Energy & Technology Review

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August · September 1994

Energy & Technology Review

Materials by Computer Design

University of California

Lawrence Livermore National Laboratory

About the Cover

Advances in precision engineering techniques have spurred the development of materials modeling at the Laboratory. As an example, the large-optics, diamond-turning machine (background photo) can routinely cut away as little as a few nanometers of material off a surface. To understand the basic mechanisms that determine how the material is removed, how surface damage occurs, and how diamond tools themselves wear, Laboratory researchers such as Christine Wu (middle photo) have been involved in studying the atomic-scale processes that define surfaces in motion. Examples include the cutting of copper (top image) and the deposition of chlorine atoms on a tantalum surface (bottom image). Such knowledge will aid in the fabrication of precise components and help to explain the properties of materials under certain conditions.

(Photo credits: James E. Stoots)

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About the Journal

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Materials by Computer Design: An Introduction

CAN novel materials with optimized properties be designed by computer? Advances in modeling methods at the atomic level coupled with rapid increases in computer capabilities over the last decade have led scientists to answer this question with a resounding "Yes."

The ability to design new materials from quantum-mechanical principles with computers is currently one of the fastest growing and most exciting areas of theoretical research in the nation and at LLNL. Our efforts are addressing problems in many disciplines, including physics, chemistry, materials science, and biotechnology.

Computer simulations are, of course, not new. Examples that have become familiar to the general public include simulating crash tests for the automotive industry, simulating aircraft in flight, and predicting the effects of earthquakes on large structures, such as bridges. (All three topics are described in the September–October 1993 issue of *Energy and Technology Review*.) In these cases and many others, computer simulations tell us not merely what might happen, but what actually will happen in the real world. This issue of *E&TR* highlights several in-house efforts involving atomic-scale computer simulations and features some of our ongoing collaborations with industrial partners. These efforts focus on simulations that explore problems at the fundamental, microscopic level.

The ultimate objective of a scientist involved in modeling and simulating materials at the microscopic level is to answer the following types of questions: What is matter really like at the atomic level? How can we modify the bonding between atoms to create novel materials with optimized properties? How can bulk materials be combined to exhibit new, desirable properties absent in the starting constituents? In addressing such questions, the scientist is armed with the set of laws that govern matter at the microscopic level, namely, quantum theory.

Matter is made of atoms, and atoms are made of nuclei surrounded by electrons. The basic laws governing the behavior of nuclei and electrons were formulated in the 1920s and are collectively known as quantum theory. Quantum theory forms the basis of our microscopic understanding of the physical universe. Equipped with the laws of quantum theory and a powerful computer, why not attack the formidable task of designing novel materials by doing calculations on every atom in the material until we arrive at the properties we need?

Unfortunately, such a straightforward approach is impossible. It is true that the quantum mechanical equations governing the behavior of electrons can be written in a relatively compact form. However, practical calculations become exceedingly difficult because of the large number of degrees of freedom and interactions between particles. Even the smallest speck of matter visible to the unaided eye contains several billions of electrons, and the complexity of their motion is enormous. Because electrons are charged and repel one another, the motion of each electron depends on the motion of all the others. To make the problem even more difficult, the laws of quantum theory tell us that each electron is described by a wave function. As a result, electrons behave like a pattern of crisscrossing waves on a rough sea. An exact calculation of a system with such mind-boggling complexity is far beyond the capacity of the most powerful computers.

Instead of attempting an exact—and ultimately impossible—calculation, scientists approximate physical laws to yield a feasible, yet somewhat inexact, calculation. The key to the spectacular success of modern quantum

simulations of materials is that the degree of inexactitude is quite small and can be controlled.

A breakthrough in the field occurred in the early 1960s with the formulation of density functional theory. The basic postulate of this important theory is that the ground-state energy (i.e., the lowest energy state) of a system of electrons moving in a given external potential can be obtained from a knowledge of the electron charge density. This concept offers tremendous computational advantages because the electron density becomes the basic variable rather than the complicated many-body wave function of all the electrons. Moreover, this powerful theory reduces the problem of describing the tangled, mutually dependent motion of electrons to one of describing the motion of a single, independent electron in an effective potential. In other words, we can describe the complex effects of all the other electrons on a single electron by an effective potential in which that electron moves. This simplified, but rigorous, description means that we can treat electrons as if they are independent of each other without seriously upsetting the result. The framework of the density functional theory gives us an extremely powerful and accurate technique to calculate the properties of materials on a first-principles, or *ab initio*, basis—that is, from the identities of the atoms making up a material and the laws of quantum theory.

Density functional theory, coupled with rapidly increasing computing power, led to an explosion of activity in the calculation of the properties of materials using the laws of quantum theory. By the early 1980s, it had become clear to the scientific community that the properties of simple crystals could be calculated with amazing accuracy using nothing but these laws. Soon, researchers began reproducing many material properties that previously could only be determined through experiments. Examples include the spectrum of atomic vibrations in solids, changes in crystal structure induced by applying external pressure, and the optical, electronic, and magnetic properties of materials. Researchers around the world reported similar successes for a wide variety of materials. What we learned is that computer calculations based on the microscopic laws of quantum theory really could tell how actual materials behaved.

But there is a catch or two to this approach. Even with the tremendous advances that emerged from density functional theory, large-scale dynamic simulations of materials and processes on a truly first-principles basis remains a formidable task. Moreover, it is not possible to apply first-principles methods to systems at nonzero temperature, where the electronic properties must be averaged over the many possible configurations of ions making up a system.

Fortunately, our first-principles knowledge of how electrons and nuclei interact in materials can be used as the basis to derive simple, yet accurate, models to reproduce the interactions. Once the model interaction potentials between atoms in materials are derived, it is possible to perform molecular dynamics simulations of complex materials processes based on the numerical calculation of atomic trajectories. Molecular dynamics simulations are usually based on empirical potentials that mimic the interatomic potentials in real materials. The simplicity that follows from using parameterized potentials is then exploited to treat large numbers of atoms (up to hundreds of millions) in more complex configurations. By controlling temperature (the mean velocity at which the constituent atoms move) during a molecular dynamics simulation, technologically interesting processes can be studied. These processes include melting, crystal growth and epitaxy, ion implantation, laser annealing, and defect motion. Thus, molecular dynamics simulations bridge the gap between quantum theory and statistical physics.

Accompanying the rapid pace of theoretical developments is another trend that is at the origin of the vitality of the field of materials physics today. In recent years, we have seen extraordinary advances in the ways materials can be synthesized. Advanced synthesis tools now allow us to fabricate materials atom by atom so that we can grow thin films, build multilayers, and construct many other products, such as fullerenes (in which the building block is C_{60}). Indeed, it is the intimate synergy between our ability to predict accurately from quantum theory how atoms *can* be assembled to form new materials and our capacity to *actually* synthesize novel materials atom-by-atom that gives the field its extraordinary intellectual vitality.

At LLNL, we are working on both sides of the equation by pursuing the theory of large-scale modeling as well as powerful methods to construct new materials with optimized properties. Many of our materials theory, modeling, and simulation activities are being done in collaboration with industrial participants in support of technology transfer initiatives.

Until now, materials design and processing have been, for the most part, empirical sciences. What this really means is that the process of coming up with an optimal material has been quite slow. For example, about one cancer drug in 40,000 has clinical significance, and perhaps one in a million would be curative. Using the old empirical methods, we can screen about ten thousand drugs a year.

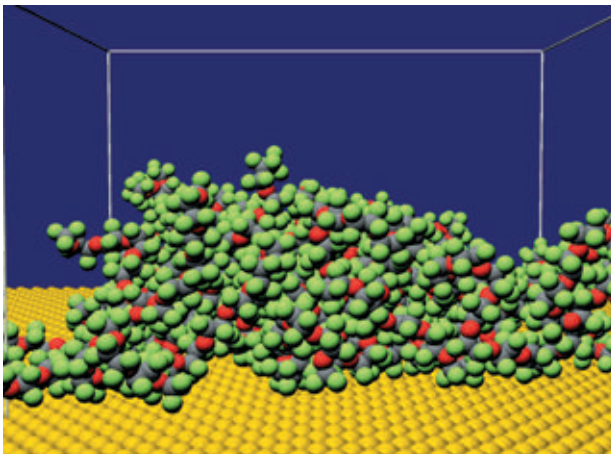
At that rate, it could take 100 years to obtain our first cancer-curing drug. Designing materials by computer will accelerate this process by improving our understanding of the mechanisms by which carcinogenic molecules cause cancer. Computers will also enable the design of drug molecules that either inhibit these mechanisms or remove the carcinogenic molecules from our body.

Consequently, in designing new materials through computer simulations, our primary objective is to rapidly screen possible designs to find those few that will enhance the competitiveness of U.S. industry or have other positive benefits to society. Examples include screening of cancer drugs, advances in catalysis for energy production, design of new alloys and multilayers, and processing of semiconductors. The expertise resident at LLNL in the applied sciences, computations, and materials modeling puts us in a unique position to address these classes of problems.

At present, we face many challenges. Engineering new electronic materials is both costly and time-consuming today. We are still unable to design new alloys and polymers to meet application-specific requirements. Being able to do so quickly and at low cost would give the U.S. a tremendous edge in the international marketplace by providing American industry with revolutionary new capabilities. The national laboratories, with their world-leading competencies in advanced materials modeling, will play a central role in this process.

For further information, contact Christian Mailhiot (510) 422-5873.

Using Computers to Build Better Computers



Lubricant PFPE

COMPUTER hard drives on the market today can store 578 megabits of data per square inch of disk surface area. Even greater storage capacity is on the horizon. One gigabit (1 billion bits) per square inch of magnetic disk has already been demonstrated in the laboratory, and the fundamental limit of storage for magnetic technology is on the order of 100 billion bits per square inch of data.

Three issues are central to increasing the storage capacity of magnetic hard drives. The first is decreasing the size of the magnetic domain that stores a bit of information. The second is creating a read/write head capable of sensing the very weak fields from the smaller domains. The third is moving the head closer to the surface of a spinning disk without introducing deleterious friction and wear.

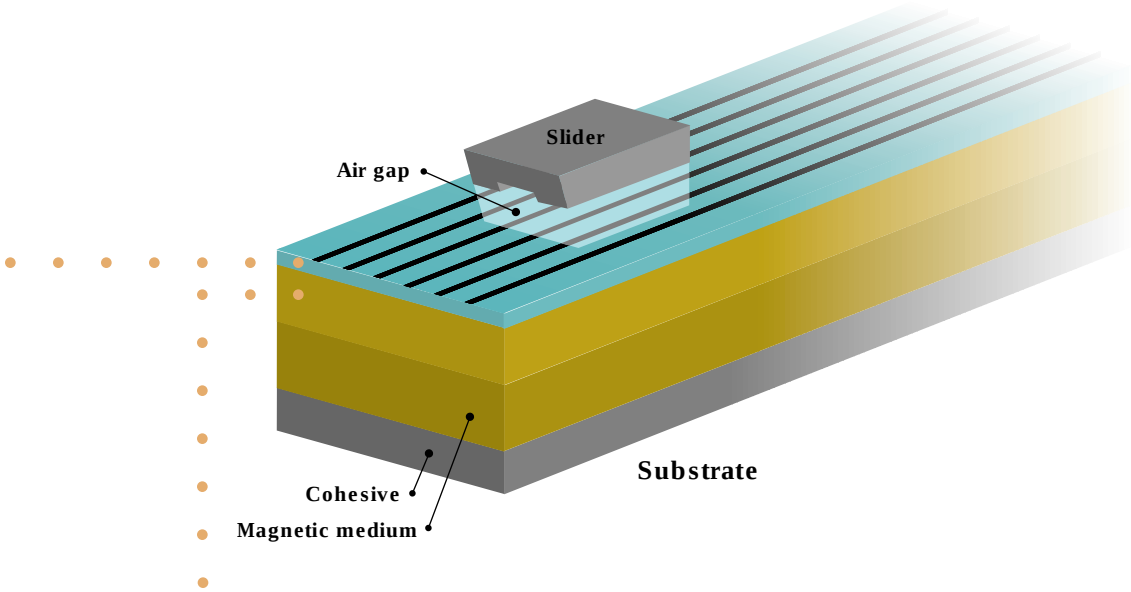
Last year, the Laboratory and IBM's Almaden Research Center in San Jose, California, signed a cooperative research and development agreement (CRADA) to study the relevant friction and wear mechanisms. The three-year agreement is valued at $1.6 million with costs shared equally by the two partners. The next-generation, super-high-capacity, hard-disk drives will increase the disk-storage capacity tenfold, to about 10 gigabits of data per square inch.

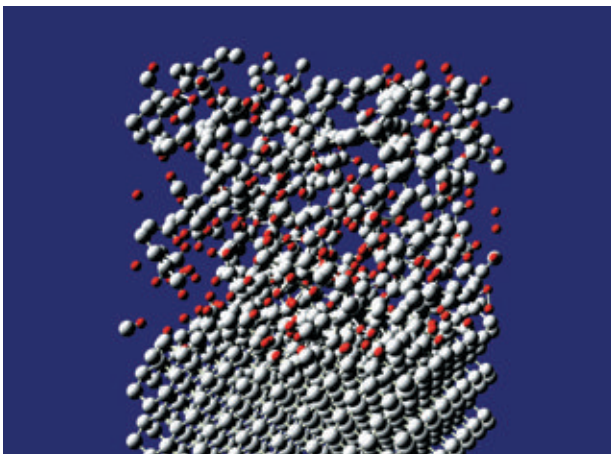
The fundamental problem associated with minimizing friction and wear mechanisms is to gain a better understanding of the underlying chemical and physical processes at the point where a disk drive's read/write head skims closest to the surface of a spinning hard disk (see figure). The interactions at this interface take place at such high speeds and short distances that atomic-level computer simulation may be the only way to envision the details of what may be happening there. Here is a case where modern computers can be applied to build even better computers. In more technical terms, this is a problem where the Laboratory's expertise in atomistic molecular dynamics (MD) modeling is being put to practical use in advancing data-storage technology itself. (The article on p. 13 gives more details on how MD modeling is used to study tribological—that is, friction and wear—processes.)

As shown in the figure, today's disk drives have a gap of only about 75 nanometers (3 millionths of an inch) between the slider, which carries the read/write head, and the disk surface. The disk also rotates very rapidly, between 3600 and 7200 rpm. Thus, the outer edge of the disk travels between 12 and 24 m/s with respect to the slider. These dimensions and velocities make the problem an ideal one for MD computer simulation. The entire slider–disk interface problem can be modeled using about 100 million atoms, which fits in the main memory available on a modern parallel supercomputer. One tool that Laboratory scientists use to analyze the enormous amount of information from these simulations is computer animation. The animated movies show the behavior of individual atoms and molecules at the slider–disk interface.

Between the magnetic substrate and the flying head is a thin coating (30 nm) of amorphous hydrogenated carbon (a:HC). The role of the carbon coating is twofold. It serves as a hard protection against friction and wear, and, because magnetic metals form strong chemical bonds with carbon, it protects the underlying magnetic substrate from corroding. In addition, a thin lubricant film (about 3 nm) is placed on top of the carbon overcoat. Increased storage capacity requires minimizing or possibly eliminating these coatings.

Researchers Jim Belak and Jim Glosli at LLNL and Michael Philpott at IBM are using MD simulation codes developed at LLNL to study the coatings and how they are modified by the tribological processes at the head–disk





Hard coating (a:HC)

The surface of a hard disk is coated with an ultrathin layer of amorphous hydrogenated carbon (a:HC) and perfluoropolyether (PFPE) lubricant to prevent friction and wear. The average spacing between the read/write head, which is carried by a slider, and the spinning disk is about 75 nm in today's technology. The need for even smaller spacing is driving our quest for increased understanding of the friction and wear properties of the protective coatings. To gain such understanding, Laboratory researchers are collaborating with researchers at IBM's Almaden Research Center to develop a molecular dynamics model of the coatings. The two images show our models of the lubricant and hard coating before contact.

interface. They have improved on an empirical model—the bond-order model—of chemical bonding in carbon films. Using this model to simulate the deposition process, they find that carbon atoms in amorphous films have a variety of local environments. When the environment is like that of diamond, the films are compact and hard. In contrast, films created at low deposition energy contain micrographitic structures. These graphitic films are soft. For the first time, understanding the microstructure of amorphous carbon films is within reach. The evolution of this microstructure controls the friction and wear rate.

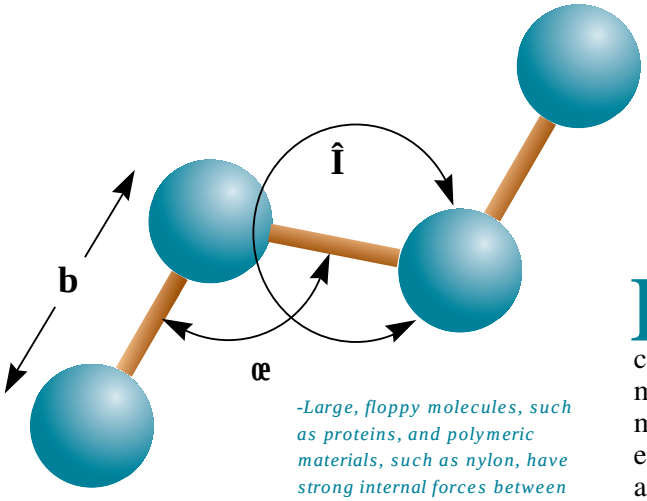
The lubricant molecules used at the head–disk interface are perfluoropolyethers (PFPEs), which present additional difficulties for modelers because no model of cohesion exists for these lubricants. We are developing one based on models used to study large biomolecules. Preliminary results show that such commercial lubricants (with a molecular weight in the range of 4000) undergo significant rearrangement in the time scale for a slider to move about 100 nm over a disk surface. This result indicates that relaxation processes in the lubricants at the head-disk interface can be studied using MD simulations.

The next goal of our joint research is to provide an understanding of the fundamental physical and chemical processes during sliding. Such work is aimed at helping the engineering of the next generation of high-capacity, hard-disk drives. The research could also lead to much larger projects involving many technologies, including surface chemistry and physics, magnetics, and materials fabrication.

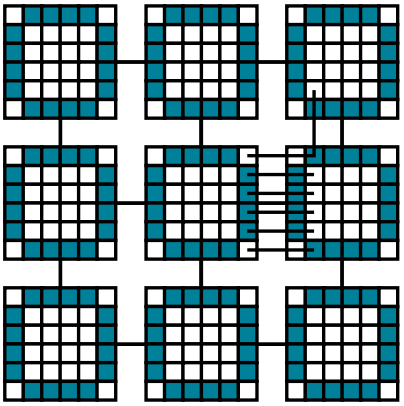
For further information contact James Belak (510) 422-6061 or James N. Glosli (510) 422-5849.

Modeling Large Molecular Systems

Laboratory scientists are developing a set of computational tools to simulate large, floppy molecules on the new Cray T3D parallel supercomputer to extend the capabilities of DuPont and Bristol-Myers Squibb.



-Large, floppy molecules, such as proteins, and polymeric materials, such as nylon, have strong internal forces between atoms that are covalently bonded and very long-range forces with atoms that are far away.



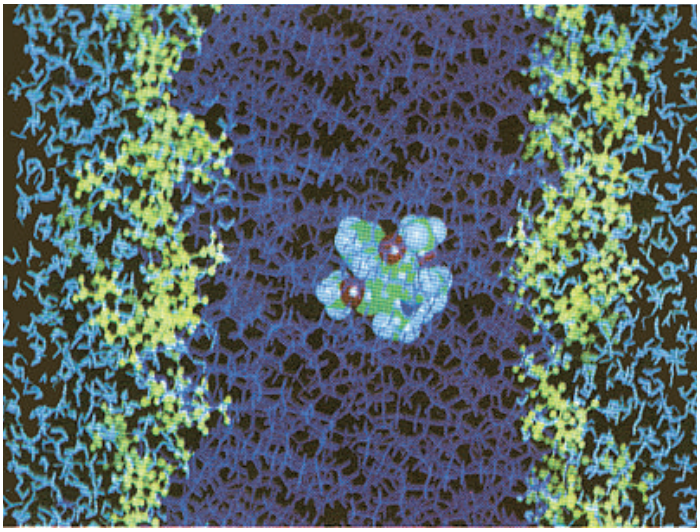
We map large molecular dynamics problems to a parallel computer by dividing the problem into smaller regions or domains.

BOTH the DOE and U.S. chemical and pharmaceutical industries need to accelerate the rate at which they can create new organic-based materials. Examples of the materials being studied include biological molecules and membranes, liquid crystals, optical thin films, and energetic materials. Conventional supercomputers now assist materials designers by giving them the ability to routinely model tens of thousands of atoms for hundreds of picoseconds (1 ps = 10^{-12} s).

However, to accurately simulate many important biological and physical phenomena, we require even more computational power. To simulate large molecular systems with long-range forces for periods as long as tens of nanoseconds and beyond (1 ns = 10^{-9} s), we need at least one or two orders of magnitude more computational power. This power will become available with the next generation of supercomputer, which uses many microprocessors to simultaneously solve a single problem.

Earlier this year, the Laboratory signed a CRADA with three industrial partners and Sandia National Laboratories/New Mexico to address specific computational issues. The goal of the CRADA is to develop the software needed for the newest massively parallel supercomputers in studies of large molecular systems with long-range forces.

In addition to the two national laboratories, the three-year program also involves DuPont, Bristol-Myers Squibb, and Cray Research. DuPont, based in Wilmington, Delaware, has had an ongoing effort in computational chemistry since the mid-1970s. This research and technology-based global company offers advanced technologies and products, such as petroleum, chemicals, polymers, and fibers. Bristol-Myers Squibb is one of the world's largest pharmaceutical companies. Its Pharmaceutical Research Institute, based in Princeton,



A simulation, performed at the Bristol-Myers Squibb Pharmaceutical Research Institute in Princeton, N.J., of a drug molecule at the center of a biomembrane.[1]

New Jersey, has a large computational chemistry effort that assists in understanding biochemical phenomena and in the development of new pharmaceuticals. Cray Research Inc., based in Eagan, Minnesota, is the nation's premiere supercomputer hardware manufacturer. The agreement with these partners will allow access to expertise and computing power that are beyond the scope of any single company or laboratory.

The use of computational science to understand, model, and develop new materials has a proven track record of getting products to market faster. Nevertheless, industry has a pressing need to expand the role that computational science plays. Thus, the partners in the new five-way CRADA will develop a new set of computational tools to examine the behavior of new materials using massively parallel supercomputers. One such computer is the T3D being developed by Cray Research. (The DOE has now leased to LLNL a T3D machine with 128 processors as part of the Industrial Computing Initiative.)

An example of the type of problem we are addressing is the transport of a drug molecule through a biomembrane. In essence, a large molecular dynamics problem such as this is mapped to a parallel computer by dividing the problem into smaller regions or domains. (See the article on p. 13 for an introduction to molecular dynamics modeling.) Each domain, containing many atoms, is treated as a separate molecular dynamics problem and is assigned to a separate processor. That is, a processor is responsible for evolving all the atoms within its domain. At the boundary of each domain are atoms that belong to neighboring domains and different processors. Care must be taken to ensure that the boundary information is communicated at each time step in the calculation so that the correct forces on the atoms are applied.

Another difficulty that arises for large biological systems with water present is that the interaction forces between atoms are very long range. In effect, every atom interacts with every other atom. This situation places serious limitations on the number of atoms we can simulate. To solve the problem, laboratory scientists are exploring an alternative method known as the fast multipole method. The main idea is that, instead of calculating the interaction of every atom that is far away, the code calculates the interaction of an atom with the field produced by distant atoms. The method saves considerable computer time for very large systems. Such savings are crucial to extend our present capabilities to solve key problems facing U.S. chemical and pharmaceutical industries.

Reference

1. T. R. Stouch, H. E. Alper, and D. Bassolino-Klimas, "Supercomputing Studies of Biomembranes," *Supercomputer Applications and High Performance Computing* **8**, 6-23 (1994).

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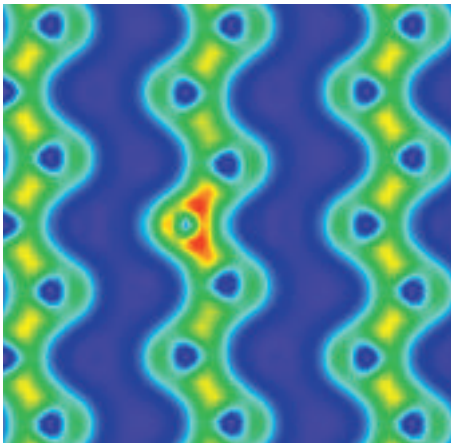
Massively Parallel Computing CRADA



Contours of electronic charge density for a boron impurity atom substituting for one silicon atom in a silicon crystal. The pileup of charge (red) around the boron atom suggests the formation of strong ionic bonds with the neighboring silicon atoms.

IN the most far-reaching technology transfer initiative to date, the Laboratory is working with industry to develop software for massively parallel supercomputers. In June 1994, Secretary of Energy Hazel O'Leary announced a $66 million joint venture involving LLNL, Los Alamos National Laboratory, and an industry group headed by Cray Research, Inc. The three-year, cost-sharing agreement, called the High-Performace Parallel Processing Project, involves Cray Research and 16 other leading industrial firms.

In one part of this endeavor, the consortium will develop software for high-performance parallel processing systems to be used in industrial applications, such as environmental modeling, materials design, and advanced manufacturing. The overall initiative, called the Industrial Computing Initiative, involves some 15 separate CRADAs. One of these projects, which teams LLNL with Xerox Corporation's Palo Alto Research Center and Cray Research, is focused on advanced atomic-level materials design. The primary objective of this project is to apply advanced *ab initio* electronic structure methods to specific physics problems of importance to research activities at Xerox, including investigations of the atomic and electronic structure of amorphous silicon and defect energetics in semiconductor materials.

To accomplish the goals of the projects, the DOE has leased two 128-processor Cray T3D massively parallel computers—one to Los Alamos and the other to the newly formed Center for Computing Sciences and Engineering at LLNL. The two T3Ds will be linked by a high-speed interconnect for collaborative work. These T3Ds can operate at peak speeds of 18 billion floating point operations per second (18 Gflops), which is comparable to the fastest vector supercomputer now at the Laboratory, but a T3D is only about one-tenth the purchase cost.

Much of the software for existing supercomputers was originally developed by the DOE laboratories for their national security missions. However, atomic-level materials modeling also benefits the economic competitiveness of the nation by focusing on industrial problems. The software that industry needs is difficult to write or upgrade from serial to parallel-style codes. New software from the Industrial Computing Initiative will help the private sector make the transition to massively parallel systems, aid industry in designing better materials, and help companies insert new products into the market faster.

Our work with Xerox and Cray Research is aimed at developing codes that simulate materials at the atomic level from first-principles, quantum-mechanical methods. Material properties—whether optical, structural, or electrical—are ultimately determined by electronic structure. The codes developed during this CRADA will extend the Laboratory's current electronic-structure codes to exploit the potential of massively parallel computers. The new capability will allow us to routinely calculate electronic structure in much larger systems and with greater accuracy than was ever possible before.

For example, the figure shows contours of electron charge density for a boron impurity atom substituting for one silicon atom in a silicon crystal. The pileup of charge (red) around the boron atom suggests the formation of strong ionic bonds with the neighboring silicon atoms. Research on defects and impurities in semiconductors will help scientists synthesize materials such as gallium arsenide and amorphous silicon. Gallium arsenide is a light-emitting semiconductor used in the diode laser found in laser printers. Amorphous silicon is used in imaging and scanning devices and in thin-film transistors that are part of flat-panel displays. Research on this and related materials could lead to a new generation of transistors in flat-panel displays for laptop computers, an area in which Japan has a dominant lead over U.S. companies.

For further information contact Christian Mailhiot (510) 422-5873 or Lin H. Yang (510) 424-4153.

Designing Better Microelectronics Devices

THE Laboratory, with its benchmark atomic-level materials theory and simulation software, has much to offer private industry in the area of microelectronics research. Only a few years ago, the idea of building a microelectronics device on an atom-by-atom basis might have seemed unrealistic. Now, that idea is within reach.

In May of last year, LLNL announced a cooperative research and development agreement (CRADA) with the Wilson Center for Research and Technology of Xerox Corporation, located near Rochester, N.Y. The three-year, $3-million project will investigate the behavior of individual atoms and molecules on the surface of microelectronic materials, such as those used in semiconductor chips. The goal is to develop a fundamental scientific knowledge of surface processes, leading to improved performance of devices used in a variety of industrial and consumer electronics products. (For more information about Laboratory research on surface processes, see the article on p. 25.)

The joint research applies quantum mechanical principles to understand what happens when a few atoms interact with a surface. That understanding is expanded to include interactions of larger numbers of atoms, then layers of atoms, and, eventually, to quantities large enough to build entire microchips. The outcome of this approach could optimize, and possibly revolutionize, the processes by which new materials and devices are made.

At Xerox, researchers shine a beam of atoms at a surface and study the results, but they need a better theoretical base to interpret what they observe. The Laboratory's expertise in computer modeling can extend the state-of-the-art capabilities at Xerox in surface etching, passivating chemically reactive surface sites, and thin-film growth. For the Laboratory, the new experimental work will be invaluable in refining new models and validating theories.

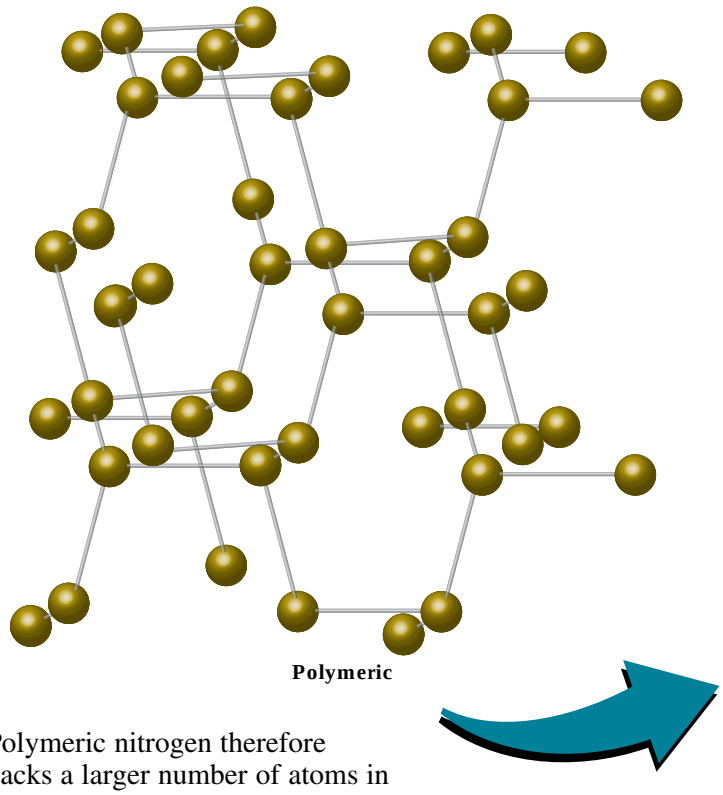
Among other benefits, the collaboration may lead to an improved theory of reactive scattering—the scattering of atoms and molecules off semiconductor surfaces. Such a theory would allow scientists to predict the behavior of etching species that come into contact with a surface and cause a chemical reaction between two materials.

To develop a quantitative theory of reactive scattering, Laboratory scientists are calculating from first principles the electronic structure of chlorine atoms on a tantalum surface. Simulating all the dynamics from first principles is beyond the current capabilities of our best supercomputers. To circumvent this problem and address the industrial process of reactive etching, Laboratory scientists are using the first-principles energy of a single chlorine atom as it reacts with the tantalum surface; from this energy, we can set the parameters of an empirical potential energy model. Forces in classical molecular dynamics simulations are represented using empirical potential models (see the article on p. 13). Classical molecular dynamics is then used to model the industrial process.

By predicting and controlling these and other types of reactions, microelectronics devices could be built one atom at a time. Down the road, this would mean higher-density and higher-performance optoelectronic and microelectronic circuitry, larger-area displays, and advanced chip designs. For now, the work is considered "precompetitive research," meaning that the results will be made available to the scientific community with the expectation of commercial benefits in the future.

For further information contact Christian Mailhiot (510) 422-5873 or David B. Boercker (510) 422-4187.

Polymeric Nitrogen: A Potential Compound to Store Energy



RESEARCHERS throughout the industrialized world are looking for alternative sources of energy to relieve the world's heavy reliance on fossil fuels. Fossil fuels are not only polluting, but they will eventually be depleted if consumed at current rates. In addition, the political realities of the post-Cold War era place renewed emphasis on the performance of conventional weapons, which could be enhanced by the creation of more energetic explosives.

One potential compound that can store energy is nitrogen, which makes up 78% of the atmosphere. Each atmospheric nitrogen atom naturally combines with another to form N_2, a diatomic molecule held together with the strongest bond known—a triple covalent bond. Theory suggests that if a volume of N_2 is sufficiently squeezed, the nitrogen will give up its diatomic structure and form a continuous network of single covalent bonds. This polymeric structure is like that observed in its chemically similar neighbor, phosphorus. At normal atmospheric pressure and temperature, polymeric nitrogen should be a highly energetic metastable solid.

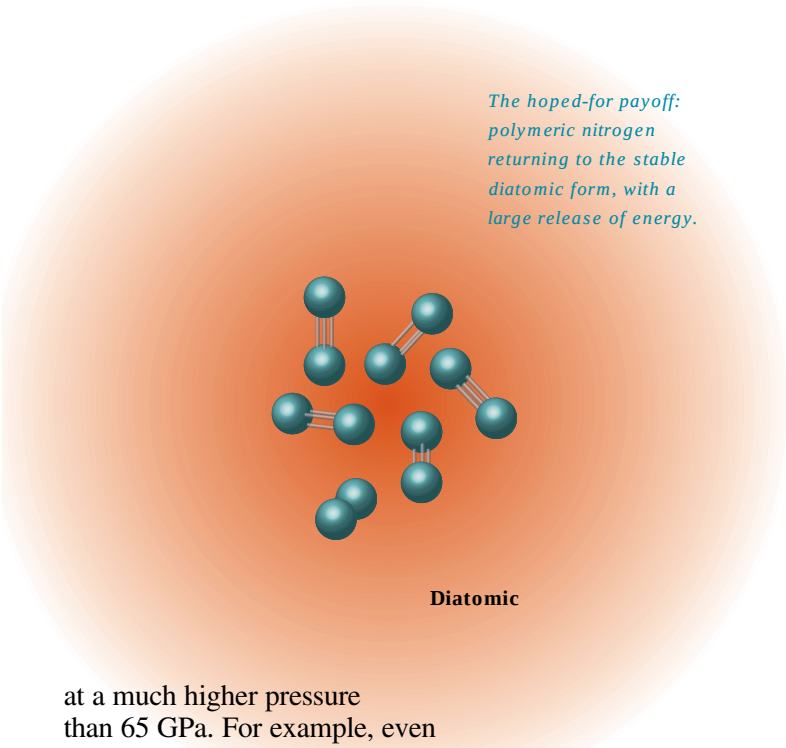
Our first-principles, quantum-mechanical calculations indicate that 1 cm^3 of polymeric nitrogen would store 34 kJ of energy—an amount virtually identical to that of diesel oil and gasoline and nearly three times that of HMX, one of the more powerful explosives in the world. Moreover, the energy released when polymeric nitrogen returns to the diatomic state would be pollution free: the sole reaction product would be environmentally benign N_2 gas.

Having only covalent bonds, polymeric nitrogen differs from most conventional liquid and solid fuels, propellants, and explosives (e.g., gasoline, liquid H_2/O_2 mixtures, and HMX). These other energy sources have covalent bonds within each molecule that alternate with extremely weak van der Waals interactions between the molecules. Polymeric nitrogen therefore packs a larger number of atoms in a given volume and can store a correspondingly larger amount of energy per unit of volume than other sources.

A decade-long history of theory and experiment in high-pressure physics has revealed trends across the periodic table of the elements. One such trend suggests that applying pressure to an elemental solid will cause it to assume the structure and bonding of a heavier element in the same column of the table at atmospheric pressure. For example, the stable phase of carbon at 1 atm is graphite, which transforms under pressure to the diamond structure. Diamonds, which are metastable solids at 1 atm, have the same structure as silicon and germanium at 1 atm.

Theory has played an important role in examining this trend. At pressures up to ~100 GPa (100 GPa = 1 Mbar = 1 million atm), some 44 phases have been encountered for the elemental solids in groups III, IV, and V of the periodic table. Well over half of these phases have been investigated theoretically, and phase identification has shown near perfect agreement with experiment.

We have predicted that, in the absence of energy barriers, nitrogen should always be diatomic below 65 GPa and polymeric above this pressure. However, energy barriers retard the effect of increased pressure and are typically quite large between two covalent phases. Therefore, the diatomic-to-polymeric transition in nitrogen should occur



The hoped-for payoff: polymeric nitrogen returning to the stable diatomic form, with a large release of energy.

at a much higher pressure than 65 GPa. For example, even when carbon is heated to 1000 K, the graphite-to-diamond transition requires roughly a factor of seven times more pressure than that predicted without energy barriers. Although energy barriers will make the synthesis of polymeric nitrogen at high pressure more difficult, they will help stabilize the polymeric phase once synthesized.

Our calculations suggest that the reverse transition (polymeric-to-diatomic) should also occur at a much lower pressure than 65 GPa—at least for a polymeric solid without defects or free surfaces. We are currently enhancing our present theoretical capabilities to determine the impact of defects and of room-temperature atomic vibrations on the metastable lifetime of polymeric nitrogen at 1 atm.

Current Research

To synthesize polymeric nitrogen, we are using one of LLNL's diamond anvil cells, a robust device with a small (~20 μm diameter) sample chamber within which pressures exceeding that at the center of the earth (~350 GPa or 3.5 Mbar) have been reached. Nitrogen at room temperature has retained its diatomic form in the diamond anvil cell up to pressures of 180 GPa. By contrast, analysis of shock-wave data imply that nitrogen becomes a fluid of single atoms at ~6000 K and at the relatively low pressure of 30 GPa. (In shock compression, a supersonic pressure wave hitting the sample induces brief conditions of high pressure and temperature.) However, laser heating in a diamond anvil cell allows more controlled access to the extremes of pressure and temperature than does shock compression.

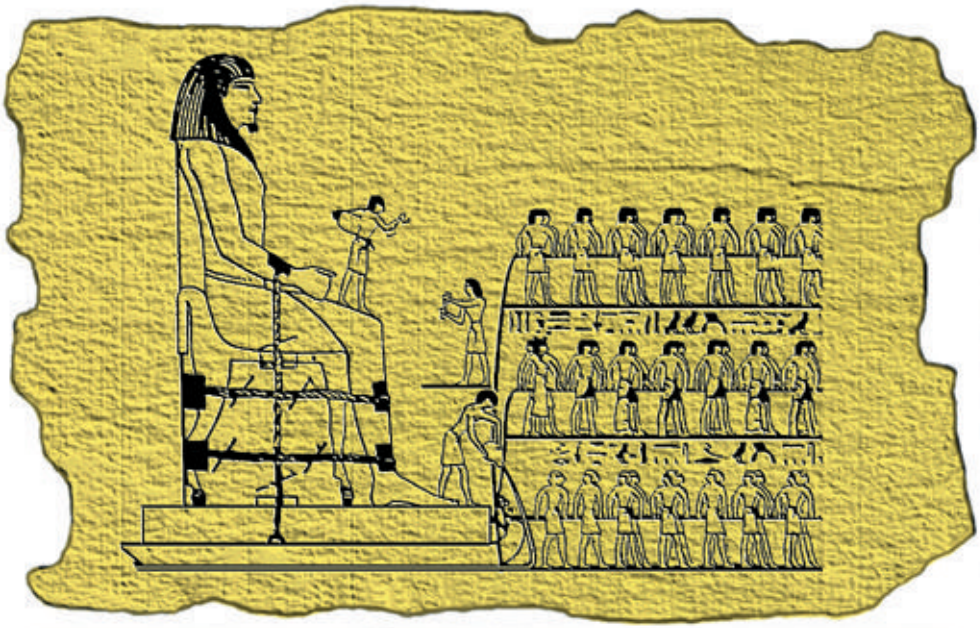
We therefore plan to heat the sample by transmitting an intense laser beam through one of the transparent diamond windows. We have already achieved 2000 to 6000 K temperatures in the diamond anvil cell. This combination of high temperature and pressures, or "hot isostatic pressing," is a tried and true materials processing technique, although so far only at pressures of tens of GPa. Our technique will extend this range in pressure by more than an order of magnitude.

To diagnose our nitrogen sample, we will use Raman scattering. When a laser beam is transmitted through the diamond anvils onto the sample, some of its photons are scattered by lattice vibrations in the nitrogen solid, leading to measurable frequency shifts in components of the beam. Raman scattering is an *in situ*, real-time diagnostic that allows us to see directly the strong triple bond that we hope to break. This diagnostic will immediately indicate the synthesis of polymeric nitrogen by the disappearance of the triple bond and the appearance of new vibrational modes.

We have begun our laser-heating efforts in the 100 GPa regime and have obtained clear indications of pressure-induced weakening of the triple N_2 bond. We are now using larger samples with a more powerful laser to minimize heat loss to the diamond anvils. With recent experimental improvements, we are confident that we can achieve ~5000 K in our high-pressure N_2 samples. After we synthesize a small sample of polymeric nitrogen at high pressure and demonstrate its stability at atmospheric pressure, production scale-up by other means will be explored.

For further information contact Andy McMahan (510) 422-7198 or Hector E. Lorenzana (510) 422-8982.

Nanotribology: Modeling Atoms When Surfaces Collide



Realistic computer simulations at the atomic level of detail are revealing new information about the basic processes that take place when materials are fabricated, as in cutting and grinding. With such increased understanding, we are developing more practical engineering guidelines for LLNL researchers and the industrial community.

TRIBOLOGY (friction, lubrication, and wear) is the science of interacting surfaces in relative motion. The word "tribology" is from the Greek *tribein*, meaning to rub. Although the term may be unfamiliar to many, its meaning is clearly conveyed among some of the oldest written records. An Egyptian painting dating back to 1880 B.C. depicts workers dragging a sled containing a heavy statue. One worker pours a liquid on the ground just before the runners to make the going easier. Leonardo da Vinci addressed the same problem when he wrote in 1519, "All things and everything whatsoever however thin it be, which interposed in the middle between objects that rub together, lighten the difficulty of this friction." An excellent source for further historical reading is Dowson's *History of Tribology*.[1]

We have first-hand experience with friction any time we walk on ordinary ground and compare the outcome with what happens when we try to walk on ice. Wear of mechanical parts—as every car owner knows—eventually leads to failure and is one of the most costly problems facing industry.

To design and engineer mechanical parts, we need a macroscopic understanding of tribological processes. However, today the tolerances of many components, such as optical devices, computer chips, and ultra-smooth surfaces, are approaching the microscopic (atomic) length scale. In fabricating such precise components, we can greatly benefit from an atomic-scale understanding of what happens when surfaces interact. The emerging field that lets us obtain this atomic-scale understanding of fundamental processes of surfaces in motion is called molecular tribology or

nanotribology. (A nanometer is one billionth or 10^{-9} of a meter; the size of an atom is about 0.3 nm.)

Recent progress in nanotribology is being driven by advances on several fronts. Of primary importance is the advent of probes that allow researchers to examine interacting surfaces at a microscopic level. One such probe is the atomic-force microscope, which has a very small tip with a radius of about 10 nm used to probe a surface. The surface force apparatus has also become a highly useful tool. Other major developments in the last decade are better models of interatomic forces, which, coupled with improved performance of computers, are giving researchers a new window into tip–surface interactions through computer simulations.

How Our Work Began

Scientists at the Laboratory became involved in the field of tribology as a result of work being done in precision engineering about a decade ago. At the time, we were exploring ways to cut materials with extreme accuracy and to obtain the best-quality surface in the process—one with very high smoothness and minimal surface damage. To meet the demand for extremely high tolerances, we developed a mechanical device called the single-point, diamond-turning machine.

Machines like the large-optics, diamond-turning machine (LODTM) at the Laboratory can routinely cut away as little as a few nanometers of material off a surface. Although diamond turning soon became a well-established technique, little was understood of the basic mechanisms that determine how the material is removed, how surface damage occurs, and how diamond tools themselves wear. Diamond turning was an obvious case where we could profit greatly from an atomic-scale knowledge of underlying tribological processes.

For special applications, diamond-turning machines can cut materials at speeds of several hundred meters per second, and the entire process of chip formation takes place on time scales much less than a single microsecond (10^{-6} s). For these and other reasons, diamond turning is a good example of a mechanical device that lends itself well to atomistic computer modeling. Following the suggestion of John Holzrichter and others at the Laboratory, we began to apply a type of modeling called molecular dynamics (MD) modeling, which explicitly takes into account interatomic motion. Such modeling gives us insights into the cutting process at very short time scales and length scales.

These days, we are using MD computer simulations to focus on several different aspects of nanotribology. For example, we are studying surface indentation of various metals and ceramics, high-speed metal cutting, and the growth of cracks in glass. LLNL has become a key player in the field of nanotribology, but it is only one of many institutions doing this type of research. Tribology issues being addressed today with MD simulations include wearless friction, adhesion and adhesive wear, and mechanical wear. Other problems range from boundary lubrication, to stick-slip phenomena (described later in this article), to junction formation and growth. For further reading on tribological processes in general, see Reference 2. Reference 3 is a review of recent progress in nanotribology.

This article describes a variety of work we have recently done to model—that is, to simulate at the atomic level—the way material is removed by mechanical means. We have developed an MD model of the cutting process, studied the process of chip formation, and examined wear mechanisms for a diamond cutting tool. Recently, we modeled the high-precision machining of glass surfaces. Our computer simulations of the indentation of a smooth glass surface are helping to explain how microscopic processes, such as the breaking and forming of interatomic bonds, give rise to macroscopic phenomena, like the plastic properties of silica glass and the ductile behavior it can exhibit under certain conditions. (In mechanics, plasticity refers to a permanent change in shape or size when a material is subjected to a stress; ductile behavior means plastic deformation without fracture.)

An underlying theme of our work is to study practical problems and materials and to ultimately transfer what we learn on the atomic scale to real-world applications that are important to the broader community of materials scientists and engineers. Molecular dynamics modeling is limited in terms of the size of the material and the period of time that can be studied. In particular, the length scale is limited by the number of atoms that can be stored in a computer's memory and the enormous amount of work required to calculate interatomic forces. For practical reasons, we typically study systems containing no more than 100 thousand atoms (a length scale of about 10 nm). In principle, however, systems containing more than 100 million atoms (100 nm) are now possible.

The time scale is limited by the time it takes for an atom to collide with a neighboring atom. This vibrational period is very short, only 10 to 100 femtoseconds (10^{-14} to 10^{-13} s). The single time step in an MD simulation must be a small fraction (about 1/25) of the vibrational period, leading to a time step of about one femtosecond. A typical long simulation runs for tens of millions of time steps (to simulate a total period of about 10 ns), requiring many days on a supercomputer.

In the next few years, we expect to routinely attain length scales of hundreds of nanometers (hundreds of millions of atoms) using more powerful parallel supercomputers. We use a parallel computer by dividing space so that each processor executes its own MD simulation for a small region. The brief on pp. 6–7 gives more details on massively parallel computing. Unfortunately, to date, no one has determined how to exploit parallel computers to study longer time scales.

The Basics of Molecular Dynamics Modeling

The molecular dynamics method was originally developed at the Laboratory in the late 1950s to study the statistical mechanical properties of a collection of atoms at equilibrium. The method is now a well-established and important tool in the fields of physics, chemistry, biology, and engineering. Recent advances in computer hardware and software allow us to simulate relatively large systems using increasingly realistic models of the forces between atoms.

In principle, MD modeling is simple. We start by identifying the position and velocities of all atoms in a system we want to model. Then we calculate the force on every atom from its neighbors and advance the positions of the modeled atoms according to Newton's equations of motion (force = mass × acceleration). During a simulation, we evaluate the response of a material—often copper, silicon, or silica glass—as it is subjected to an external force by following the response of each atom. Examples of external forces include stress fields, moving boundaries, and heat baths.

Despite the simplicity of MD modeling, the number of users and applications today remains limited; in addition, many researchers do not use it to its full potential. The reason for this underuse is that this type of modeling can be "overkill" in that it is too expensive and requires too much detail for solving most practical problems. Furthermore, there is a certain art in selecting the appropriate boundary conditions and constructing interatomic-force models.

Consider, for example, Figure 1, which shows the boundary conditions we use in many of our simulations of indentation and cutting of a clean metal surface by a diamond-like tool. In this figure, the dashed line forms a box surrounding all the atoms that are represented. This box is called a simulation cell, which is our "window" on the system being modeled. Both the metal surface and the V-shaped diamond tool above it have "handles" to position the surfaces relative to one another. These are the dark circles forming the boundary. In practice, we keep the tool fixed in the rotational direction and slide the work surface from left to right during a simulation of cutting.

Immediately next to the boundary atoms is a region in which the atoms are constrained to be at room temperature. From an atomic point of view, temperature is a manifestation of the vibrational energy of the atoms. The role of the thermostat atoms in our tribology simulations is to draw away heat generated at the tip of the tool, mimicking a much larger piece of material than is represented in the illustration. The remaining atoms represented by open circles make up the Newtonian region, meaning that these atoms are free from further constraint and move according to

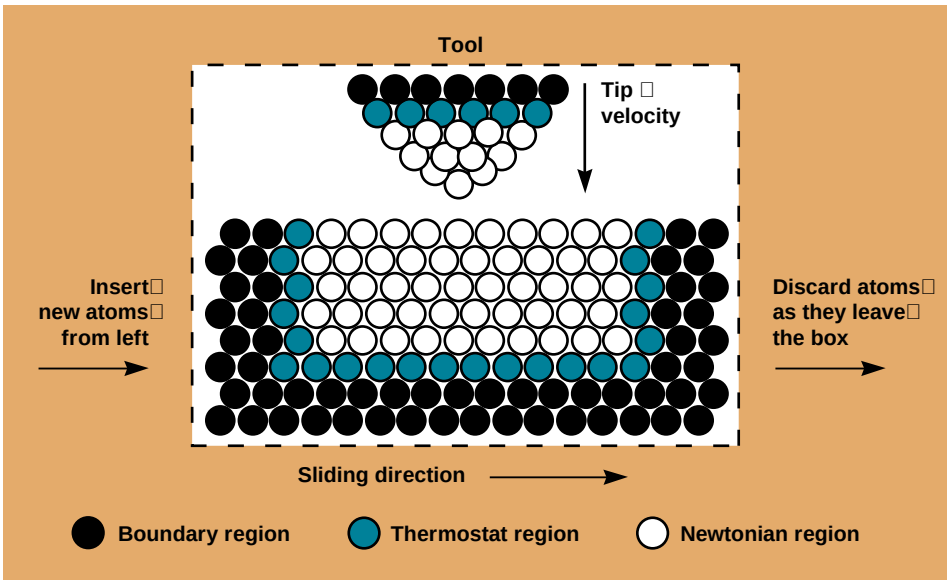


Figure 1. Geometry of a tool tip and work piece for a molecular dynamics (MD) simulation of indentation or cutting. The box, represented by the dashed line surrounding all the atoms, is our "window" into the system being modeled. Only the atoms in this box are evolved during an MD simulation. The top and bottom layers of boundary atoms (dark circles) are rigid and serve as "handles" to position the tool relative to the surface. The next layer of atoms (gray circles) are maintained at room temperature. Their purpose is to draw away heat produced at the tool tip. The remaining atoms (open circles) are free from constraint; that is, they obey Newton's equations of motion. Deformation processes in this interior region are the ones of interest in our MD simulations.

Newton's equations. The tribological processes in this region are of interest in the MD simulation.

In many cases, we would like to simulate cutting or scraping over lengths that are far greater than the dimensions of the dozen or so atoms shown in Figure 1. However, as mentioned earlier, following the motion of a large number of atoms is prohibitive in terms of computer time and cost. To help overcome this problem, we use a relatively simple approach. We allow atoms to leave the simulation cell at the "downstream" end (to the right in Figure 1 as the simulated work piece moves under the tool). At the same time, we periodically insert new atoms from the left at the upstream boundary. This approach restricts the population of atoms simulated at any given time, while allowing us to model nanotribological processes in a much larger work piece. The extension of this model from two to three dimensions is straightforward.

MD Simulations at LLNL

Indenting Surfaces

One of our first simulations involved the indentation of a metal surface by a blunted, triangular diamond tip moving vertically at a constant velocity ranging from 1 to 1000 m/s. Keep in mind that in this and all of our subsequent work, our objective is to understand—at a more microscopic, atomistic level than was previously possible—what is happening when surfaces in relative motion interact with one another.

Figure 2a is a "snapshot" of what happens when the tool indents the first three layers of metal. The interatomic forces in a metal arise from two effects: the interaction between electrons localized on the atoms, and the interaction of atoms with free electrons. We use an embedded-atom model of the metal that incorporates both of these effects. In this figure, the atoms are shaded by the local value of stress. At first, the surface responds elastically (deforms without permanent loss of size or shape), and we see circular regions of constant stress, called the Hertzian stress field, which is well known from elasticity studies of contact mechanics. When the tool is pushed in further to indent six layers of metal, as in Figure 2b, the surface begins to flow plastically, and we obtain shear and discontinuity. (See Reference 4 for an introduction to dislocations and plastic deformation.) In a 2D simulation like this one, dislocation edges are clearly visible within the metal along the darker-colored slip bands that appear at 60-degree angles with the surface. In a close-packed metal such as this, the atoms behave like hard spheres (for example, billiard balls), and slip

(a) (b)

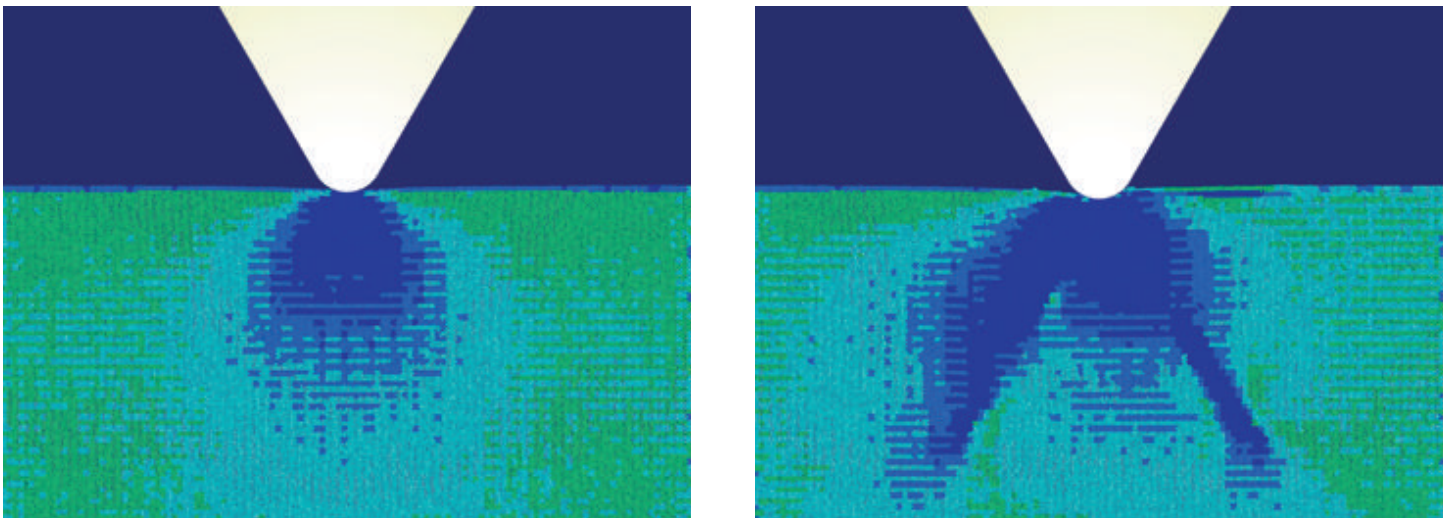


Figure 2. Two frames from our two-dimensional MD simulation of the indentation of a metal surface. The atoms are shaded by the local value of stress. (a) When the tip is pressed three layers into the surface, the response is entirely elastic; that is, there is no permanent change in size or shape of the material. The circular regions of stress are well known from continuum elasticity studies of contact mechanics. (b) When the tip is pressed six layers into the surface, the material yields plastically by creating dislocations along slip bands visible at ±60 degrees from the horizontal surface of the metal. The plastic deformation means that the metal's change in shape remains when the tool tip is removed from the surface.

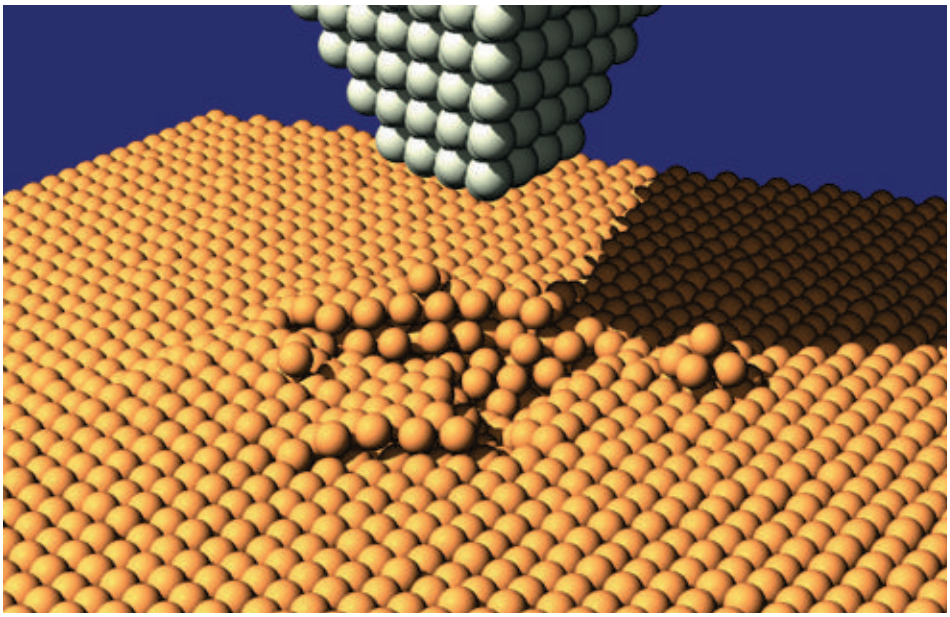
is analogous to sliding stacks of billiard balls over each other.

A 3D simulation of the indentation of copper gives us a slightly different picture. Figure 3a is an image we obtained after copper was indented at a rate of 1 m/s, and the simulated tool was withdrawn from the surface. (Slower rates, typical of experiments performed in the laboratory, are beyond the current capabilities of MD simulations.) In a 3D simulation, we do not see the distinctive bands of dislocation that were observed in a 2D simulation. Moreover, there is relatively little distortion at the metal surface. Instead, we find a small pileup of atoms on the metal surface, a few atoms in interstitial positions (between regular lattice positions), and a small dislocation loop (observable in Figure 3a as the "step" or ledge of atoms on the surface) extending to the bottom of the crater.

Figure 3b helps to explain the difference between our 2D and 3D simulations. Here, the atoms are colored according to the initial layering before the computer experiment. This cross section at the moment of full indentation of the copper surface shows that very little surface distortion has actually occurred. Remarkably few atoms have bulged out around the tool. Instead of distinctive dislocation bands, we see disorder only within a few layers of the sides and bottom of the tool tip. This localized disorder arises from point mechanisms (interstitials, vacancies, and so forth) of plasticity.

There are many other ways to display the results for such a simulation. One of the best and most revealing is by means of a graph, called a loading curve. Figure 4 shows the load (instantaneous force in nanoNewtons) on the diamond-like tool as a function of depth of indentation (shown here as the number of layers indented) for the simulation in Figure 3a. The very rapid

(a)



(b)

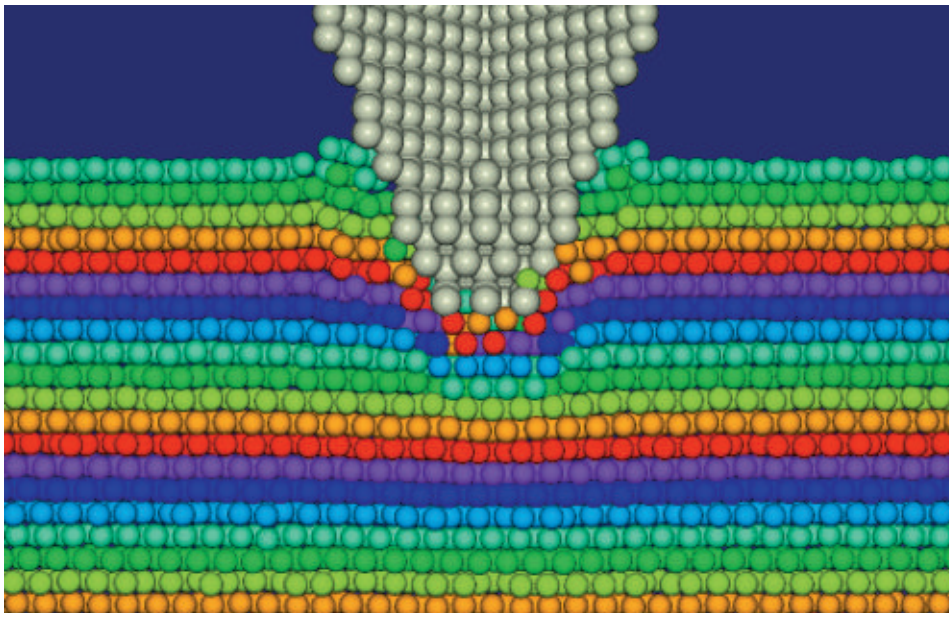


Figure 3. (a) Three-dimensional simulation of the indentation of a clean copper surface. The tool was pressed into the surface to a depth of seven atomic layers and removed to the position shown. The mechanisms of plastic deformation (permanent change in shape) include a small pileup of atoms on the metal surface, a few atoms in interstitial positions, and a small dislocation loop (observable as the "step" of atoms on the surface in front of the indent) extending to the bottom of the indent. (b) Cross section through the center of the tool for the simulation shown in (a). The copper atoms are shaded according to their initial depth. (The shading pattern repeats every eight layers.) Remarkably few atoms have bulged out onto the surface around the tool. Through elastic and plastic deformation, the surface is able to accommodate nearly the entire volume of the tool.

fluctuations in load—which look like "noise" on the curve—arise from the rapid motion of surface atoms repeatedly colliding against the tool atoms. The larger peaks and valleys are far more interesting in terms of what they reveal.

At first, the load rises linearly as the metal surface responds elastically. After indenting about 1.5 layers of copper, the load drops abruptly when the elastic stress is relieved. This abrupt drop, called "critical yielding," is reminiscent of what is observed in the laboratory. The first yielding in the simulation corresponds to a single copper atom popping out onto the surface from under the tool tip and relieving the stress energy. With more indentation, more of these point events take place. After indenting seven layers of copper, the tool is stopped. At this point, the surface accommodates nearly all the tip through elastic and plastic deformation, and there is little pileup of atoms around the tip, as observed in the cross section in Figure 3b. When the direction of the tool is reversed (lifted from the surface), the load quickly drops to zero, as expected. However, the load suddenly rises once again as the tool is removed further. This unexpected rise is caused by annealing at the surface of the metal so that the material returns to more intimate contact with the tool, and the load rises.

Our results from simulations using silver as the indented material are quite similar to those just described for copper. However, because silver is softer, the yielding occurs at a smaller load than for copper.

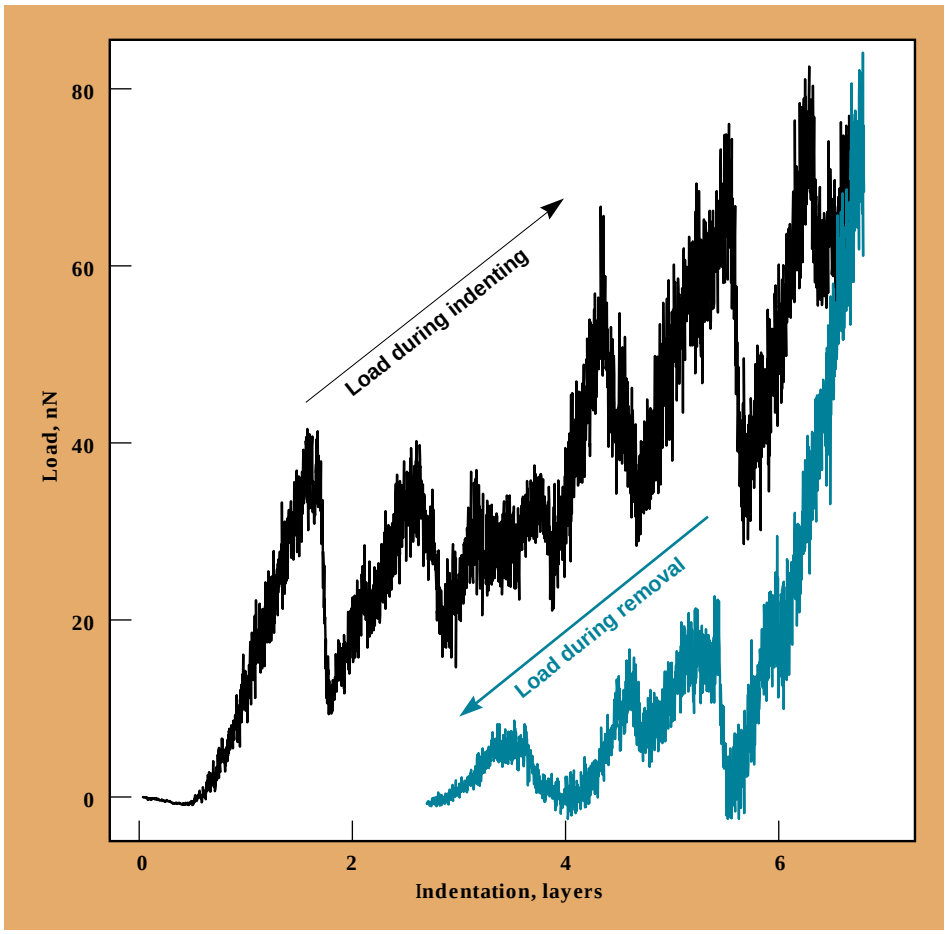


Figure 4. The load (normal force in nanoNewtons) on the diamond tool as a function of depth of indentation for the simulation shown in Figure 3a. The abrupt drops in the loading curve correspond to individual plastic events, such as an atom popping out onto the surface from beneath the tool tip. After indenting seven layers, the direction of the tool is reversed, and the load quickly drops to zero as is expected. However, on further removal, the load suddenly rises again. This unexpected rise is caused by annealing at the surface so that the material returns to more intimate contact with the tool, and the load rises again.

Cutting and Chip Formation

Cutting is a widely used process in fabricating components. To obtain a more basic understanding of what happens when a metal is cut, we use a simplified geometry. We idealize our model slightly by limiting the motion to two dimensions or thin, periodic slabs in three dimensions. This idealization, known as orthogonal cutting, assumes that the material being cut is sufficiently wide that edge effects have essentially no influence on the results.

We have simulated orthogonal cutting in both two and three dimensions. The 2D simulations more accurately model the length scales and time scales that are common in laboratory experiments using single-point, diamond-turning machines. In this type of simulation, cutting speeds range from about 10 to 100 m/s. We have also varied the sharpness of the rigid tool tip used for cutting. We have used tool-edge radii of curvature ranging from 1 to 20 nm. Our bluntest tip (20 nm) approaches the sharpest real-life tool tip, which has a radius of curvature of about 35 nm.

Figure 5a is a single frame from a computer-animated movie of our three-dimensional MD simulation of orthogonal cutting. The copper

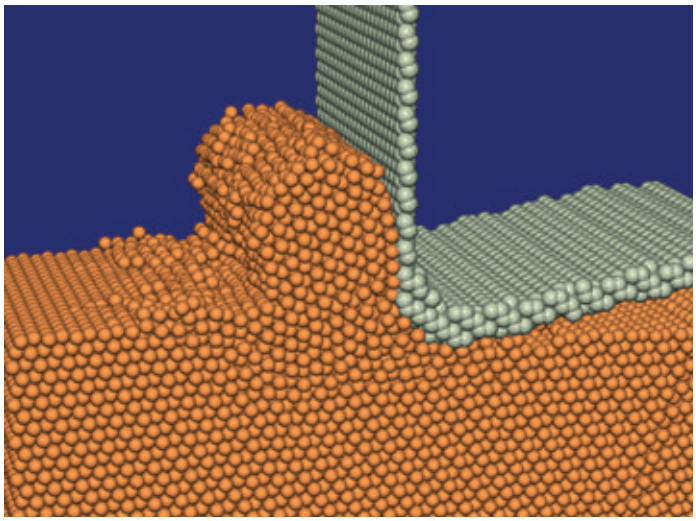
material flows from left to right at 100 m/s. In this simulation, the carbon atoms in the diamond-like tool are not permitted to move, so they serve as our fixed frame of reference.

Figure 5b is a projection in two dimensions of all the atomic positions in Figure 5a. This type of projection makes it easier to see some important effects. During our simulation of cutting, the system forms a chip. The chip is reminiscent of what is actually observed during real experiments. The chip remains crystalline, but it has an orientation different from that of the surface. Regions of disorder among the atoms are apparent in front of the tool tip and on the surface in front of the chip. Unlike our 3D studies of point indentation, dislocations readily form during orthogonal cutting. Unlike the single point in our indentation simulations, the cutting tool in the orthogonal cutting geometry forms an infinite line, like a knife edge. This geometry provides much more energy for the creation of dislocations.

Our calculations show that the cutting force strongly depends on the sharpness of the tool. This relation is also observed experimentally. Dull tools (those with a large tip radius) require larger forces to achieve the same depth of cut as sharp tools. A good measure to quantify our observations is the work (force × distance) performed by the cutting tool divided by the volume of material removed, also known as the specific energy. This energy increases dramatically with decreasing depths of cut. For our shallowest (nanometer-scale) cut, the specific energy exceeds the energy required to vaporize the material, though the material remains a solid.

The dependence of specific work on depth of cut has been observed in macroscopic metal cutting for many years and is known as the size effect. However, the macroscopic size effect is much less dramatic than the size effect observed in our simulations or in experiments using single-point, diamond-turning machines. The transition between macroscopic and microscopic behavior occurs at a length scale of a few micrometers, comparable to the average grain size in most metals. We interpret this result as a change in the mechanisms of deformation, from grain-boundary sliding and motion of *existing* dislocations at the macroscopic scale to the creation of *new* dislocations and other point mechanisms of deformation at the microscopic, atomic scale. These dislocation-creation and point mechanisms of deformation consume

(a)



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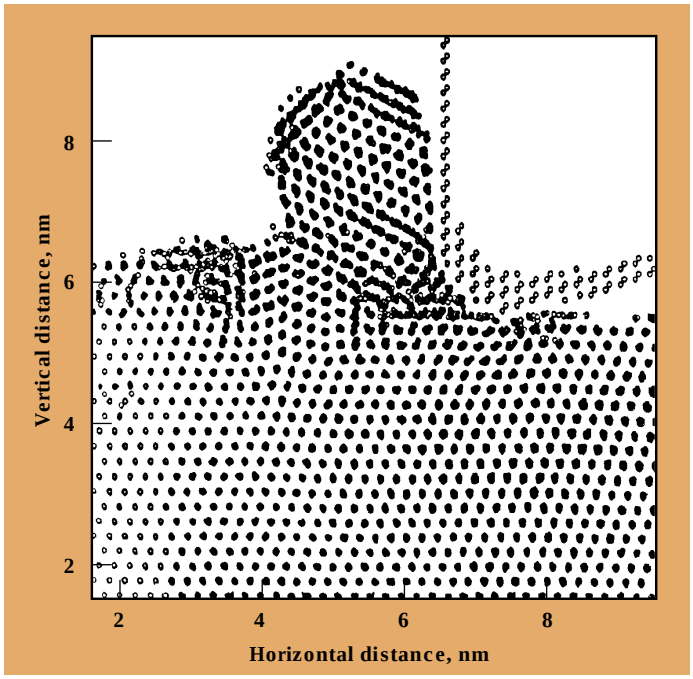

Figure 5. A 3D simulation of orthogonal cutting of copper (a) after the formation of a chip and (b) with all atomic positions projected into two dimensions. In this MD simulation, the carbon atoms in the tool are not permitted to move, and the copper material is flowing from left to right. The chip remains crystalline, and regions of disorder are seen in front of the tool tip and on the surface in front of the chip. These regions of disorder, clearest in (b), are connected by a zone of intense shear.

significantly greater energies, leading to the observed size effect.

In contrast to copper, materials like silicon and iron are not considered machinable with diamond tools. The reason is that the diamond tool wears rapidly, and it becomes difficult to maintain contour accuracy. The increased wear occurs for all materials that form strong chemical bonds (covalent bonds) with carbon. We have investigated and identified some of the underlying processes that give rise to these effects.

In covalent materials like silicon, the nature of interatomic forces is much different from that in metals. The strength of a covalent bond depends on the local environment, and the material forms an open structure. Our basic method is the same as that for cutting copper, except that now we evolve not only the silicon surface material but also the carbon atoms in the diamond tool to allow for tool wear. We have found that both copper and silicon show ductile behavior during cutting; however, the underlying mechanisms that allow this behavior are very different for the two materials. Whereas a copper chip remains crystalline, a silicon chip is transformed into a completely different state.

Figure 6 is a cross-sectional view, just as the one in Figure 5b, but this time of a silicon-cutting simulation. In this case, the diamond wedge is cutting at a speed of 540 m/s. Although no wear of the tool is apparent yet, a single layer of silicon atoms has coated the diamond tip. Chip formation occurs between this layer of silicon atoms and the crystalline surface. In related simulations of diamond asperities (abrasive tips) scraping a silicon surface (as in grinding processes), we found that the diamonds wear by forming small clusters of silicon carbide, which remain on the silicon surface.

In Figure 6, the silicon material in the chip and in the first few layers of newly cut surface appears to be amorphous or possibly to have melted. The temperature in the chip, calculated from the vibrational motion of silicon atoms, is comparable to the melting temperature of bulk silicon. However, the silicon atoms in the chip are not diffusing, which demonstrates that the material is, indeed, in a solid state.

We have developed the following idea to explain chip formation in crystalline silicon. Because of the nature of covalent bonds in crystalline silicon, the energy needed to shear the crystal is enormous. In fact, less energy is required to transform the crystal into an amorphous solid and to shear the amorphous solid than to shear the crystal. The interplay between the energetics of different deformation processes and the dependence on length scale may explain the transition from brittle to ductile behavior that is observed in ceramic materials.

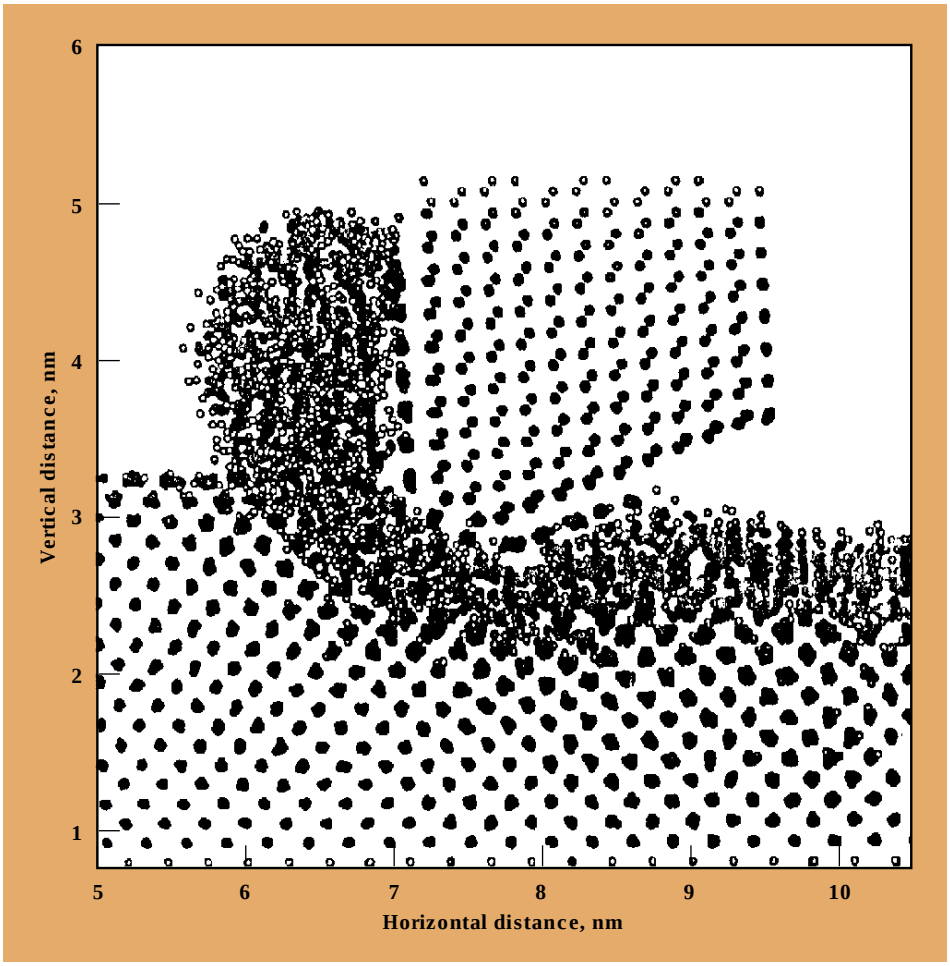

Figure 6. A 3D simulation of orthogonal cutting of silicon. As in Figure 5b, all the atomic positions are projected into two dimensions to make certain features more visible. Unlike copper, silicon is transformed from a crystalline state into an amorphous state during cutting. Both the chip and the first few layers of newly machined surface are amorphous. A thin layer of silicon atoms also coats the diamond tool. The chip forms between the bulk silicon and this thin coating.

How Cracks Propagate in Glass

The ability to precisely machine ceramic surfaces like silica glass affects

many different fabrication technologies and is central to constructing a wide range of sophisticated optics systems. At LLNL, the Laser Program needs to make very high-quality mirrors, and we need to know more about special materials, such as ceramics, used in modern devices and equipment. We are applying MD methods to examine deformation processes at the atomic scale in these materials.

The main difficulty is that glass and ceramic materials are brittle. Anyone who has seen a rock impact a windshield or a pane of window glass knows about the property of brittleness. This property can result in cracking, subsurface damage, and other kinds of costly damage during precision machining. However, a growing body of experimental evidence suggests that glass and ceramics can exhibit both ductile and brittle behavior during grinding, depending on the size of the abrasive used. In particular, there is an abrupt change in the surface smoothness of glass with a smaller abrasive size. In other words, with a smaller depth of cut, even glass can behave in a ductile manner. If we could better understand and manipulate this ductile-to-brittle transition, we could improve the economics associated with fabricating ceramic components.

To address this problem, in 1993 we began simulating fused silica glass with no impurities. In silica, four oxygen atoms surround each silicon atom to form a tetrahedron. Each oxygen atom is shared with two silicon atoms to form connected tetrahedra. Amorphous silica glass is a random network of these interconnected tetrahedra. To study the nanometer-scale deformation of fused silica, we pushed a diamond tip with a radius of about one nanometer into a smooth silica surface, as shown in Figure 7. We found that the silica surface responds much more elastically than did either the copper or silicon surfaces. For indentations up to 1.25 nm, we observe no plastic deformation. At an indentation of 1.25 nm, a significant rearrangement of the silica network occurs directly beneath the tool tip. This rearrangement, an example of which is shown in Figure 8, leads to a decrease in the slope of the loading curve. When the tool is removed, the unloading curve does not follow the loading curve, as it does for elastic indentations up to 1.25 nm. The area between the two curves is a measure of the work performed by the tool in rearranging the silica network. These calculated loading and unloading curves are strikingly similar to those observed experimentally.

It is essential to learn more about cracks for a better understanding of deformation in glass. To simulate the propagation of a crack into a silica surface, we put a notch on the top surface of the glass and let the computer simulation pull apart the sample at a constant velocity. The critical stress for crack propagation depends on the geometry and length of a pre-existing crack. Longer cracks, for example, yield at lower applied stress than do shorter cracks. In the simulation shown in Figure 9, we observed the crack length to elongate by 30%, stop, and then yield again at lower stress. This "stick-slip" phenomenon has been observed during crack propagation in fiber-reinforced materials. The sticking is determined by the microstructure. In our case, the crack stopped after entering a large void. The void permits additional stress relaxation,

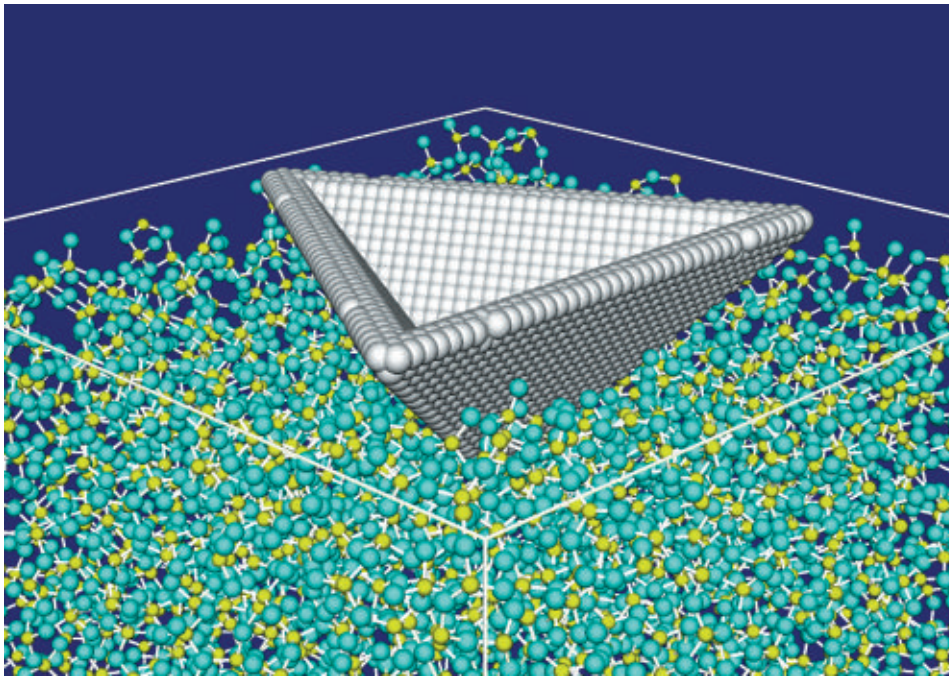

Figure 7. Surface indentation of fused silica (glass). Amorphous silica glass forms a random network of interconnected tetrahedra. A silicon atom (shown here as a yellow ball) is located at the center of each tetrahedron; an oxygen atom (blue ball) is located at each of the four corners. During our simulated indenting of a silica surface, we do not observe the abrupt drops in the loading curve that were seen in copper (Figure 4). Instead, the response of a silica surface is almost entirely elastic up to 1.25 nm. After 1.25 nm, there is a slight change in slope of the loading curve, indicating the onset of plastic deformation.

and the crack tip halts until sufficient stress builds up again.

In related new work, we are modeling crack propagation in silica in the presence of water. Water has the interesting property of enhancing the propagation of cracks in silica by replacing silicon–oxygen bonds with terminal hydrogen atoms.

New Directions: Bridging the Gap

Our atomic-scale simulations of deformation in materials such as copper, silicon, and glass are beginning to give us new insight into specific microscopic processes. However, most macroscopic processes—those we must understand to engineer mechanical parts—are a complicated mix of many different microscopic processes. Orthogonal cutting with a single-point, diamond-turning machine is an almost unique exception to the rule. The reason we are able to model this type of cutting so realistically is that both the length scale (tens of nanometers) and time scale (tens of nanoseconds for cutting speeds of up to 100 m/s) overlap in actual diamond-turning experiments and computer simulation.

Another important example of such overlap is friction and wear at the interface between a computer hard disk and the head used to read and write information on the disk. The space between a flying head and a spinning magnetic disk is less than 100 nm in today's technology, and the space will soon shrink to about 10 nm. A problem this size fits into the main memory of modern parallel supercomputers, allowing us to simulate all the atoms and molecules at the head–disk interface and their response when the head collides with the surface. Moreover, because modern disks spin at high rates of about 5000 rpm, collisions occur on the nanosecond time scale attainable in MD modeling. Extending our MD model to this industrial process could lead to greatly increased storage capacity for next-generation computers, as is described in more detail on pp. 4–5.

In the future, we plan to apply the microscopic, atomic scale, understanding that we have been acquiring to solve macroscopic engineering problems. To do so, we need a bridge between the microscopic world of atoms and the macroscopic world of our everyday experience.

For example, in designing a car or bridge, it is obviously not practical to simulate the motion of every atom in the structure. Instead, a practicing engineer treats a car or bridge as a continuous material. The behavior of a car crashing into a wall is simulated by calculating the response of every small volume that makes up the car, in the same way that we calculate the response of every atom in an MD simulation. These small volumes are assumed to be so large that they contain a vast number of atoms—far too many to simulate individually. The quantities we use to describe the small volumes, for example density and temperature, are the same as those we use to describe our everyday macroscopic world. These quantities represent, in an average way, what the atoms inside the volume are doing.

The way such a continuum mechanics simulation represents materials with widely different behaviors, such as metals and glasses, is to tabulate the particular behavior of interest for that particular material. For instance, when a thin wire is pulled with a certain force, it stretches. However, the precise amount of stretch depends on whether the material is plastic or metal or glass; that is, it depends on the atomic structure of the material. Such a tabulation of material behavior is known as a "constitutive relation," and, in practice, a separate relation must be specified for every behavior that might arise in a simulation.

Continuum mechanics simulations are extremely useful when the amount

(a) (b)

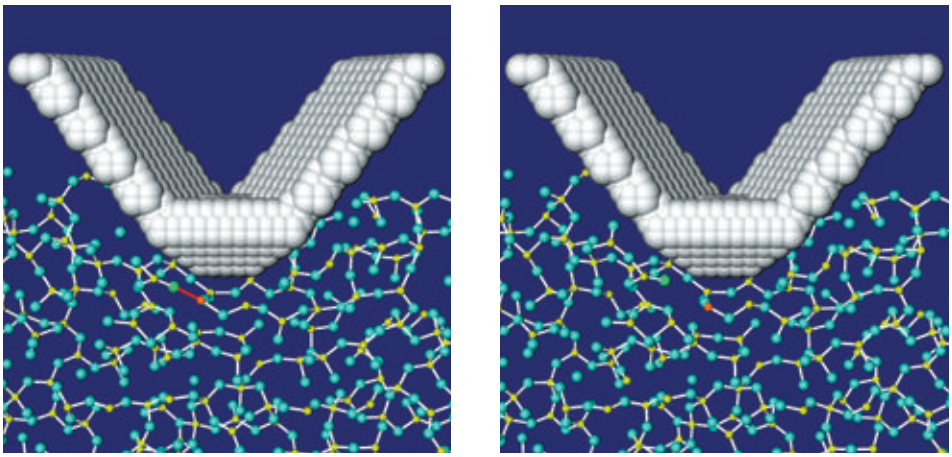

Figure 8. A cross-sectional plot through the center of the diamond tool for the simulation shown in Figure 7 immediately before (a) and immediately after (b) the onset of plasticity when the material yields. The bond shaded in red in (a) is one of the bonds that breaks when the silica network rearranges.

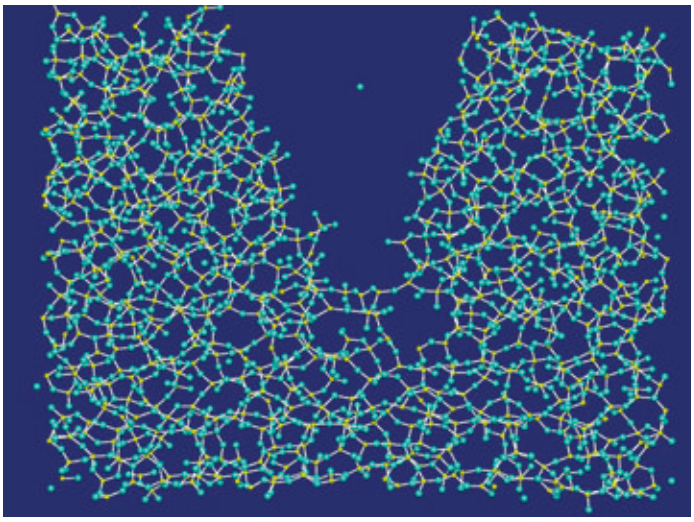

Figure 9. Large-scale, or macroscopic, plasticity in silica is dominated by the propagation of cracks. We simulated the mechanism of crack propagation by creating a notch on a silica surface and pulling the material apart at a constant velocity. Our calculated critical stress (the stress required to move the crack tip) agrees well with experiments. We also observed a novel stick-slip phenomenon. As the crack tip enters a large void, such as the one just below and to the right of center, the tip momentarily halts as the stress is lowered, then the crack continues to propagate again.

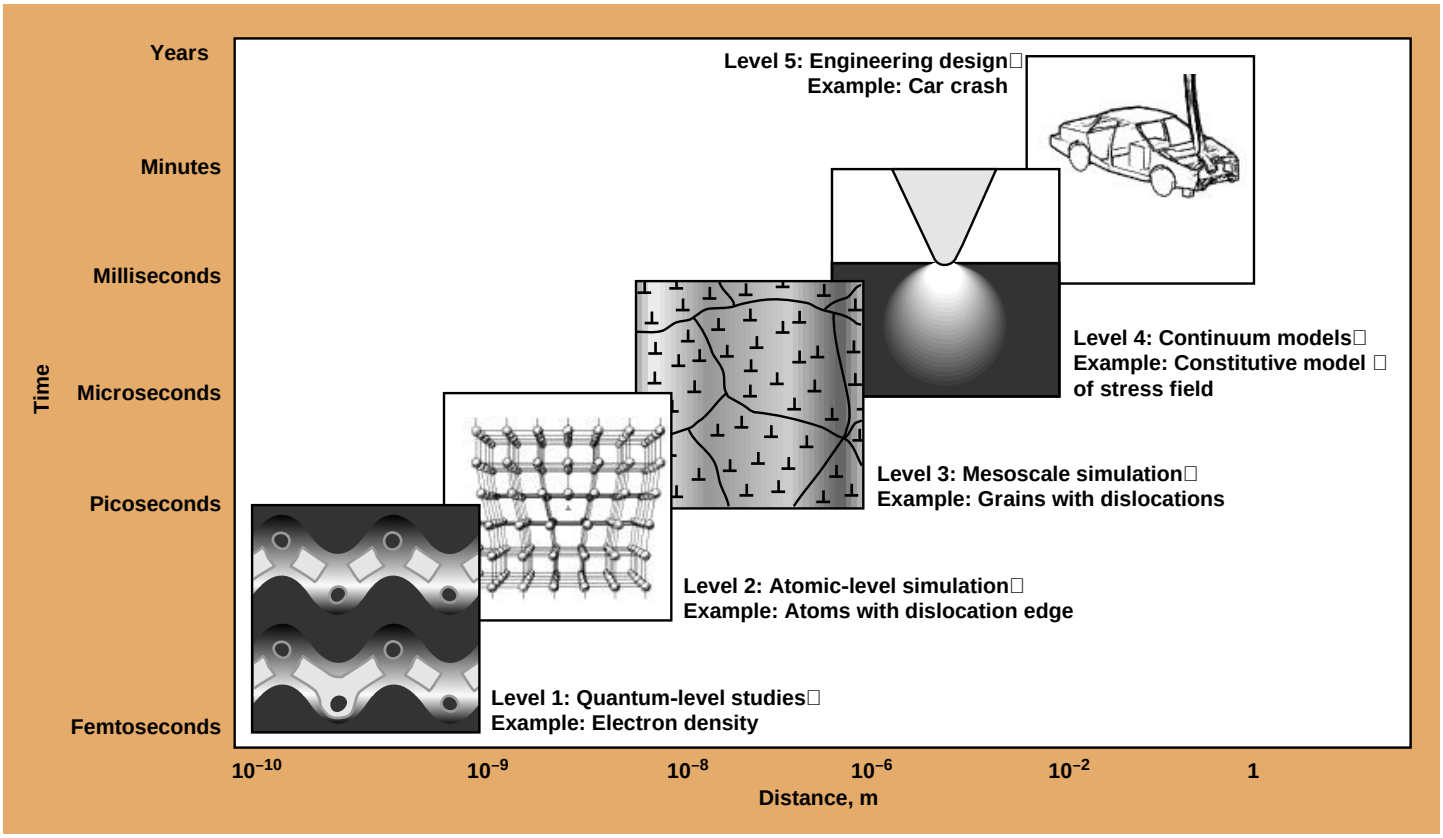

Figure 10. Multiscale modeling. This schematic shows the different types of studies and models needed to simulate various materials problems. At the shortest length and time scale, quantum studies (Level 1) look at electronic structure, such as electron density. Level 2 simulations take into account that the world is composed of atoms. This is the type of simulation we have applied in our studies of nanotribology. Level 3, referred to as mesoscale simulation, is concerned with objects that define microstructure, such as grains with dislocations. Level 4 is concerned with continuum models, such as stress-strain relationships. Continuum models are, in turn, extremely useful for solving practical, Level 5 engineering problems, such as a car crashing into a wall. Our new work will focus on Level 3 and 4 modeling to bridge what we are learning from atomic-scale studies to real-world engineering problems. (This illustration was adapted from W. A. Goddard et al.[5])

of deformation is small. Unfortunately, a serious problem arises when the deformation we want to study is severe. In such cases, the local material microstructure (grain size, dislocation density, and so forth) changes, and the constitutive models used prior to the severe deformation are no longer valid. Furthermore, we have no way to predict which new constitutive model to use without knowing the new microstructure of the material.

To address this challenging problem, we are developing a methodology known as multiscale modeling. To illustrate this approach, Figure 10 shows a hierarchy of different types of models that are used to simulate various problems. At the macroscopic level, continuum models (shown as Level 4) take into account regions of stress and strain. They are extremely useful for solving practical engineering problems (Level 5), such as a car crashing into a wall. However, continuum models, by themselves, do not account for the fact that the world is composed of atoms (Level 2) and that interatomic interactions are determined by electronic structure (Level 1).

To bridge the gap from the microscopic, atomistic level to the macroscopic, engineering level, we will use large-scale MD simulations to study the atomic-scale origins of microstructure interactions and to develop models for mesoscale studies (Level 3) of microstructure evolution. In mesoscale simulations, the objects we study are those that define the microstructure—that is, dislocations and grain boundaries. In such simulations, the atoms do not appear explicitly, as they do in MD modeling. Next, we will calculate material constitutive relations (Level 4) from our new mesoscale simulations to understand the connection with microstructure. This type of approach will allow us to predict the evolution of microstructure when an object is subjected to a macroscopic stress or strain, and hence predict the new constitutive model to use at the continuum mechanics level.

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Key Words: crack propagation; materials fabrication—copper, fused silica glass, silicon, silver; molecular dynamics (MD) modeling; single-point diamond turning; tribology research.

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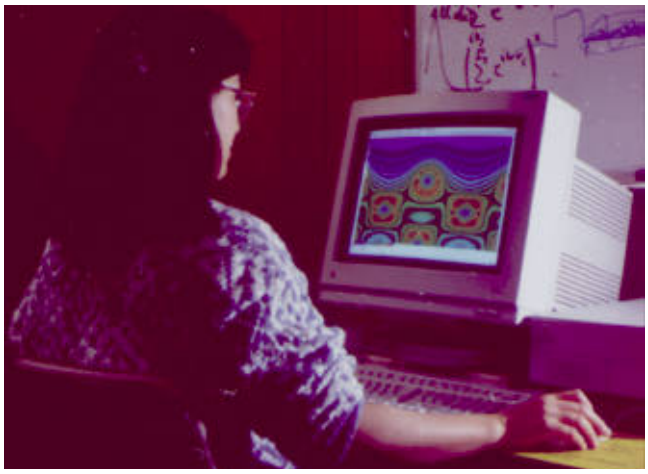
Toward Improved Understanding of Material Surfaces and Interfaces



Our atomic-level modeling of material surfaces and interfaces will impact the design of future materials.

THE surface of a material, whether it is a sheet of paper or a silicon wafer, defines the boundary of an object. Consequently, the properties of that surface determine how a second material will interact with it. For example, the words on this page result from a marking material, such as ink or toner, being deposited on the paper surface in specified patterns. For the printing process to be successful, the interaction between the marking material and the paper must be characterized by strong adhesion and minimal diffusion.

An understanding of surface properties and of how different materials interact has numerous other applications. Specifically, in the microelectronics industry, the complex integrated circuits that form the core of a computer are built on the surfaces of semiconducting wafers, or chips. Chip fabrication involves adding thin layers of material to the surface, transferring the physical layout of the integrated circuit onto the chip, and selectively removing material to form circuit features. Combinations of these steps may be repeated hundreds of times to fabricate millions of transistors on these chips, which are often smaller than a few square centimeters. Features on individual transistors can be smaller than the wavelength of visible light (~415 nm), and they promise to become even smaller as technology advances. Consequently, an atomic-level (tens of nm) understanding of the surface properties of semiconductor devices is essential to their design and production.

The Field Advances

Surface science and materials engineering have made remarkable progress in recent years as a result of new atomic-scale deposition and diagnostic techniques. The deposition techniques, which allow atoms of one material to be added onto the surface of another, have given industry the ability to grow extremely thin films whose thickness can be controlled to within a single atomic diameter (~0.3 nm). New diagnostics, ranging from scanning tunneling microscopy to low-energy electron diffraction, can locate the positions of single atoms and can, therefore, provide unprecedented detail about the surfaces and interfaces of materials.

In addition to the development of these techniques, the close synergy between experimental and theoretical activities has demonstrated the power of computational methods to predict accurately the formation and structure of materials surfaces. The success of these methods may soon allow materials to be custom designed at the atomic scale.

The Laboratory Gets Involved

About five years ago, we began building new capabilities in atomic-level materials modeling. These capabilities were based on our previous work in computational and theoretical condensed-matter physics, which we traditionally used to provide data about materials properties to the Weapons Program. We have been very successful in transferring our expertise to industrial applications, as can be measured by our ability to partner with industry through the CRADA process. To date, we have four CRADAs with U.S. industry in materials modeling (see pp. 4–9), and we expect at least two more to begin in 1995.

Our work in computational and theoretical materials physics complements experimental work in surface science by providing insights into observed phenomena and by addressing issues that we cannot see or measure directly. Examples include:

- The atomic geometry and electronic structure of surfaces and interfaces.
- The attachment sites and binding energies of chemically adsorbed atoms and molecules on surfaces.
- The effects of defects and impurities on the physical and chemical properties of surfaces.
- The prediction of novel properties of multilayer materials.

As fabrication techniques become more sophisticated, atomic-level theory will play a critical role in the design of new materials. By providing a framework for selecting from an ever-increasing number of possibilities, our calculations will focus experimental efforts along paths with the highest probability of success.

Computational Methods

We use several computational methods to address issues in surface science. The most rigorous are known as first-principles, or *ab initio*, electronic structure methods. These are based on the local-density approximation model, and they rely solely on quantum-mechanical principles. The only input to these calculations is the chemical identity of the atoms that comprise the surface or interface. (For a more detailed description of these methods, see the article on pp. 33–38.) Calculations done with these methods can reveal the locations of the atomic nuclei at equilibrium as well as the energies and spatial distribution of the material's electrons. These methods can also be used to determine the forces exerted on the atoms, from which we deduce the motion of the atoms using the laws of classical physics.

Molecular dynamics is the general computational method used to track the positions and velocities of individual particles (atoms or groups of atoms) in a material as the particles interact with each other and respond to external influences. The motion of each particle is calculated by solving Newton's equation of motion, force = mass × acceleration, where the force on a given particle depends on the interactions of the particle with other particles. (For more details on molecular-dynamics methods, see the article on pp. 13–24.)

To determine the forces on the atoms in molecular dynamics calculations, we employ one of two methods: *ab initio* methods, or model force laws. With *ab initio* methods, the rearranagement of the local electron density must be calculated each time the atoms move a very small distance. Because of the speed limitations of present-day computers, we can track the motion of only a few hundred atoms for a short period of time.

For larger-scale calculations, we use model force laws to approximate the forces among the atoms. These force laws, which have been validated by a limited set of experimental data and by results from *ab initio* calculations, allow us to perform molecular-dynamics calculations more efficiently than is possible with *ab initio* methods. If the force laws are accurate, the calculations can yield valuable insights into the dynamic processes that occur at surfaces, but they do not yield information about the electronic properties of those surfaces. Ultimately, we choose the method that best balances the amount of time required to perform the calculation against the accuracy and nature of the information required.

Surface and Interface Formation

We follow three steps to model how surfaces and interfaces form. First, we calculate the structure of a chemically pure, or clean, surface at equilibrium. We next determine the reaction of the surface with additional atoms deposited on top of it. If the atoms bond, an interface will form, and we then determine the structure and properties of this interface.

Surface Relaxation

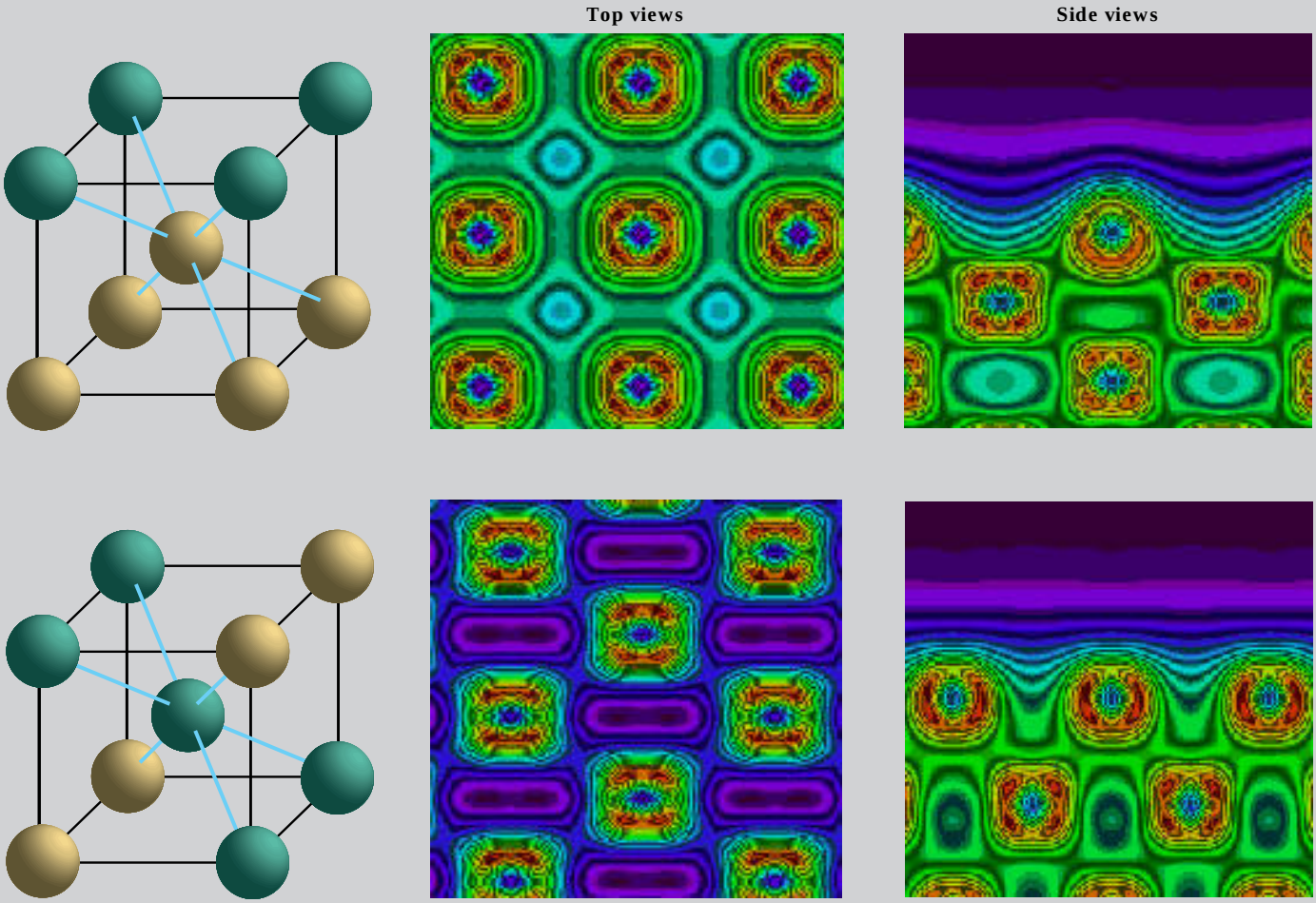
The first step in the calculational process is to determine the structure of a clean surface of a material. As a convenient starting point, we can imagine slicing a crystal in half between two planes of atoms. Initially, the atoms on the surface occupy the same positions as in the original

Understanding Tantalum Surfaces

Tantalum, like all crystalline materials, is composed of a number of atoms arranged in a regular pattern that is repeated throughout the material. In tantalum, the atoms form a body-centered cubic pattern, with one atom at each corner of a cube and one atom at the center of the cube. If we arrange these body-centered cubes side by side and top to bottom so that the face of any given cube coincides with the face of one of its neighbors, we can form a crystal of tantalum.

We can form many different tantalum surfaces depending on where we slice the crystal. If we slice the crystal between the planes of atoms parallel to one of its cubic faces, we have a surface such as the one shown at top left. Slicing through the body of the cube along the face diagonal would produce a surface like that shown at bottom left. In both cases, the green atoms would become the atoms in the topmost layer of the surface.

The electron-density distributions of the relaxed surfaces are shown from the top and from the side for both surfaces. The top layer of atoms on both surfaces is pulled downward, so the separation between it and the second layer of atoms is reduced. For the surface shown at top left, the separation is reduced by 12%; for the surface shown at bottom left, the separation is reduced by only 2%.



crystal, but they will tend to move because they will no longer feel the forces of the atoms that were above them. After new equilibrium positions for these atoms are established, the surface is said to be "relaxed." The goal of our calculations is to predict the structure of the relaxed surface in order to develop a microscopic understanding of chemical bonding at surfaces.

We use *ab initio* methods to calculate the atomic geometry of clean surfaces. This geometry, however, can vary widely depending on the planes of atoms between which the crystal was sliced. There can also be large variations in the nature of the surface relaxation among different classes of materials because of different bonding mechanisms. For example, in simple metals, the electrons responsible for bonding are distributed almost uniformly throughout the crystal. In contrast, the electrons in semiconductors are not as uniformly distributed and tend to pile up between pairs of atoms to form highly directional covalent bonds.

Atom Deposition and Interface Formation

After we understand the structure of a clean relaxed surface, we introduce additional atoms onto that surface. Atom deposition is a more complicated problem to model because atoms generally react differently at different surface sites. The structure of an atom overlayer will depend not only on the chemical nature of the surface and on the surface temperature, but also on the density of the additional atoms. Sometimes atoms will react with the surface to create a chemical species that is no longer strongly bound to the surface. In this case, some of the substrate material will eventually vaporize, resulting in an etched surface. If the atoms bind with the surface, continued deposition will eventually form an interface.

To simulate atom deposition and interface formation, we use molecular-dynamics calculations with model force laws. In our calculations, we first simulate several layers of atoms in a relaxed surface. We then project additional atoms one at a time toward the substrate, calculating the trajectories of these atoms and all the atoms in the substrate. After a number of atoms have built up on the surface of the substrate, we compare the structure of the simulated interface with experimental results.

Current Research

We are currently involved in a number of research efforts in modeling material surfaces and interfaces. Work in this field promises to revolutionize such areas as microelectronics and manufacturing through the development of new materials and fabrication processes.

Etching Tantalum with Chlorine

We are currently collaborating with the Wilson Center for Research

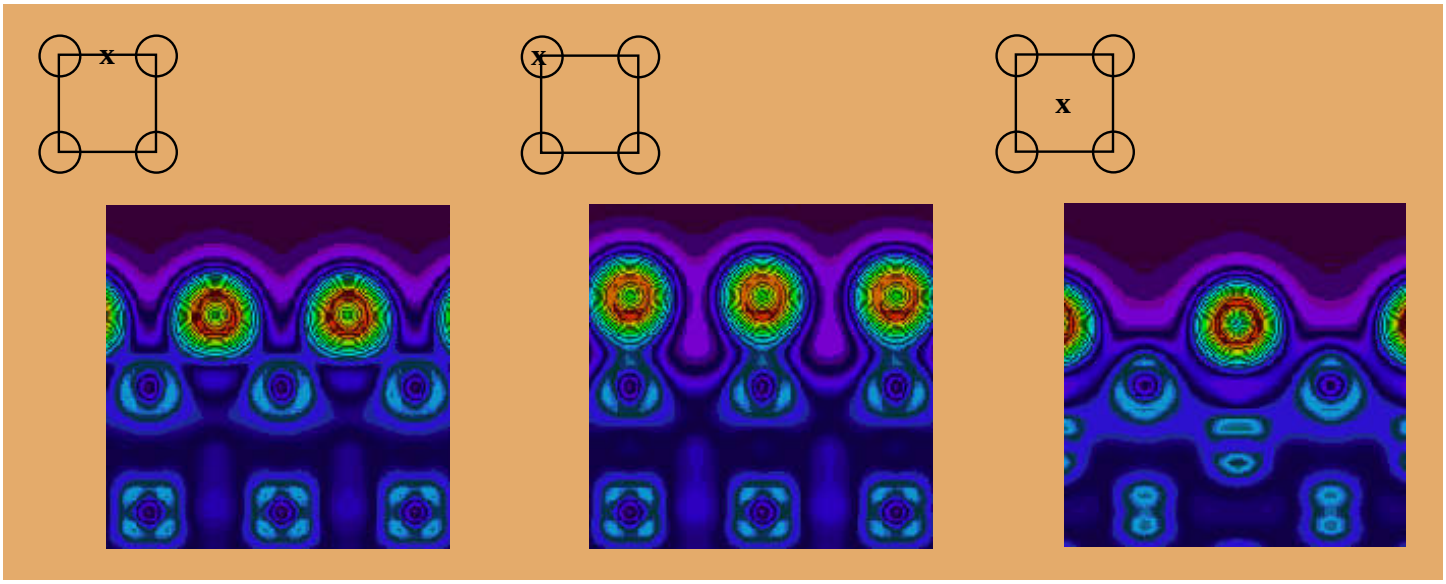


Figure 1. Adsorption of chlorine atoms at three binding sites on a relaxed tantalum surface. (This surface is illustrated in the top figure on p. 27.) The sketches above the figures are top views of tantalum atoms; an "x" indicates the location of the deposited chlorine atom. The figures, which are side views of the tantalum surface with chlorine atoms on top, indicate the electron-density distribution. The density is highest near the atoms, and the accumulation of electrons between the atoms is indicative of bond formation. We used this information to determine the preferred binding site of chlorine (shown in left-most figure).

and Technology of Xerox Corporation to model the etching of tantalum with chlorine. Tantalum has applications in thermal ink-jet printers and flat-panel displays, and the ability to etch tantalum selectively is key to the fabrication of such devices. Chlorine is a potential candidate for etching, although the interactions between chlorine atoms and tantalum surfaces are not fully understood at the microscopic, quantum-mechanical level. An ideal etchant would react strongly enough with the tantalum atoms to remove them from the surface, but not so strongly that it would damage those portions of the surface that are not to be etched.

Our first goal is to understand the structure of clean tantalum surfaces. Fortunately, tantalum surfaces relax in very simple ways. When a tantalum surface is exposed, the relative positions of the atoms in the surface plane do not change. Rather, the whole layer simply moves vertically until the forces are balanced. Using *ab initio* calculations, we modeled the relaxation of two tantalum surfaces and discovered that the degree of vertical movement varies considerably with the crystalline orientation of the surface (see the box on p. 27 for a description of these surfaces).

Next, we calculated the properties of six chlorine-binding sites on two tantalum surfaces. Figure 1 shows our results for one of these surfaces. In addition to finding the preferred binding sites, we are also constructing a model force law that can be used in molecular-dynamics simulations. This force law will allow us to predict the behavior of chlorine atoms that come into contact with a tantalum surface (see also the article on p. 9).

Metal–Semiconductor Interfaces

Understanding the interface between a metal and a semiconductor is critical to the microelectronics industry. In an integrated circuit, thin metallic films are deposited on semiconductor surfaces. If the number of metal atoms deposited on the insulating surface of a semiconductor is so small that they are isolated from one another, no electric current can flow along the surface. However, if the number of metal atoms surpasses a critical value, the metal atoms in the overlayer will start to interact and become conducting. In advanced microelectronic devices, the electrical properties of the metal–semiconductor interface are critical elements in the design process.

Simple models predict that the transition from insulating to conducting behavior will occur when the separation between metal atoms is nearly equal to that in a normal conducting wire of the same material. In such a case, the transition would depend only on the nature of the metal atoms and would be independent of the surface properties of the substrate. To test this model and to determine the threshold at which a metal overlayer becomes conducting, we performed *ab initio* calculations for gold and sodium atoms deposited on a semiconductor commonly used for optoelectronic applications, gallium arsenide.

Figure 2 shows the electron-density contours for low and higher coverages of gold atoms on the surface of gallium arsenide. At low coverage, the electrons are localized near individual gold

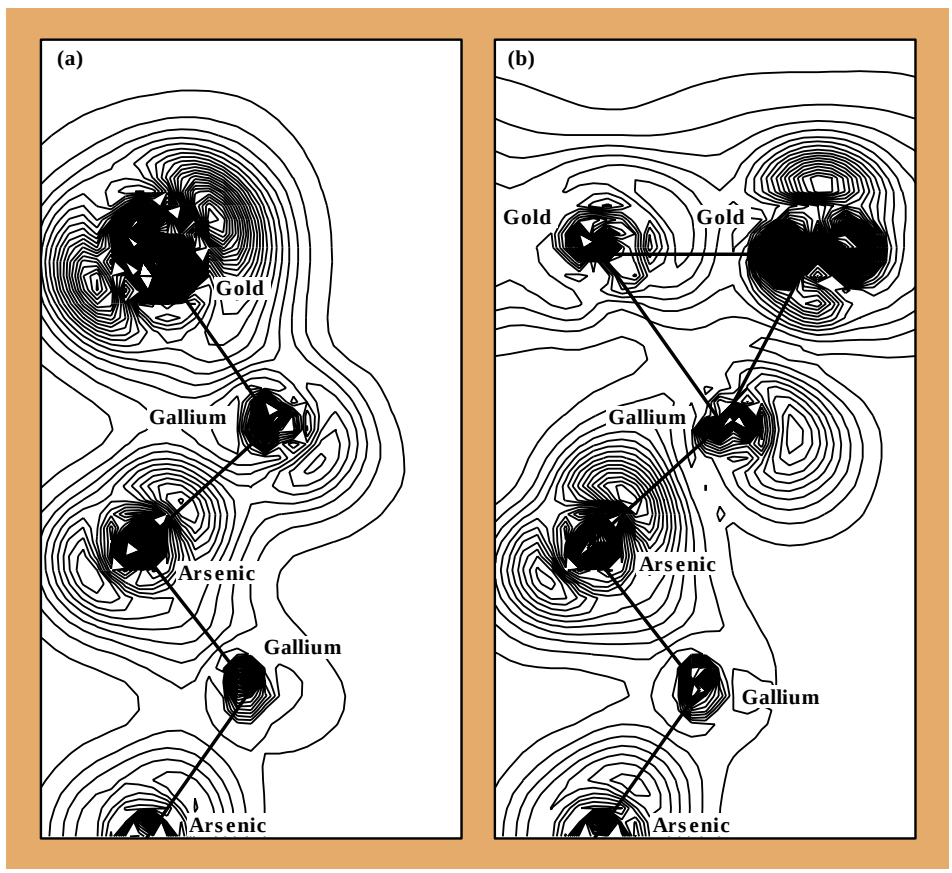


Figure 2. Side views of the electron-density contours for gold atoms deposited on a gallium arsenide surface. At low coverage (a), the electrons are localized near individual gold atoms, and the surface is insulating. At higher coverage (b), the electrons are more uniformly distributed in the gold overlayer, and the surface becomes conducting.

atoms and cannot move easily along the surface. At higher coverage, the electrons are more evenly distributed along the surface, as in a metal, and can move easily to conduct electrical current. We find that the gold overlayer becomes conducting near the ideal coverage, as predicted by simple models.

However, calculations for sodium indicate that the nature of the transition can depend on the strength of the electronic interactions between the gallium arsenide surface and the additional atoms. Figure 3, which compares the bonding of sodium and gold atoms at equal coverage on a gallium arsenide surface, illustrates this difference. The sodium atoms are pulled much closer toward the surface of the gallium arsenide than are the gold atoms, indicating that sodium interacts more strongly with the surface than does gold. Contrary to the simple model, we find that sodium only becomes conducting on the gallium arsenide surface at coverages twice that of gold.

Molybdenum–Silicon Multilayers

Being able to simulate the relationship between particle deposition and interface formation is particularly important when dealing with multilayer structures made of alternating layers of different materials. Multilayer structures, some with layers as thin as 5 nm, have applications in advanced lithographic techniques for transferring circuit layouts onto semiconductor chips. One multilayer structure in which we have particular interest is that composed of molybdenum and silicon. This multilayer structure is used in highly reflective x-ray mirrors, whose performance depends on the sharpness of the interfaces and on the layer thicknesses.

Interestingly, when molybdenum atoms are deposited on top of silicon layers, the interfaces formed are far less abrupt than those formed when silicon atoms are deposited on top of molybdenum. To investigate this asymmetry, we performed two molecular-dynamics simulations (see Figure 4). For one, we deposited molybdenum atoms on a silicon slab; for the other, we reversed the process. Although the force law that we used for these simulations was approximate, the calculations nevertheless shed some light on the reason for the structural asymmetry of the interfaces.

Each atom in a bulk crystal of the metal molybdenum is surrounded by 14 closely neighboring atoms, whereas each atom in the semiconductor silicon is covalently bonded to only 4 neighboring atoms. When a molybdenum atom is atop a silicon substrate, it will have only a few neighbors, so it will attempt to surround itself with more neighbors by burying into the substrate. A silicon atom, in contrast, will remain atop the molybdenum surface because it already has a sufficient number of neighbors. The better we understand the microscopic mechanisms determining interface thickness, the better we will be able to guide the fabrication of high-performance mirrors.

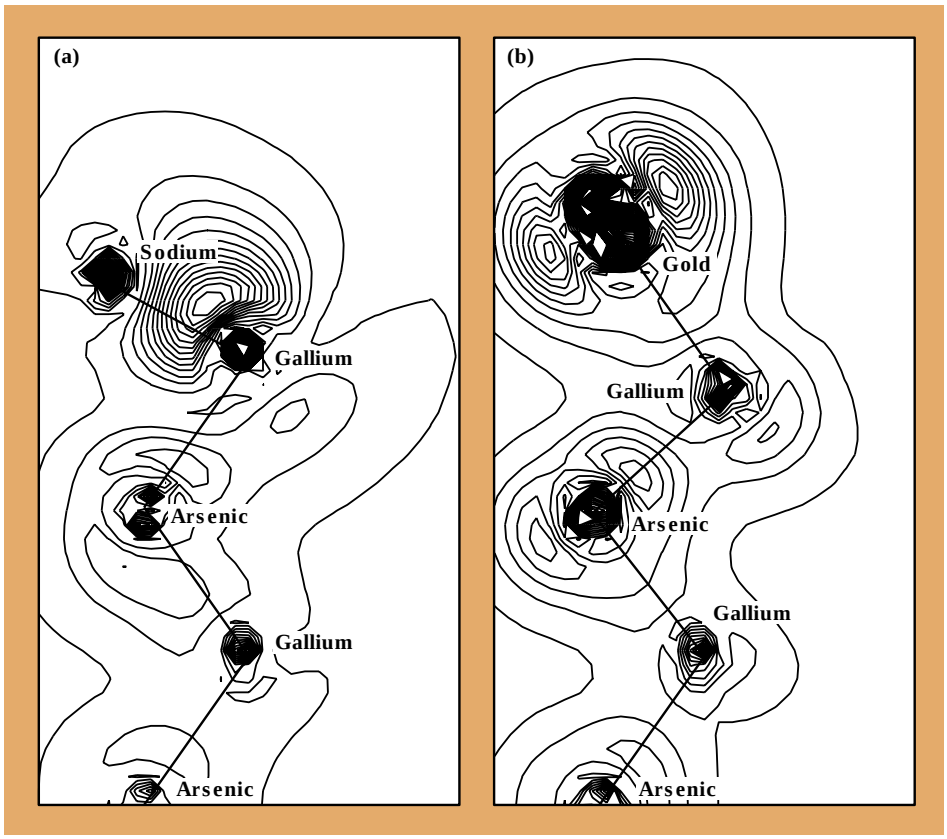


Figure 3. Side view of the bonding of sodium (a) and gold (b) atoms to a gallium arsenide surface. The sodium atom interacts more strongly with the surface than does the gold atom. As a result, the sodium overlayer becomes conducting at a higher coverage than for gold.

Conclusion

LLNL has developed significant expertise in the field of atomic-level materials modeling and design. We

are currently involved in several exciting collaborative projects that promise to speed the development of novel materials for the microelectronics industry. As our calculational methods improve and as computers continue to grow in power and memory, the size and complexity of the materials design problems we can address at the atomic level will scale with them.

The emergence of massively parallel computing environments will eventually make simulations of realistic, complex systems routine. The opportunities provided will revolutionize atomic-level, quantum-mechanical simulations of materials and processes, making true atomic engineering of devices and products a reality.

Work funded by the Department of Energy's Assistant Secretary for Defense Programs and Director of Energy Research.

Key Words: atomic structure; bonding; computational methods—*ab initio*, model force laws, molecular dynamics; crystal structure; interfaces; materials modeling; semiconductors; surfaces.

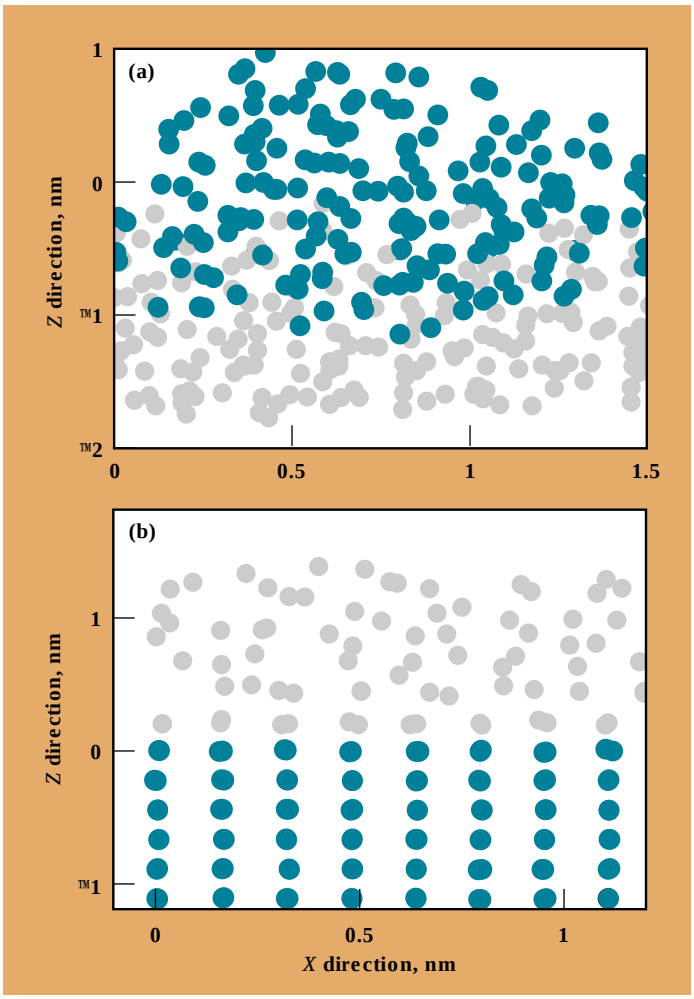
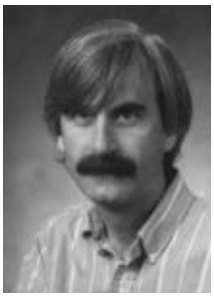
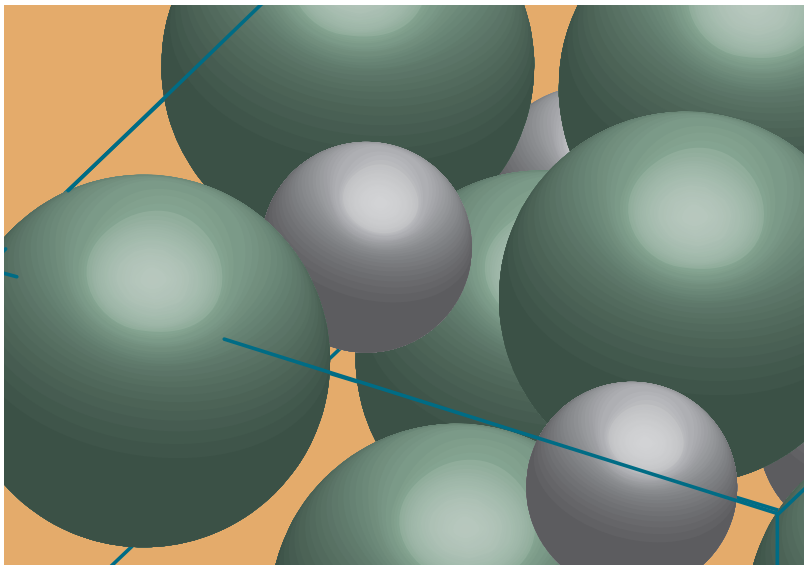


Figure 4.
Molybdenum–silicon interfaces. (a) Side view of a silicon slab (gray dots) after 192 molybdenum atoms (blue dots) were deposited on it. The delineation between the molybdenum and silicon is not abrupt because many of the molybdenum atoms intermix with the silicon. The atoms that were deposited last begin to form a layer of pure molybdenum. (b) Side view of a molybdenum slab upon which 80 silicon atoms were deposited. Here, the interface between the molybdenum slab and the silicon layer is abrupt at the atomic level.



For further information contact David B. Boercker (510) 422-4187, John E. Klepeis (510) 422-6103, or Christine J. Wu (510) 424-4096.

Predicting the Structural and Electronic Properties of Scintillators



We are modeling the properties of scintillators and related materials so that we can guide the synthesis of new materials with improved radiation detection capabilities.

FOR numerous applications, detecting high-energy gamma and x-ray radiation is valuable. Examples include:

- Distinguishing brief showers of secondary particles from infrequent events, such as cosmic rays passing through the earth.
- Monitoring the radiation dose to a patient undergoing medical tomography.
- Identifying sources that may threaten the environment or the safety and health of the public.
- Seeking out covert nuclear weapons.

However, because high-energy radiation cannot be directly detected efficiently, it is more convenient to convert it into photons in the visible or ultraviolet range. These photons can then be readily detected and counted by such means as a photomultiplier. A necessary step in the detection process then becomes the means to convert the high-energy radiation into visible light. Scintillators, materials that emit flashes of light in response to ionizing radiation, are used for just this purpose (see Figure 1).

In the detection process (Figure 2), the incoming radiation interacts with the scintillator's electrons and loses energy by creating electronic excitations in the crystal. These excitations then decay, leading to the emission of photons in the visible or ultraviolet range.

Scintillators are typically wide-gap insulators, such as ionic salts, in which the primary electronic excitation is the creation of electrons and holes (the absence of electrons in normally filled electron states). The size of the energy gap between the empty and filled electron states greatly influences the frequency of the light emitted; a wider gap corresponds to a higher frequency of light. Scintillator materials are often dense, containing deep multi-electron cores (as in the case of barium, lead, and bismuth),

and have many electrons that can produce many excitations. Sometimes, they are even deliberately doped with impurity atoms to create defects that can enhance the radiative decay of electron–hole pairs.

We are modeling the properties of scintillators and related materials like phospors for the purpose of guiding the synthesis of new scintillators. These new scintillators should have a high density of electrons to absorb energy and a fast and efficient luminescence (light emission) to ensure high sensitivity and time resolution. They should also be transparent enough at relevant emission wavelengths to allow the light to pass unattenuated to the detector, and "hard" enough to resist radiation damage by the detected particles after extended use.

Although we can already calculate some of the properties of new materials, we are also studying known materials in order to enhance our predictive capabilities and thereby more accurately model new materials before they are synthesized. For example, we could calculate defect properties, including accurate excitation spectra, to compare with optical absorption and emission measurements in order to identify unknown and troublesome defects in a new material. We could also model useful impurity defects, which would be introduced deliberately into the material.

Modeling a scintillator material is a two-part strategy. First, we determine the material's structural and electronic properties—that is, its atomic structure as a function of density and its electron excitations versus structure, including, for example, electron band structures and electron–hole interactions. Then we use these properties to predict whether a material will be suitable for a particular application or will have characteristics that render it useless.

Structural properties are important because they affect a material's absorption and emission characteristics and its response to heat, pressure, and other external and internal forces. Applying pressure to a material induces volume compression, distortion, and changes in strength, density, and the microscopic arrangement of atoms. Structural changes such as these in turn cause changes in the electron states. The most important electrons are those in the atoms' more energetic outer orbits that are shared among the material's many atoms. To calculate the dynamics of these itinerant electrons (the electron band structure), we must determine the allowed quantum-mechanical states available to them. To do this, we use computational methods based on a model called the local-density approximation (LDA). These methods, together with subsequent corrections to the LDA model—such as those describing electron–electron interactions in more detail—also help us to determine electron–hole interactions and to predict how various materials will function as scintillators.

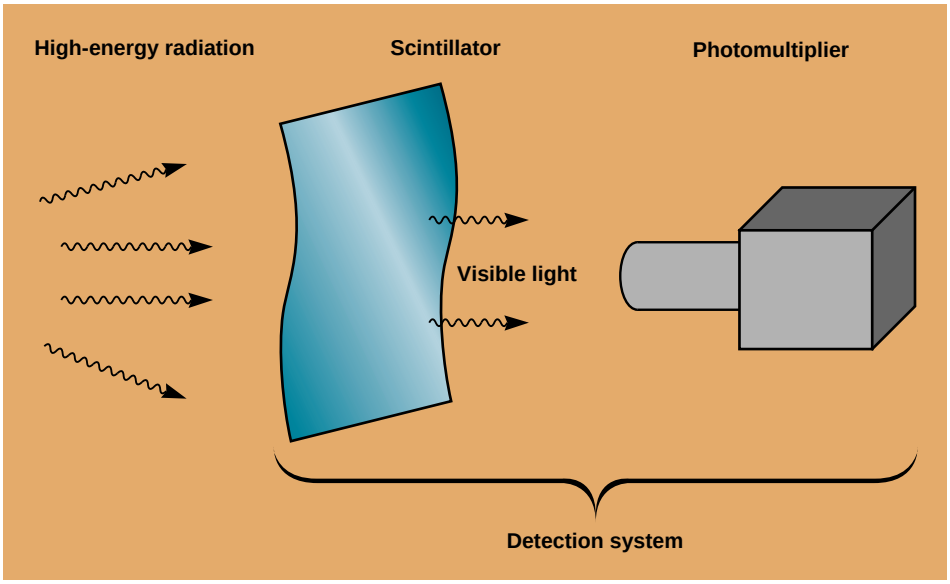


Figure 1. Scintillators are used to convert high-energy radiation into visible or ultraviolet light. These photons can then be readily detected and counted by such means as a photomultiplier.

The Local Density Approximation Model

Computational methods based on the LDA model can be used to determine both the atomic and electronic structures of materials, including potential scintillator materials such as lead fluoride, barium fluoride, the cesium halides, and lithium fluoride. For example, these methods can be used to determine properties such as a material's crystal structure (e.g., cubic or orthorhombic) and density, internal atomic coordinates, possible structural phase transitions, and associated transition pressures. They can also be used to describe the atomic structure near a defect and, very importantly, the relation between a material's structure and its electronic properties. In contrast to the atomic structure, the electronic structure

deals primarily with the dynamics of electrons in a solid, specified by the wave functions and energies of the electron states.

Determining Scintillator Structure

To determine the atomic structure of a scintillator, or any other material, we determine the total energy of its electrons and then minimize that total energy with respect to the atomic coordinates and crystal unit-cell dimensions. To determine the total energy, we first consider each electron separately, treating it as if it were moving in an average potential field created by all the remaining negative and positive charges in the crystal. We then apply a unique functional of the electron density, obtained from a sum over all the electrons, which yields the material's total energy. Although the exact form of this functional is unknown, we can get an exceptionally accurate and practical approximation to it using the LDA model.

We currently have two very accurate LDA-based methods for treating the motion of electrons—the pseudopotential method, which applies only to the valence electrons in a solid and therefore to its "pseudo" nuclear potential, and an all-electron method, which applies to all electrons in a solid and therefore to its true nuclear potential.

The Pseudopotential Method

The pseudopotential method eliminates the atom's deeply bound core electrons and the potentials that bind them, allowing us to focus solely on the relevant structural, electronic, and optical properties of the valence electrons, which are the ones active in the chemical bonding of materials. This method also allows us to employ powerful mathematical tools (such as Fourier analysis, where the electron wave functions are described in terms of plane waves) to study problems at the small cost of slight approximations.

Although the pseudopotential method simplifies the description of the valence electrons, we use psuedopotentials that are norm-conserving; they leave this description unchanged in the chemically important bonding regions. Such norm-conserving pseudopotentials are highly transferable; that is, they can be used to predict the chemistry of an atom in a wide range of situations (e.g., bulk, surface, adsorbate). Because norm-conserving pseudopotentials do not rely on prior experimental knowledge about a chemical element, we can construct one for every element in the periodic table.

All-Electron Methods

When the pseudopotential approximation is not sufficiently accurate for a material, as is the case with some transition metal and actinide elements (some of which are candidate scintillator materials), we can use all-electron methods that explicitly treat both the deep and shallow core electrons as well as the valence electrons.

All-electron methods work equally well regardless of the degree to which the electron states are localized or extended; therefore, they are immediately applicable to a wide range of materials. They are also useful for materials whose relevant

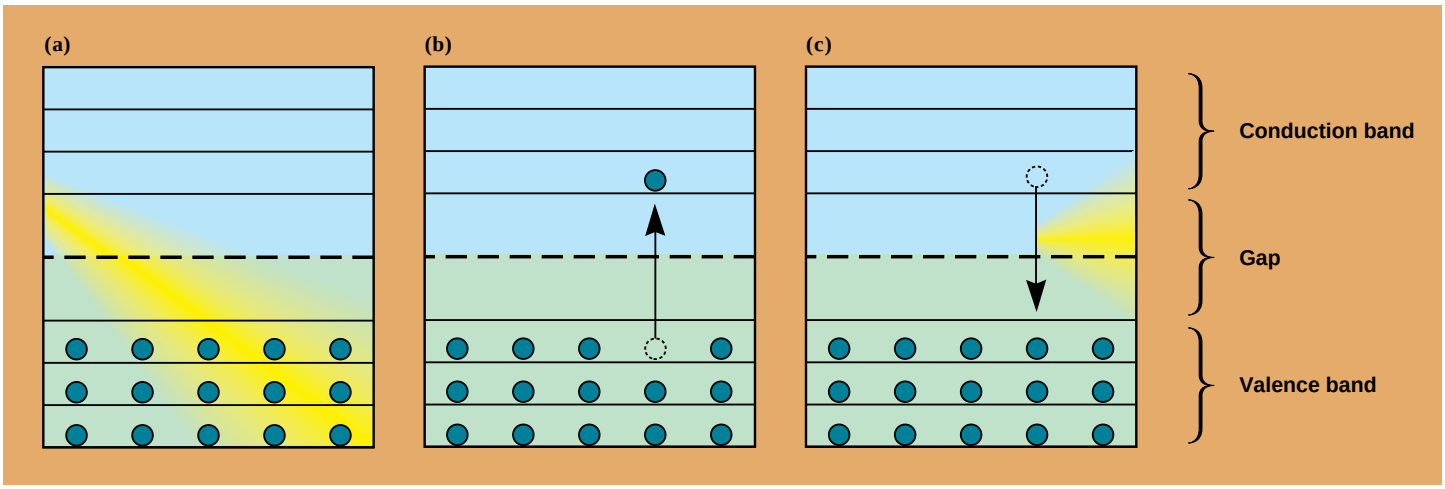


Figure 2. Schematic of the scintillation process. (a) Incoming radiation (such as light) enters a crystal. Note the filled (low-energy) and empty (high-energy) states of electrons delineated by the Fermi energy (dashed line). (b) The radiation absorbed by the crystal excites its electrons (one promotion shown) from filled to empty states. (c) When the electrons later become de-excited, the electron and hole in (b) recombine, and readily detectable radiation is emitted from the crystal.

properties depend specifically on the core electrons and for materials at pressures where the shallow core electrons of the compressed atoms may participate in the chemical bonding.

All-electron methods are also computationally efficient for systems with small numbers of atoms. However, they are mathematically complex and not as amenable to the mathematical tools used in conjunction with pseudopotentials. One consequence of this complexity is a rapid degradation of computational efficiency for complicated structures. The pseudopotential method is usually more efficient for systems such as surfaces, interfaces, and defect structures. On the other hand, the description of the electronic wave functions obtained from all-electron calculations is more convenient for identifying the chemical nature of the electronic states. Chemical analyses of these states often provide important insights into the properties of materials such as scintillators. Ultimately, the benefit of having expertise with both pseudopotential and all-electron methods is that we can use the most suitable method for any given problem. In this way, the methods complement each other. They also serve as a check on each other when both are applicable.

Describing Electron–Electron Interactions

The LDA model treats each electron as being approximately independent from all other electrons, but they are, in reality, not independent. An electron or hole polarizes a material by interacting with other electrons. Some induced polarization also occurs as other electrons move away from a given electron, creating a polarization cloud that changes the energy of the electron. This change, which occurs for all electronic states, is called the self energy. Although self-energy effects are approximately included in the LDA model, the proper way to treat such effects is by means of a quasiparticle approach. A quasiparticle can be either an electron plus its polarization cloud or a hole plus its polarization cloud. These effects are critical for an accurate treatment of electronic excitations, but the LDA model is more than adequate for treating most structural properties.

To appreciate the differences in accuracy between the LDA and the quasiparticle approaches, one has only to look at lithium fluoride, a luminescent insulator that has the widest known band gap of any material except artificial systems such as noble-gas solids (Figures 3 and 4). Experiments indicate that lithium fluoride has a band gap of 14.1 to 14.2 eV between its conduction and valence bands. The width of the fluorine valence-band is approximately 3.5 eV. The shallowest fluorine core electrons lie roughly 21.5 eV below the valence-band maximum. According to the LDA model, the band gap is 8.9 eV, the valence bandwidth is 3.1 eV, and the core electrons are 19.5 eV below the valence–band maximum. On the other hand, the quasiparticle results, which are considerably better than the LDA results, yield a band gap of 14.2 eV, a valence bandwidth of 3.7 eV, and a centroid for the core electron band that is 21.5 eV below the valence-band maximum.

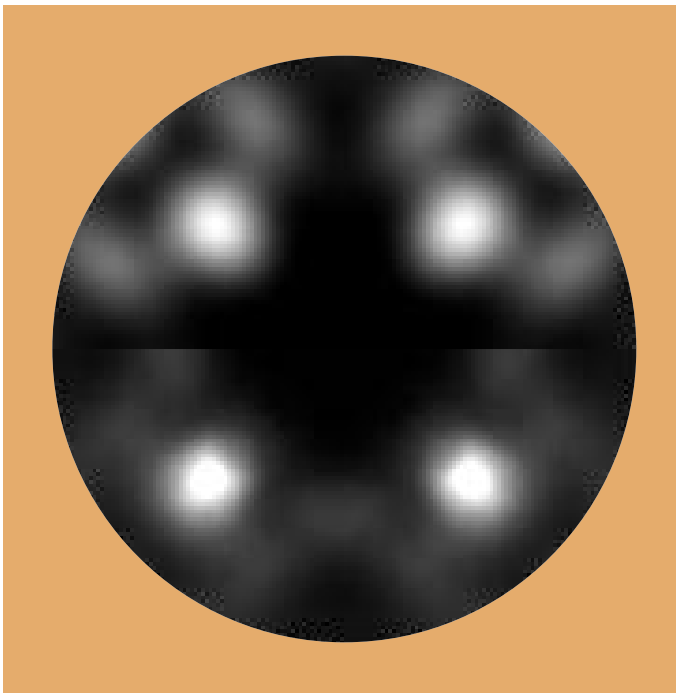


Figure 3.
Experimental (top half) and simulated (bottom half) angular distribution patterns for photoelectrons excited from a lithium fluoride crystal. Areas of high electron intensity appear brighter. The two patterns, which show significant correspondence, would appear indistinguishable if the theory and experiment agreed perfectly.

Describing Electron–Hole Interactions

If we want to describe the excitations in scintillators, we need to do more than describe just one electron or one hole even within the quasiparticle approach. We need to describe electron–hole interactions since the important electronic excitations are electron–hole pairs. When one of these electron–hole pairs decays in a radiative process, scintillation occurs. Such decay occurs when an electron falls into the hole state, refilling the vacancy left by a previous electron. It can also occur during atomic motion, as a nonradiative

process, or during the emission of light, as a radiative process.

In the case of electron–hole pairs, we also need to describe the coupled motion of the two particles (electron and hole) and are already working on approaches to do just that. For instance, the same theory that has been applied to fullerene solids[1] (which are not scintillators) can also be applied to scintillators.

Current Projects

We have used our all-electron LDA method to calculate the atomic structure of barium fluoride and lead fluoride, both of which can exist in one of two phases (either cubic or orthorhombic—see Figure 5) at low pressures. The cubic phase is observed to be the most stable (the lowest energy) experimentally, and our calculations reproduce this observation correctly. We have also calculated the pressure at which lead fluoride transforms from the cubic to the orthorhombic phase and find that it agrees with the experimentally measured transition pressure. In the case of the orthorhombic phase, there are a large number of independent structural parameters that describe the atomic structure of the material. Once again, the calculated structural parameters agree well with experiment. This high level of agreement is an example of the quantitative accuracy of LDA calculations and is well documented. Thus, even in the absence of experimental measurements, we can have confidence in calculated structural quantities. This confidence is important because all other properties of a material depend on the atomic structure.

Cubic barium fluoride is known experimentally to be a fast scintillator, whereas cubic lead fluoride has not been observed to scintillate. However, there is some controversy as to whether the orthorhombic form of lead fluoride luminesces. To address this controversy and to provide insight into the materials properties that distinguish efficient and poor scintillators, we have calculated the electronic band structures of both forms of barium fluoride and lead fluoride. The calculated energy bands for cubic barium fluoride, as well as the chemical nature of the electron wave functions, are consistent with the observed luminescence in this material. The calculations for the orthorhombic phase indicate that it should also be a fast scintillator. Those for cubic and orthorhombic lead fluoride again indicate that the energy bands for the orthorhombic phase are very similar to those of the cubic phase; therefore, the luminescence characteristics of both phases should also be very similar. Because our calculations are for pure, defect-free crystals, we believe that any observed scintillation in orthorhombic lead fluoride is likely the result of defects or other structural imperfections.

Future Directions

First-principles, quantum-mechanical methods afford the calculation of the energies of defect excitations in addition to band gaps. This is of great practical interest because the optical

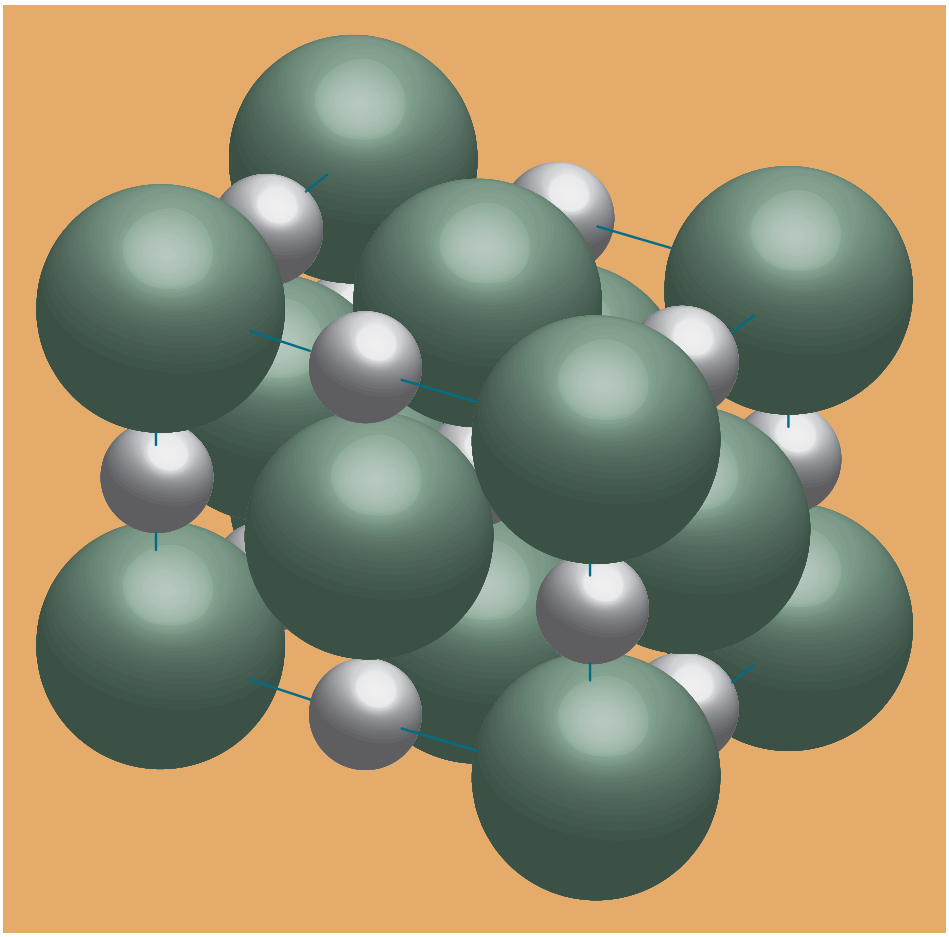


Figure 4. Unit cell of lithium fluoride, which is used for many scintillator and dosimetry applications, including Laboratory dosimeters. The box enclosing the fluorine (green) and lithium (gray) atoms is intended only as a guide.

properties of a material can be tailored by introducing defect levels inside the fundamental band gap. Accidental defects can also degrade the performance of a scintillator. At present, no one can calculate defect excitations accurately, so we have to generalize the quasiparticle method to handle this problem. The first application of this method, to a chlorine vacancy in lithium chloride, yielded an accurate estimate of the frequency of light absorbed by this defect. Eventually, it should be possible to predict defect properties for a wide range of materials, thereby advancing the development of new scintillators.

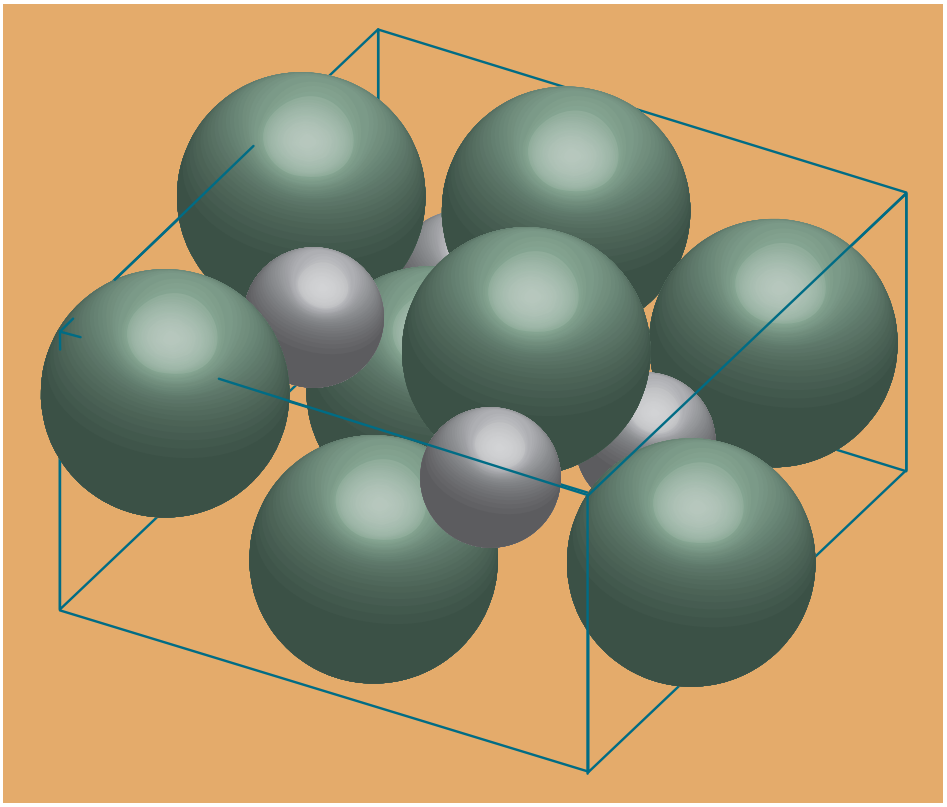


Figure 5. **Unit cell of the orthorhombic phase of lead fluoride, which has potential scintillator applications. The connecting lines that define the box enclosing the fluorine (green) and lead (gray) atoms are intended only as a guide.**

Work funded by the Department of Energy's Assistant Secretary for Defense Programs.

Key Words: electrons; local-density approximation; pseudopotentials; quasiparticles; radiation detection; scintillators.

Notes and References

1. All research on fullerene solids had been completed as of the date of this writing, but a document describing the work has not yet been published. For more information on fullerene solids, contact Eric Shirley (301) 975-2349.

For further information please contact John E. Klepeis (510) 422-6103, Eric L. Shirley (301) 975-2349, or Michael P. Surh (510) 422-2087 (clockwise from upper left).

***Ab initio* methods**	Methods based on the local-density approximation model used to reveal locations of atomic nuclei at equilibrium as well as energies and spatial distribution of a material's electrons.
All-electron model	Model based on the local-density approximation used to calculate the motion of all electrons in a solid.
Atomistic	Of or relating to atoms. In modeling, atomistic simulations are concerned with length scales on the order of 10^{-8} to 10^{-9} m.
Constitutive relation	A tabulation of the behavior, such as the force required to stretch a certain distance, of a particular material that depends on its constitution or structure. The variety of behaviors of different materials, such as metals and glasses, enters continuum models through constitutive relations.
Continuum model	A model, useful for solving practical engineering problems, that treats an object or structure as a continuous material. Such models take into account, for example, regions of stress and strain, but they do not simulate the atomic structure of the system.
Ductile	Deformation of a material without fracture.
Elastic	Deformation of a material without permanent loss of size or shape.
Interstitial	In a crystalline material, atoms or ions that occupy spaces between other atoms or ions in the crystal lattice are called interstitial.
Local-density approximation model	Model used to determine the atomic and electronic structures of materials. These include crystal structure and density, internal atomic coordinates, structural phase transitions, and associated transition pressures.
LODTM	Large-optics diamond turning machine at LLNL.
Mesoscale simulation	A simulation concerned with the objects that define the microstructure of a material, such as dislocations and grain boundaries.
Model force laws	Laws used to approximate the forces among atoms. These laws are useful for larger-scale calculations, where *ab initio* methods would be too time consuming.
Molecular dynamics (MD) simulation	A modeling tool to study the statistical mechanical properties of a collection of atoms. In an MD calculation, atomic motion is simulated by solving Newton's equations of motion ($F = m \times a$) for a large collection of atoms.
Multilayers	Structures made of alternating layers of different materials, some as thin as 5 nm.
Nanotribology	The science of fundamental surface processes at the atomic scale, also known as molecular tribology. See tribology.

Plastic A permanent change in shape or size when a material is subjected to a stress.

Polarization cloud The region around a charged particle (when embedded in a gas of electrons) into which the electrons are either attracted or repelled.

Pseudopotential model Method based on the local-density approximation used to calculate the motion of only the valence electrons in a solid.

Quasiparticle method Method used to calculate the self energy of an excitation by including the effects of the polarization cloud. The complete excitation—an added electron or hole plus its polarization cloud—is called a "quasiparticle."

Relaxed surface A material surface in which the atoms are at equilibrium.

Scintillator A material that emits flashes of light in response to ionizing radiation. Such materials are used to identify brief showers of secondary particles, monitor radiation doses, and identify environmentally threatening sources.

Self energy The reduction in energy of an electron or hole as other electrons move away from it.

Tribology The science of interacting surfaces in relative motion, namely friction, lubrication, wear, and adhesion.

Valence electrons Those electrons active in the chemical bonding of materials.

Nanotribology: Modeling Atoms When Surfaces Collide

Molecular tribology, or nanotribology, gives us an atomic-scale understanding of the fundamental processes that take place when surfaces in relative motion interact. Researchers at LLNL and elsewhere need to know more about these processes to design and build many ultra-precise components, including optical devices, very smooth surfaces, and computer chips. We are applying a type of realistic computer modeling developed at LLNL, called molecular dynamics modeling, to study what happens when different materials, such as metals and glass, undergo cutting, grinding, cracking, and other processes associated with fabrication. We have found, for example, that both metals and ceramics behave in a ductile manner when we simulate machining on the nanometer length scale. However, the mechanisms underlying deformation are quite different in the two types of materials. Metals, such as copper, remain crystalline and deform through dislocation mechanisms. In contrast, covalent materials, such as silicon, transform into an amorphous state, which flows. We are applying such information to develop more practical engineering guidelines for researchers at LLNL and in the industrial community.

Contact James Belak (510) 422-6061.

Toward Improved Understanding of Material Surfaces and Interfaces

Our capabilities in theoretical and computational condensed-matter physics allow us to gain an atomic-level understanding of the structure, formation, and electronic properties of the surfaces and interfaces of a wide variety of materials. So far, we have simulated such experimentally observed phenomena as the relaxation of metal and semiconductor surfaces and the growth of metal–semiconductor interfaces. Recent applications of our work include the etching of tantalum with chlorine for thermal ink-jet printers, the deposition of molybdenum and silicon atoms for x-ray mirrors, and the metallization of thin films on semiconductor surfaces. As the computing environment grows and matures, we will be able to custom design materials at the atomic level solely from the identities of the atoms and the laws of quantum mechanics.

Contact David B. Boercker (510) 422-4187, John E. Klepeis (510) 422-6103, or Christine J. Wu (510) 424-4096.

Predicting the Structural and Electronic Properties of Scintillators

Scintillators, materials that emit short flashes of light in response to ionizing radiation, are used to detect high-energy radiation (charged particles, x rays, or gamma rays) from various sources. We are modeling the properties of these materials for the purpose of guiding the synthesis of new scintillators with improved detection capabilities. Our calculational tools include methods based on the local density approximation (LDA), such as pseudopotential and all-electron methods, and quasiparticle approaches. We have used our all-electron LDA method to calculate the atomic structure of barium fluoride and lead fluoride, both of which can exist in one of two phases (either cubic or orthorhombic) at low pressures. Our calculations have accurately reproduced the experimentally observed structural properties of these materials. We have also provided insight into their electronic properties. Ultimately, we want to calculate the energies of defect excitations. This is of great practical interest because the optical properties of a material can be tailored by introducing defect levels inside the fundamental band gap.

Contact John E. Klepeis (510) 422-6103, Eric L. Shirley (301) 975-2349, or Michael P. Surh (510) 422-2087.