theory is valid only for structures with size considerably larger than the lattice spacing; the case where the size is comparable to that spacing offers a worthy mathematical challenge.

Photorefractive materials are electro-optic crystals in which absorption of photons triggers a charge migration resulting in a spatial modulation of the material's refractive index through a space-charge-field-induced electro-optic effect. There are some exciting mathematical problems related to the theory of propagation of conjugated waves in photorefractive materials, especially in self-pumped conjugators. Electro-optic crystal chemistry (in particular, altering crystals by cooking them in a specific atmosphere) and crystal growth may greatly benefit from the close attention of mathematical scientists (see Chapter 4). Better understanding of crystal growth in general and electro-optic crystal growth in particular, including adequate mathematical modeling of the processes, may substantially accelerate the technological development of photorefractive materials.

Along with quantum-well semiconductor structures, organic and polymeric materials (OPMs) seem to constitute the most promising group of NLO materials (see Chapter 3). One advantage of OPMs is that some have record-high radiation damage thresholds. The main theoretical areas in need of investigation for these materials are quantum calculations of the polarizability of an individual molecule (for example, a molecule oriented by an external field in high temperature can he "frozen" by cooling through the material phase transition) and calculations of macro-susceptibility as determined by microscopic order parameters and by the micro-susceptibility (polarizability). The resulting systems are extremely complicated. The theory involves heavy mathematical machinery (including complicated wave-function calculations and group theory). Further progress in the area will undoubtedly depend on the efforts of applied mathematical scientists.

One issue that is common to most of the NLO materials discussed above and that may require a strong mathematical effort is substantially increasing the radiation damage threshold. For many materials, this is an important goal. For materials for a new generation of more powerful lasers, it is very important. A detailed theory of optical breakdown in NLO materials needs to be developed for this; it must include, among other things, a theory of stimulated scatterings (in particular, stimulated Brillouin scattering—SBS) and must address multi-photon absorption (MPA) and plasma formation during the self-focusing process. In particular, it must present a theory that includes SBS and MPA of the collapse of the solution of a three-dimensional nonlinear Schrödinger equation.

With the emergence of laser sources of coherent radiation in a fundamentally new x-ray domain—x-ray lasers—a completely new host of NLO materials and effects can be

envisioned. Recent results show that third-order NLO phenomena of considerable amplitude (including, for example, nonlinear refractive index) can be expected both in an x-ray laser plasma and, most interestingly, in solid-state materials. The theory of these effects will have to include quantum transitions of (initially) bounded electrons, both between atomic shelves and into a free-electron continuum. This poses new mathematical challenges that are (initially) related to the fast relaxation of hard-driven electrons in the continuum.

Lastly, one of the most fascinating recently discovered phenomena in the nonlinear interaction of light with atoms and ions is that high-order harmonic generation (HHG) spectra deviate drastically from perturbation theory predictions. The physics of this phenomenon has two major components: phase-matching conditions and the nonlinear response of individual atoms. It has recently became clear that the major features of HHG, and, in particular, its plateau, result mainly from general properties of nonlinear atomic response. Yet, there exists no simple model or theory that explains even those major features. A number of multiparameter theoretical models of the single-atom response to intensive optical fields in HHG have been suggested; most of them reproduce qualitatively the gross picture of the process. The most successful theoretical approach thus far has been direct numerical simulation using Hartry-Slater approximation of the atomic Schrödinger equations for many-electron atoms. It requires, however, a tremendous amount of calculation, provides little insight into the physics of the process, and hardly allows for general conclusions. A great theoretical challenge is to develop a mathematical and physical model that describes the major features of the phenomenon and identifies the most substantial factors resulting in HHG.

# 8

# MATHEMATICAL AND NUMERICAL METHODS

## INTRODUCTION

There are three hierarchical levels of understanding, corresponding to three levels of spatial detail, into which models of materials can be organized. The microscopic level is concerned with the properties and evolution of assemblages of large numbers of atoms and molecules, often arranged as a crystal. The macroscopic level deals with bulk averages across microstructure and is the domain of continuum mechanics and thermodynamics. The mesoscopic level is intermediate to the other two. Each of these levels has its own set of concepts and materials parameters. In principle, these parameters can be derived from properties of a lower level or measured experimentally. In either case, they provide an appropriate basis for the quantitative description of matter at the level in question, while omitting details of behavior important only at a lower level. A theory of materials consists in the calculation of material behavior within each level and the application of parameters calculated on one level to a more macroscopic one.

Within each level, the challenge is to predict phenomena from appropriate equations of motion or conditions of equilibrium. On the microscopic level, the dynamics of atoms and molecules are described by Newton's law or Schrödinger's equation. On the macroscopic level, materials properties are generally represented by a set of partial differential equations that express energy, mass, and momentum conservation and are formulated to represent the symmetry of the material to which they are applied. On the mesoscopic level, theoretical approaches are less well defined. Ginzburg-Landau and Langevin equations, however, are being used increasingly. In the Ginzburg-Landau approach, the free energy of the material is expanded as a power series of a quantity, called the order parameter, and its gradients. The value of the order parameter shows the local state (or phase) of the material (Landau and Lifshitz, 1969). In the Langevin approach, particle dynamics is modified by an interaction with a random force that represents an interaction, the details of which are undeterminable or nonessential (Parisi, 1988). Frequently, there is no sharp boundary between the mesoscopic and macroscopic levels, except the degree to which an application may demand further constraints in modeling.

The complete formulation of a materials science problem is often too complicated, involving the entire atomic or molecular structure and focus. Mathematical modeling is needed to simplify the problem while preserving the relevant physics; the model can then be studied via mathematical and computational tools. At each level, models typically lead to nonlinear equations; solutions of these equations can exhibit coherent structures, chaos, or complex patterns. Understanding the models and their solutions presents formidable analytical and numerical challenges that require extending existing methods, developing new approaches, and incorporating techniques from other fields.

Some mathematical research areas with materials science applications are summarized below. Sometimes, an opportunity is specific to a material, property, or phenomenon. Often a problem area is generic, spanning the hierarchy of materials modeling.

## MICROSCOPIC SCALE

In analyzing and predicting the phases of a material and the nature of transitions between these phases, an electronic structure calculation (Callaway, 1991) is an important tool. Typically, electronic structure calculations are used to develop models of interatomic forces and to predict the zero-temperature configuration, that is, the crystal structure, of a large number of atoms and molecules. In these areas, algorithms are needed that can handle complicated materials efficiently and effectively.

Improved electronic structure methods and approximations are needed to treat systems with a large number of atoms or molecules. This is particularly true for such complicated structures as polymers, alloys, ceramics, and materials in which defects such as surfaces and dislocations are present. Improving the calculations of alloy properties will probably require the development of radically new methods because disorder is generally present in these materials. Determining microscopic forces between defects is an example of an especially fundamental and challenging calculation.

Improving many electronic structure methods requires going beyond the local density approximation to density functional theory. Density functional methods are based on a theorem that says the ground-state electronic energy is a universal functional of the electronic density, but that theorem provides no information on the nature of the functional. Mathematical analysis expresses the functional in pieces that are exactly known and lumps the unknown parts into a piece that is approximated, known as the local density approximation. This latter piece contains the dominant part of the electronic correlation energy, which is intrinsically a quantum many-body effect. Accurate computation of the electron structure of many materials requires improved approximations of this energy. How to do this has been the object of research for a number of years. Can bounds or inequalities be established for this part of the energy? and How must the assumptions be changed for different classes of systems? are natural questions to ask.

A general issue in electronic structure calculations is the effective utilization of parallel computers. The use of parallel computers for electronic structure calculations has been developing slowly because of the size of the computational codes, uncertainty in possible computational gains, and the difficulty in adjusting well-developed procedures to novel computational environments. Most parallel computing in this area has involved the joint efforts of a materials theorist, an applied mathematician, and a computer scientist.

Ab initio electronic structure calculations for clusters, which are common activities of the quantum chemist, are an example of a situation where strong coupling appears between treating the electron correlation energy properly and using parallel computers. The major difficulty with these methods, as with their counterparts used in condensed matter physics (mentioned in Chapter 2), is the need to correlate many electrons. Knowing how to effectively exploit parallel computers for such intensive calculations would be beneficial.

In recent years, electronic structure calculations and the study of quantum many-body phenomena have been attempted by Monte Carlo methods (Doll and Gubernatis, 1990; De Raedt and von der Linden, 1992). The quantum mechanics imposes significant constraints on the nature and utility of the algorithms used. In almost all cases, these algorithms possess what is called the sign problem, in which the transition probabilities needed in the Monte

Carlo step become negative (Schmidt and Kalos, 1984; Loh et al., 1990). In some algorithms, approximate procedures allow useful calculations to be performed; in others, the sign problem is so bad that the study of the models believed to be basic for understanding the materials, such as high-temperature superconductors, are essentially prohibited. The sign problem is a significant factor limiting the advance of theoretical many-body physics.

The study of phase transitions and their dynamics sits in a branch of physics called statistical mechanics. This branch plays an important and useful role in many areas of materials research. From the specification of the interactions between many particles (obtained from electronic structure calculations or from assumed models), statistical mechanics attempts to predict the macroscopic behavior associated with these particles and their interactions. While many exactly solvable models and exact results exist, most predictions are based on approximate theories, and there is always a need to develop better approximations and methods.

In quantum mechanical problems, where the above mentioned density functional theory is used, the Kac-Feynman path integral is also often used as the basis for analytic and numerical work (Feynman, 1972). In classical statistical mechanics, analogous mathematical constructs called Wiener integrals and density functionals exist. A Wiener integral represents the motion of particles by the trajectories of these particles as they undergo Brownian motion. Density functionals describe the spatial distribution of matter when the location of one or more particles is given (Feynman, 1972). These classical statistical mechanics constructs are used, for instance, in polymer research and in the theory of melting of solids and freezing of liquids. What is lacking is a complete understanding of how to perform systematic approximation of these density functionals and how to gauge the effects of approximations on predicted properties.

One of the most remarkable developments in the modern theory of statistical mechanics has been the renormalization group method. This method is a prescription for the systematic removal of irrelevant length or energy scales from a problem (Wilson, 1975). Successfully applied to many second-order phase transition problems, some electronic structure problems, and some polymer problems, its applicability has been limited by its computational needs, an incomplete understanding of its mathematical structure, and the lack of a prescription for applying its concepts to a wider spectrum of problems. The increased use of renormalization group methods in some areas has brought with it the need for more insight into dealing with asymptotic series and their resummation.

For equilibrium behavior, computer simulations have provided important insights, and, with the use of parallel computers, many of these simulations now involve tens of millions of particles. The physics of a phase transition, however, leads to difficulties in performing such simulations, difficulties that become more severe as the transition is approached. For Monte Carlo simulations of second-order phase transitions, recent algorithmic breakthroughs involving the use of Monte Carlo moves of clusters, as opposed to moves of single particles, have reduced the computing time for such simulations by orders of magnitude (Swendsen and Wang, 1987; Wolff, 1989; Hayes, 1993).

These algorithms were first developed for Ising models, the physical variables (spins) of which assume discrete values, and were later extended to other models, including the XY and sigma models, the variables of which assume continuous values. To date, however, these

algorithms fail for a class of problems characterized by "frustrated" interactions. In a frustrated system, the minimal energy configuration, say for a local arrangement of spins, becomes impossible to satisfy because of the constraints imposed by the minimal energy configuration of a neighboring region. Frustration leads to the existence of many local minima of the energy with values very close to the global minimum. This condition radically alters the dynamics of the system, renders its analysis difficult, and makes simulations increasingly difficult as the temperature is lowered.

A comparably challenging class of problems, involving random systems, is often called the spin-glass problem after physical systems in which low concentrations of atoms with magnetic moments are randomly positioned in a material and induce an interaction between each other that varies in sign. The problem is one of optimizing a nonlinear function of a large number of variables, which is an issue throughout materials research. Polymer problems and protein folding problems are solved by optimizing nonlinear functions (see Chapter 3). How does one know that the global minimum has been reached? and What techniques can one use to reach it efficiently? are major questions awaiting answers. One recent approach uses a random walk in the function to be minimized; from a series of extrema that are generated, the global minimum can be determined with high probability as the number of walks increases (Berg, 1993).

Theoretical work on the microscopic level has concentrated on predicting the properties of a system at or not far from equilibrium. Yet, the synthesis, processing, and use of many materials often occurs under conditions far from equilibrium. Both the analytical and the computational treatments of such problems are underdeveloped. Problem areas include the kinetics of chemical reactions. The kinetics of chemical reactions is an inherently nonlinear area and therefore presents a considerable challenge.

Molecular dynamics is increasingly used to study the kinetics of phase transitions and other nonequilibrium problems. A limitation of this method is that often the physical time simulated by these calculations is short compared to the time scale of the phenomenon of interest. Can this method be modified to extend the simulation to longer physical times? Part of the problem is that many time scales may be present in the problem. Can the longer scales be studied without computing time being taken up by the shorter scales?

## MACROSCOPIC SCALE

Applied mathematicians have had a large impact on materials science at the continuum level. For example, applied mathematicians did the asymptotic analysis of the stress field near a crack-tip, which has yielded catalogs of figures of merit (stress intensity factors) for fracture prediction based on simple crack models (Babuška and Miller, 1984; Vasilopoulos, 1988; Sumaratna and Ting, 1986; Reitich, 1991). Surface-stability analysis of moving interfaces has led to an increased understanding of microstructural growth during solidification; see two subsections, Phase Transformations and Pattern Formation and Dendritic Growth, in Chapter 4. Finite-element and finite-difference methods are routinely used to map stress concentrations in many load problems. Much research in this area is already in progress, yet much remains to be done. In particular, improvements are needed

in both the analysis and numerics of partial differential equations, especially nonlinear ones.

Improving ways to generate adaptive grids is important in many problems associated with the growth and processing of materials, where the boundaries are often complicated. In these problems, a moving interface (marking the separation of a liquid and solid) or a free-moving boundary (marking the extent of solidification) can develop complex spatial structures and become unstable (Huang and Glicksman, 1981a, b; Langer, 1987; Gollub, 1991). These interface developments define the material's mesoscale structure, which in turn determines the material's macroscopic parameters and behavior. These problems often are associated with nonlinear diffusion processes and place great demands on finite-difference and finite-element methods because of the need to track the fronts and simultaneously to capture structure and patterns developing at increasingly reduced length scales. Improved numerical methods for such problems are needed.

A fascinating feature of many interface and growth problems is the occurrence of self-similar structures (Voorhees, 1985; Voorhees and Schaefer, 1987; Hardy et al., 1991). Analysis and computation would benefit from a clear understanding of the conditions under which self-similar structures occur and knowledge of the geometric details of those that can occur. Many materials problems involve phenomena on disparate time and spatial scales, resulting in stiff partial differential equations. To further complicate the situation, in some problems the partial differential equations change type, for example, from elliptic to hyperbolic, as time evolves (Keyfitz and Shearer, 1990). Much work on the theory and numerical solution of partial differential equations under these challenging conditions awaits attention.

Often in materials research, the scientist is interested in inferring from measurements made on a macroscopic level information about the mesoscale. For instance, acoustic measurements may lead to inferences about the location and geometry of a crack in a material, which in turn may lead to a prediction of whether the crack is one likely to initiate fracturing of the material. This and related situations are inverse problems and are inherently ill posed. Ill-posed problems are a class of problems of mathematical interest for which improved methods would significantly influence present understanding and characterization of materials. Ill-posed problems also are basic to such bread-and-butter tasks as parameter fitting of models.

The complete solution of a problem is not always essential or desired. Of interest may be only what happens at long or short times, long or short wave numbers, and so on. This simplification leads to the use of asymptotic expansion methods. Of course, once the terms in an asymptotic expansion have been produced, the next natural thing is to sum this series to extend the solution, say, from long-time behavior to the earlier behavior leading to it.

Characteristic of materials modeling on the macroscopic level is the use of constitutive relations. Familiar cases are the relations between current and electric field and between stress and strain, in which quantities such as conductivity and elastic stiffness, respectively, appear. These quantities are a way of specifying the properties and behavior of the material on the macroscopic scale. With new material types being developed and studied, extending current constitutive models and developing new constitutive models become important. A context in which this is the case is a new family of viscoelastic

materials (Renardy et al., 1987). In general, the viscoelastic response of materials, especially of polymers, needs more attention. Plasticity has been and continues to be an important area of investigation. Today, nonlinear behavior in materials, including nonlinear optical behavior, is at the forefront of investigation.

## MESOSCOPIC SCALE

Between the microscopic and macroscopic scales is the mesoscale, with many significant materials problems. On this scale, the materials scientist is concerned primarily with characterizing and controlling the microstructure of a material in ways that allow one to predict macroscopic properties. The mesoscale structure is usually a long-lived state of the material that is far from equilibrium. At the mesoscopic level, most materials are inhomogeneous, and macroscopic descriptions usually require an average over, or an explicit treatment of, the microstructural detail.

The technique of "homogenization" of the microstructure-level partial differential equation appears useful for such mesoscale problems. Further development of homogenization procedures appears warranted. In some respects, homogenization methods build on an older body of work, effective medium approximations, that for a long time has been the subject of considerable analytical efforts. Lord Rayleigh himself pondered such problems (Rayleigh, 1892).

A material's mesostructure exhibits polycrystalline, phase-separated, and other variations in properties over regions that are too large to be treated microscopically but are sufficiently large that they have the same properties and parameters as the macroscopic bulk material. The basic question in effective medium theory is, Given the properties of the constituents, what are the properties of the aggregate? On the microscopic level, the same question is asked in the theory of alloys: Given the properties of the individual atoms or molecules, what are the properties of the combination? Not surprisingly, these two areas share approximation techniques (Gubernatis, 1978), but considerable attention has been given to the development of bounds and variational principles with regard to effective medium approximations, issues that have not been focused on as much at the microscopic level. Today, many applications require that one consider the effective nonlinear response (elastic and optical) of a material to external forces. Analysis of extreme responses and the development of statistical theories of fracture are also needed. The question of what structures produce optimal response properties is also of current interest.

As a phase transition evolves in time, phases nucleate, separate, grow, and disappear. As a material interface or free-moving surface becomes unstable, rich complex structures evolve into columnar grains, lamellar eutectics, dendritic growths of fractal structures, and other structural features. Both views of microstructural evolution, that of evolving phase transitions and that of instability development in interfaces and surfaces, point to the often exceptionally complex mesoscopic morphology of materials. See Chapters 4 and 5 for examples.

In Ginzburg-Landau (GL) theory, the free energy is expanded as a power series of a quantity called the order parameter. If the material is inhomogeneous, terms with the

gradient of the order parameter are included. The various terms in this expansion are adjusted to be consistent with the symmetry of the material. The resulting expressions can be used to investigate the phases of the material. From some microscopic models, the leading terms in this expansion can be explicitly obtained and the associated parameters identified with quantities that are calculable or measurable. This remarkable situation is true for the Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity (Fetter and Walceka, 1971; see also the section Superconductivity in Chapter 4) and the theory of lattice vibrations (Maradudian and Fein, 1962; Cowley, 1964). The nature of the martensitic transformation has recently been successfully investigated in this manner (Krumhansel and Gooding, 1989; see also the Chapter 4 section, Martensite and Shape-Memory Materials). It is expected that similar methods of analysis will be fruitful in other areas of materials science in the future.

One research need presented by the GL approach is for a way to avoid redeveloping it on a case-by-case basis. Another research challenge arises when minimizing the GL energy functional to obtain the order parameter's power series structure, and therefore the structure of the material; this may present nonconvex minimization problems with no or non-unique solutions, about which more understanding is needed.

One approach to the kinetics of phase transitions is to make the order parameter time dependent and allow it to evolve in time under the action of forces taken to be proportional to gradients of the GL energy functional. These forces may be supplemented by viscous terms and random forces. There are also related approaches, expressing time-dependent position and momentum and that include viscous and random forcing terms, based on Langevin equations. The theorist is now faced with solving sets of nonlinear dissipative stochastic partial differential equations that are first-order in time. Such partial differential equations have been the subject of considerable analysis. However, the analysis needs to be made accessible, and more efficient and effective numerical algorithms need to be developed to integrate these equations.

A number of interesting materials problems exist for which a GL approach is ineffective. An example of such a situation is microphase separation in block copolymers in the strong segregation limit (see Chapter 3 sections, Block Copolymers and Interfaces in Polymer Systems). There is much work to be done in developing effective methods to treat mesoscale phenomena.

## POTENTIALLY APPLICABLE MATHEMATICAL SCIENCES DEVELOPMENTS

The preceding three sections have focused on mathematical opportunities in materials science that require the extension of existing methods or the development of new approaches. In the present section, developments in the mathematical sciences are identified that might be applicable to materials problems but are not yet widely exploited.

As already mentioned, parallel computing provides important opportunities for electronic structure calculations. Such applications are only one example of the need and potential for parallel computing in materials science research. Opportunities exist for

parallel computation of material properties and behavior in nearly every area of computational materials science. From the algorithmic point of view, there are two issues. The first is that mathematicians have developed and implemented parallel versions of many basic linear algebra methods, finite-element and finite-difference methods, fast Fourier transforms, sparse-matrix methods, and so forth. Much of this off-the-shelf technology could be used in materials science calculations, but little of it is known to the materials scientist. Expanding the awareness and use of state-of-the-art parallel computation capabilities and expertise in the materials science community would be an important contribution. The second issue is that efficient use of parallel architectures generally requires rethinking the algorithm on the global scale. Directly porting a serial or vector algorithm to a parallel computer typically leads to disappointing performance gains. Many of the equations, boundary conditions, geometries, initial conditions, and so on that are germane to materials problems differ from those traditionally addressed by applied mathematicians in such applications as hydrodynamics. These issues underscore an obvious area of opportunity for interdisciplinary collaboration between materials scientists and mathematical scientists.

Wavelets (Chui, 1992), neural networks (Hertz et al., 1991), and cellular automata (Wolfram, 1983) are topics of mathematical research in which there is currently great activity. These areas are finding applications is such fields as image enhancement, signal processing, and DNA sequencing. While they are still relatively unknown to the materials community, they could have a place in materials science. Some ways in which these areas might he able to assist the materials scientist are examined below.

A natural use of wavelets would be the compression of the vast amount of data produced by experiments and simulations. One can also ask to what extent wavelet transforms (or their generalizations) could be used in place of the Fourier transform that has been used routinely in materials research for over a century. Can analysis and computations based on wavelets yield information that is hard to obtain by Fourier analysis? In electronic structure analysis, could wavelets be an attractive alternative to plane-wave and Wannier bases, which emphasize, respectively, the delocalized or localized nature of the electron? Electron density often exhibits spatial characteristics intermediate between the two (delocalized and localized).

The fields of neural networks, cellular automata, and statistical mechanics have many conceptual and model interrelationships with potential benefits for materials science. Spin-glass-like problems (Binder and Young, 1986; Fischer and Hertz, 1990) involve the optimization issues that arise in neural networks that can "learn"; an algorithm that can learn how to solve a problem while in the process of solving it may open possibilities in materials processing and synthesis. If these processes were adequately modeled, could one specify desired properties and have the network adjust the experimental controls to produce them? Can neural networks be used to determine the optimal processing conditions?

Monte Carlo simulations of Ising models and related models are examples of stochastic cellular automata. With the specification of very simple rules for going from one stage of the calculations to the next, both stochastic and deterministic automata can produce rich patterns reminiscent of mesoscale structure. To what extent can these structures be better understood by simple automata models than by the more complex and difficult-to-analyze models normally used? Statistical mechanicians already have considerable

experience with this type of problem.

A form of deterministic cellular automata, the lattice gas method for solving partial differential equations, is successful in solving hydrodynamics problems (Doolen, 1991). With lattice gas methods, simulations of fluid turbulence are available that provide direct checks of many approximate theories. Calculations of fluid flowing through a porous material, a problem important for oil recovery from sandstone, have also been successful. These methods have been applied to the study of phase-separation and chemical-reaction kinetics.

A strength of these methods is the ease with which they can handle complicated boundaries and boundary conditions. Because of the ability to use millions of cells, these methods have the potential of more easily tracking fronts and thus may be a considerable asset in solving moving interface and free-boundary problems associated with solidification and grain growth. The methods also adapt well to parallel computers; specialized computers that perform just this type of calculation could be designed.

A basic problem with lattice gas methods is determining whether the rules specified are sufficient to ensure that the calculated phenomena correspond to physical phenomena. To what level of accuracy do lattice gas methods solve the Navier-Stokes equations, the diffusion equation, and so forth? For fluid problems, the answer appears to be on relatively firm ground. This correspondence follows from analyses analogous to those used in statistical mechanics for determining macroscopic behavior in the kinetic theory of gases, from which the Navier-Stokes equations for a collection of interacting particles can be derived. For other physical systems, more analysis and understanding are needed.

Many of the concepts and methods of probability and statistics used in materials science are products of mathematical sciences research done much earlier in this century or previous centuries. Yet, probability and statistics sport many newer concepts and methods that may influence the analysis and design of materials experiments; see, for example, Chapters 9 and 10 in National Research Council (1991d). What impact might methods of nonparametric function estimation, modeling, and simulation have on the interpretation and analysis of materials experiments and simulations? Recently, Bayesian methods of statistical analysis have been used successfully in several areas of materials science, including optimization of the design of neutron scattering interferometers (Sivia et al., 1990), analysis of reflectivity data (Sivia et al., 1991), and solving ill-posed problems associated with the use of quantum Monte Carlo calculations (Gubernatis et al., 1991). The saying "With enough parameters one can fit anything" recedes into the background as these methods estimate not only what fit to the parameters is most probable but also what is the most probable number of parameters needed (Sivia and Carlile, 1992).

The ubiquitous need for nonlinear optimization has been highlighted several times in this report. Nonlinear optimization is also used in comparing theory with experiment (see, for example, the Modeling Protein Structure and Dynamics section of Chapter 3). Such optimization problems are especially challenging because of noise and the incomplete nature of the data.

# 9

# RECOMMENDATIONS

## INTRODUCTION

The preceding chapters provide both an overview and some details of recent and current activities in an assortment of materials science areas where mathematical modeling, analysis, and computation play key roles, and they identify areas of mathematical research in which increased activity would accelerate materials research. However, the purpose of this report is not merely to focus in an abstract way on promising directions for collaboration between materials scientists and mathematical scientists, but also to encourage both communities to increase such collaboration for their mutual benefit and for the general benefit of the nation, including the practical benefits to industry and the strengthening of economic competitiveness and national security. Clearly, both the mathematical and materials sciences have much to gain from each other. An increase in collaboration would improve existing materials science models and produce better qualitative and quantitative understanding. In addition to stimulating new mathematical and statistical developments, such collaboration would provide mathematical scientists with new problems whose real-world relevance would bring excitement and practical application. The committee believes that a considerable amount of modern mathematics and statistics would be useful in resolving problems of materials science but is not utilized because materials scientists are unaware of those mathematical and statistical results and mathematical scientists are unaware of the potential applications.

Unfortunately, as summarized in Chapter 1, obstacles to collaboration now exist with inhibiting effects that should not be underestimated. To increase awareness of this situation and stimulate thoughtful approaches to improving it, the committee identifies in this chapter what it views as the main obstacles to increased collaboration between the materials science and mathematical sciences communities. The committee's conclusions are based on information gathered in the course of this study, including input from scientists (see appendix) whose work is at the interface between materials science and the mathematical sciences, and the knowledge and experience of the committee's members. This chapter closes with the committee's recommendations to universities, government, industry, and professional societies on how to enhance and further increase collaborative efforts between the two communities and how to attract students and young researchers to such work.

### Acknowledging Obstacles to Collaboration

The committee sees the following as the main obstacles to collaboration:

1. In many cases, successful interaction with materials scientists requires mathematical scientists to learn more physical science. A significant investment of time and effort is required to clear this hurdle.

2. Mathematical scientists and materials scientists are typically educated with and use different technical languages. Time and effort are required to surmount this language barrier. The mathematical scientist should learn enough of the technical language and jargon of the materials scientist to understand what needs to be accomplished in materials science. The materials scientist should focus much of the discussion on mathematical modeling in order to minimize linguistic discord.
3. Cultural, perceptual, and attitudinal differences between the mathematical and materials communities may lead to unrealistic expectations, with subsequent frustration that causes disillusionment with the collaborative process. This is an obstacle of attitudes that can be circumvented by more effective communication. Materials scientists want to analyze and to understand materials phenomena, whereas mathematical scientists want to develop mathematical theories and computational methods. Goals for any collaboration must be clarified at the outset. Preliminary discussion should help to identify the common interest and to show how each party is likely to benefit from the interaction.
4. Since there is a significant chance that useful research might never emerge from a collaborative effort, both sides are often reluctant to begin talking with each other. This impediment can be overcome by recognizing that both sides of a potential collaboration need to contribute an initial increment of time to facilitate understanding and useful communication.
5. Departmental structures in most universities too often discourage mathematical research by materials scientists and materials-oriented research by mathematical scientists by not providing motivating rewards such as tenure, promotion, and salary increases. Overcoming this obstacle requires that such structural disincentives be transformed into incentives that stimulate, encourage, and reward individuals for undertaking cross-disciplinary efforts between the mathematical sciences and materials science.
6. The last obstacle to collaborative research between materials science and the mathematical sciences is the shortage of funding. This obstacle is particularly important because a great deal of initial investment in time and effort is necessary before a collaboration can be established.

### Fostering Increased Collaboration

As noted in Chapter 1, the traditional boundaries between disciplines sometimes needlessly constrain the development of unorthodox ideas and new theories. The National Science Foundation recognized this in establishing a number of interdisciplinary science and technology centers, many of which include several institutions and often several disciplines (National Science Foundation, 1993, 1992). In particular, materials science is today a vast

and growing body of knowledge based on the physical sciences, engineering, and mathematics but is not obliged to conform to their limits.

Despite the obstacles noted above, successful collaboration between materials scientists and mathematical scientists has taken place and is taking place. This collaboration has led to substantial progress in both fields. Much of this progress, mentioned in Chapters 2 to 8, has been possible only through close interaction between members of the two fields. Fruitful collaborative efforts have occasionally sprung up and have involved imaginative and creative researchers on both sides who have had the curiosity and eagerness to expand their horizons. However, as Chapters 2 through 8 also indicate, numerous opportunities exist for new collaborations between members of the two communities, with a concomitantly large potential for benefit both to the research communities themselves and to strategic national interests. Thus ensuring the scientific vigor, technological strength, and economic health of the nation argues in favor of stimulating and facilitating new collaboration between mathematical scientists and materials scientists.

## RECOMMENDATIONS

**Universities, government, industry, and professional societies have important roles to play in fostering the kind of interdisciplinary mathematical sciences research and education that will enhance progress in materials science**. Since, as was emphasized in Chapter 1, cross-disciplinary collaborations require long-term commitments, all of these communities should strive to provide the means by which long-term collaborative commitments between the mathematical and materials sciences can spring up and thrive.

Having taken into consideration input from the contributors listed in the appendix, **the committee makes the following recommendations on how to enhance and further increase collaborative efforts between the two communities.**

### Universities

The university has perhaps the major role to play, both in encouraging collaboration and in attracting students and young researchers to the mathematical sciences-materials science interdisciplinary area. The committee sees challenges and opportunities at all levels.

1. Seminars led jointly by a mathematical scientist and a materials scientist should be given. Such seminars would both enhance understanding and collaboration and stimulate interest in students and young researchers. Since such joint efforts are very time consuming, recognition of the value and the effort should be reflected in teaching assignments and faculty evaluation.
2. Temporary reassignment, faculty exchanges, and joint appointments in which mathematical scientists would reside in materials science departments and vice versa, should be encouraged. Such reassignment or exchange may sometimes result in a

productive, long-term career switch. The visiting scientists should be encouraged to teach courses to students and young researchers in the host department. Such courses would be useful in attracting students to this interdisciplinary area. To be effective, these assignments should be included in accrued credit toward normal sabbatical leaves and regarded favorably in merit and promotion reviews.

3. Young faculty members in the mathematical sciences and in materials science should be encouraged to collaborate in research with colleagues in the other discipline. This approach will require that explicit recognition be given in merit and tenure reviews to the young faculty member as an important contributor to the synergistic effort. In many universities, the pressure to attain tenure inhibits young researchers from entering this cross-disciplinary area at a time when they could have a great impact, and thus it is a major barrier to be overcome.

Basic mathematics courses in universities generally do not generate the excitement and awareness of frontier issues in research that are more commonly conveyed in basic physical sciences courses. One consequence is that potential scientists and engineers lose interest in and appreciation for the mathematical sciences, a circumstance that contributes to the communication problems pointed out in this chapter and in Chapter 1. Students in introductory courses should be made aware of cutting-edge mathematical sciences questions that pertain to important materials science research issues. Doing that would also help to raise awareness of the value of quantitative methods in materials science and in general.

### Federal and State Government

Government funding plays a major role in facilitating cross-disciplinary work between the mathematical sciences and materials science, in attracting young researchers to the area, and in enhancing research collaboration at this interface. While federal and state support of individual investigators and small groups should remain the primary approach to funding, some specific actions to enhance collaborative efforts should complement that approach:

1. The most important recommendation is that funding agencies should make special efforts to ensure that interdisciplinary proposals involving mathematical and materials scientists receive careful and appropriate consideration. There is currently a perception that such proposals can "fall through the cracks." The review of an interdisciplinary proposal needs to be coordinated between the agency programs for the different disciplines involved. Reviewers familiar with research issues at the interface should be selected. Also, there should be specific earmarking of funds for joint mathematical-materials proposals and fellowships.
2. The participation of mathematical scientists in programs of government materials research laboratories and materials research groups should be encouraged.

3. Workshops and topical meetings that bring together mathematical and materials scientists from universities, national laboratories, and industry should be supported.
4. Priority should be given to supporting mathematical scientists who are keen on interacting effectively with materials scientists, that is, to those mathematical scientists who have learned or are learning the requisite physical science, and who have penetrated or are in the process of penetrating the jargon barrier in order to conduct a collaborative effort involving the two disciplines.
5. Postdoctoral fellowships that bring mathematical scientists into materials programs should be supported to help attract young researchers to the area. The leveraging effect of interdisciplinary postdoctoral fellowships is large.
6. An on-line glossary of terms used (sometimes in different ways) by different research communities could be made available nationwide as one step toward alleviating the communication problems between the mathematical and physical sciences and engineering communities.

### Industry

Although it does not presume to tell industry how to conduct its business, the committee makes the following recommendations, believing that while the roles that can be played by the various materials industries will differ greatly, there are some common opportunities:

1. Mathematical scientists should be encouraged to take sabbatical leaves and summer employment in industrial materials laboratories; conversely, industrial scientists and managers should be welcomed as adjunct faculty or visitors in university mathematical sciences departments.
2. Industrial firms should employ young mathematical scientists as consultants, making a long-term, several-year commitment (as some firms currently do for young engineering faculty); in doing this, firms should recognize fully that the initial years of employment will involve a substantial investment in educating such consultants in industrial problems.

### Universities, Government, and Industry Together

The recommendations made above would not be complete without the inclusion of joint recommendations to industry, universities, and federal and state governments, all of which stand to benefit from materials science research.

1. A program should be established that offers sabbatical leaves for mathematical scientists to visit industry and government materials science laboratories, and for mathematical scientists from materials science industries or national laboratories to visit universities.
2. A postdoctoral program should be offered to enable young mathematical scientists to work jointly with a materials science industrial company and a university for two years.

Both of these programs should be funded jointly through university, industry, and government sources; federal and state governments should initiate the programs.

### Professional Societies

Cognizant of the important role of materials, professional societies in mathematical, engineering, and physical sciences disciplines have given increasing emphasis to materials science and processing at their meetings. These efforts should continue and should be expanded.

1. Professional societies should cooperate in sponsoring and developing programs in materials-related areas; for example, topical meetings and workshops could be jointly sponsored, or a joint national meeting could be organized.
2. Professional societies should encourage the publication of special issues of professional journals and of volumes that focus on advances made possible by collaborative work in the mathematical sciences and materials science. They should strive to ensure that more professional rewards and recognition accrue to contributors to such work.

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