# Theory and Modeling in Materials Science

*How do scientists understand and predict the behavior of materials? Four recent studies demonstrate how a sound theoretical framework combined with effective models of material structures and mechanisms are providing solutions relevant to Laboratory programs.*



These materials scientists use a variety of approaches to solve materials problems described in this article. (Left to right) Standing: Daniel Calef, modeling of aerogels; Lloyd Chase, division leader; and William Gourdin, physically based models of tantalum deformation. Sitting: Larry Fried, molecular dynamics and phenomenological modeling of high explosives; and Tomas de la Rubia, kinetic Monte Carlo modeling of ion implantation and defects in silicon.

**E**VER since our ancestors first used tools to make tasks easier, understanding the properties of materials has been a practical concern. The challenge of explaining how modern materials behave is driven by the vast range of new materials and processing methods that are available and by the demands placed on performance, sometimes in harsh or unusual environments.

The cessation of nuclear testing and the advent of science-based stockpile stewardship as a primary Laboratory mission increase the challenge. Today, we need to predict changes in the structure and properties of materials in stockpiled warheads and the effects of these changes on how weapons perform. Success in fulfilling the stockpile stewardship mission will also provide far-reaching benefits to other Laboratory programs and the commercial sector.

One way scientists study material properties is by applying fundamental physical and mathematical principles to form the basis of models. By combining models with spectacular advances in computational technology, we can often shed light on the mechanisms that determine how a material behaves. Furthermore, theory and modeling in materials science are often directed toward predicting, not just describing, the properties of materials. Models have progressed to a point that they can often tell us not only what happens, but how or why it happens.

Lawrence Livermore scientists have an arsenal of tools and devices to model the behavior of materials without always resorting to experiments that can be expensive. On the other hand, experiments are usually used to validate models, so theorists and experimenters often work together.

Today in the Chemistry and Materials Science Directorate we are addressing increasingly complex phenomena and a broad range of problems in materials science relevant to Laboratory programs. Examples of our current modeling capabilities include:
- The evolution of microstructures, such as the formation and growth of voids produced by radioactive decay or irradiation of materials.
- The performance and degradation of high explosives and polymers.
- Alloy properties, such as phase diagrams.
- Analysis of spectroscopic scattering data.
- Metals processing.
- Corrosion damage.

These topics and many others also have important applications in defense, industry, and other sectors. The diverse materials we model include aerogels, alloys, ceramics, high explosives, metals, and polymers, to name only a few. The breadth of our modeling capabilities means that we cover length scales starting from atoms and electrons at the submicroscopic level, to grains and grain boundaries at intermediate lengths, to finished components at the opposite end of the spectrum.

## About Length Scales

The concept of modeling on all relevant length and time scales is fundamental in our research; Table 1 illustrates the concept. Materials generally have a wide range of internal structures that determine their behavior and performance. Our objective is to predict, explain, and sometimes control properties across the full range of material structures, which span spatial dimensions from a fraction of a nanometer to meters. (A nanometer is one billionth of a meter; a typical atom is about 0.3 nm in diameter.)

At the shortest lengths and times relevant to materials properties, atoms and electrons determine characteristics such as a material's hardness, conductivity, and optical properties. Sometimes we are able to calculate the behavior of a material based on quantum-mechanical theory alone. In that case, we call the process a "first-principles" calculation because we essentially do not use or need any experimental input. About all we need to know is the atomic numbers of the atoms involved and sometimes their positions. First-principles calculations increase our understanding of materials by allowing us to make predictions, reveal trends, test hypotheses, and analyze experimental data.

First-principles calculations form the basis for many of our modeling activities at Livermore.[1] Examples include the properties of metals and alloys, the behavior of surfaces and interfaces, and the modeling of experimental measurements. Because first-principles theory and modeling were discussed extensively in the *August/September 1994 issue of Energy & Technology Review*,[2] this article emphasizes the other approaches.

At increasing length scales in Table 1, we study the properties associated with larger structures by using approaches such as molecular dynamics (MD), kinetic Monte Carlo, or phenomenological models. Models associated with greater lengths are increasingly based on the empirical or measured responses of materials to stress, deformation, temperature, and other factors. By combining several approaches, we can deal with the wide variety of physical properties we need to assess. Illustrating diverse approaches to modeling across a range of material structures and properties, the following four examples of recent accomplishments are only a few of our many modeling efforts in progress.

## Defects in Silicon

Over the last 30 years, exponential growth of the semiconductor industry has been driven toward denser packing of smaller components that make up a silicon chip. To develop the silicon chips required for microelectronics components in the 21st century, we need to understand more about how defects are produced and how dopants diffuse in silicon.

Dopant atoms are required to make silicon usable for manufacturing

semiconductor devices. During manufacturing, dopants are routinely implanted (using ion accelerators) into very precise regions of a silicon wafer. This process damages the silicon wafer by introducing defects that must be removed. At the high temperatures used for the removal process, the defects and dopant atoms interact and diffuse over long distances. Dopants therefore can end up at destinations different from their intended location in a wafer. When that happens, the defective devices are not suitable for the marketplace.

We are creating a "virtual laboratory" to study this problem and to model other types of radiation effects in materials. Our strategy is to use an experimentally validated hierarchy of theoretical and computer simulation tools to span many length and time scales, from picoseconds to minutes. At the shortest lengths (at atom level) and times (up to about a nanosecond), we use MD simulations based on forces between atoms that accurately reproduce relevant properties of the material. Over time, defects in silicon can aggregate to form larger structures,

**Table 1.** Theory and modeling activities at Livermore cover all of the length scales associated with material structures.

| Material structure | Length scale | Primary theory or model used |
|---|---|---|
| Atomic or electronic | Angstroms ($1\ \text{Å} = 10^{-10}$ m) | QM |
| Simple defects (vacancies, point defects, interstitials) | Angstroms to nanometers ($1\ \text{nm} = 10^{-9}$ m) | QM MD KMC |
| Extended defects (dislocation, cores, small voids, clusters, and precipitates) | 10 to 100 nm | QM MD PM |
| Nanoscale to microscale structures (grain boundaries, grains, precipitates) | 10 nm to 100 µm ($1\ \text{µm} = 10^{-6}$ m) | QM MD PM Phen |
| Polycrystallines, composites, and interfaces | Micrometers to meters | PM Phen |
| Continuum (i.e., auto or bridge) | Varies | CM |

*Quantum mechanics (QM)* forms the rigorous theoretical basis for studies of electrons and atoms, chemical bonds, molecular structures, interfaces, and defects—the smallest structures that determine how a material behaves.
*Molecular dynamics (MD)* calculates the motions of atoms or molecules combining Newton's laws of motion with quantum-mechanical understanding, e.g., modeling the collisions of high-energy particles with the atoms of a solid undergoing radiation damage.
*Kinetic Monte Carlo (KMC)* models are used to study how atoms and defects in a material diffuse spatially by discrete jumps. The probability of a jump is determined by temperature and energy barriers for the movement.
*Physically based models (PM)* are based on physical concepts that emulate the behavior of material structures, e.g., dislocation movement, grain-boundary sliding, crystallographic twinning, and material movement.
*Phenomenological models (Phen)* use mathematical relations without any known physical basis to describe experimental observations.
*Continuum models (CM)* treat structures, such as a car frame or beams of a bridge, as a continuous or homogeneous material, e.g., the process of forging an automobile bumper.

like dislocations. To study how such structures evolve over longer times (minutes or hours), we use kinetic Monte Carlo simulations. In this work, we have a collaboration with scientists at AT&T Bell Laboratories, which allows us to develop a new capability to support other Laboratory programs.

Recent computer simulations based on our models are giving us a clear and consistent physical picture of the production and evolution of damage in silicon under energetic-beam bombardment. A typical simulation begins with a cube of silicon made of about one million atoms in a normal lattice arrangement. Then we simulate the bombardment of the top of the cube with high-energy ions to implant arsenic, boron, or other dopant atoms. Figure 1 shows the defects—that is, displaced atoms—in a silicon cube. We can simulate the full range of beam energies that are typically used to process silicon devices, from about one-tenth of an electron volt to several thousand electron volts. As the energy increases, the amount of total damage increases, as expected, but we also find that the size of the largest defect clusters increases.

Our simulations produce images that look as though they come from a high-resolution microscope. We validate the simulations by comparing them with damage observed in actual materials, as shown in Figure 2. Comparisons like this confirm that our computer-aided design package accurately predicts experimental results.

Our work on semiconductor devices also applies to a range of other problems. For example, the walls in nuclear power plants undergo radiation damage from neutron bombardment. Similar processes may occur in nuclear weapons components. Our simulations can help predict the performance of materials used in weapons, existing fission power plants, and fusion plants that may be developed in the future. Because void formation is also seen in

metallic nuclear fuel rods and other structures, the modeling of defects and voids has applications to these problems as well.

## Deformation in Tantalum

Anyone who has attempted household plumbing knows that copper tubing becomes more difficult to work by hand after repeated bends. This phenomenon, known as work hardening, occurs in many metals. The increase in strength is caused by interactions between lattice defects called dislocations.

Dislocations consist of extra or unequal planes of atoms, like an extra sheet of paper slipped part way into a stack of sheets. Another handy way to imagine dislocations is to think of them as "wrinkles" in the regular arrangement of atoms in a metal crystal—much like wrinkles in a rug. Imagine creating a small wrinkle at one end of a rug and then pushing the wrinkle along to the other end. In a similar manner, atoms in a metal lattice can be moved relative to each other by creating a dislocation and then moving it through the crystal. Like a wrinkle in a rug, dislocations are long, string-like

defects. When many are present, they tangle like spaghetti. In metal, the more dense the tangles, the more energy is needed to deform it.

Copper belongs to a class of common metals with a simple structure known as face-centered cubic—a cube of atoms with an additional atom on each face.

Another group of metals, including iron and tantalum, has a body-centered cubic (bcc) structure with atoms at the corners of a cube and one atom in the center. Because these metals are technologically important, their mechanical behavior is of considerable interest.
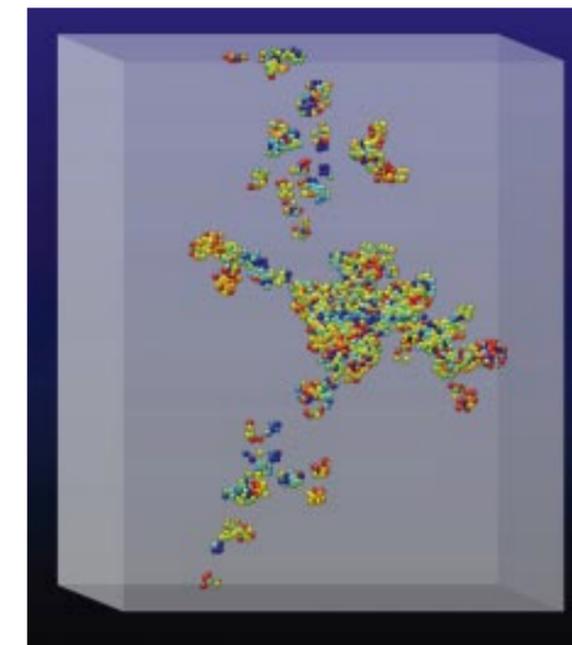


**Figure 1.** Monte Carlo computer simulation of displaced atoms in a cube of translucent silicon after implantation with 15-keV arsenic ions. The unaffected silicon atoms are not shown here. The atoms in blue are under tensile stress and represent areas with vacancies; the atoms in red are in compressive stress and indicate the presence of interstitials. The large mass in the middle is an amorphous zone; i.e., the crystalline order has been destroyed.
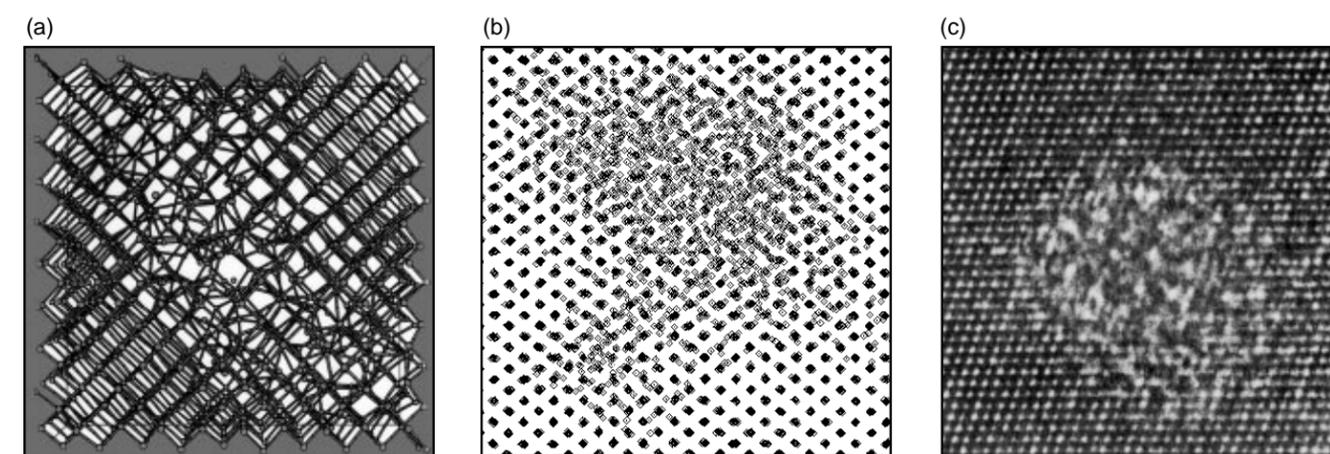
(a) 

(b) 

(c) 

**Figure 2.** (a) Three-dimensional plot of damage created by a 25-keV platinum ion in silicon. A highly disordered, amorphous region is surrounded by crystalline material. (b) A two-dimensional projection of the atoms in (a). (c) An experimental high-resolution electron micrograph done elsewhere[3] of the impact of a 100-keV bismuth ion in silicon. Although the exact conditions of the simulation and experiment are not identical, this type of comparison helps us to validate the simulation and to interpret the experimental observation.

Our goal is to understand the mechanical behavior of bcc metals and to include enough physics concepts in the model so that calculations can be meaningfully extrapolated to new conditions. The problem is beyond the reach of quantum mechanical calculations. Instead, we are using physically based models that are realistic in representing the actual processes that control deformation. Tantalum is a good test case for this work because it is ductile, shows substantial work hardening, and has important defense applications.



**Figure 3.** How to envision the two barriers to plastic flow in tantalum: The distance along the bottom refers to the distance traveled by a moving dislocation when a material is deformed. The Peierls barriers are associated with the motion of isolated dislocations (analogous to wrinkles in a rug). The larger obstacles occur where dislocations intersect.

**Figure 4.** Our model accurately reproduces experimental values of stress (force applied per unit area) and strain (relative change in dimensions) for various strain rates (rates of deformation) in unalloyed tantalum at room temperature.



Our model for tantalum accounts for both yield stress (force per unit area at which it begins to permanently deform) and work hardening. Previous explanations said nothing about work hardening and did not explain it for this class of materials. We suggest that there are two (or possibly more) barriers to moving a dislocation, as illustrated by the humps in Figure 3. At first, a dislocation in tantalum must move as if it were isolated, and enough force must be applied to overcome a series of small barriers. In the analogy of wrinkles in a rug, even if no other wrinkles block the path, some force is still required to move an isolated wrinkle. (The material in front of a wrinkle must be lifted as it moves forward.) After moving a certain distance, however, a dislocation may encounter a barrier produced by other dislocations. The force to overcome this barrier increases with deformation and accounts for work hardening in a natural way.

Our model combines the two mechanisms, yield stress and work hardening, and is able to describe which one dominates at different stages and under different conditions of deformation. Figure 4 shows how well the model can reproduce the observed mechanical behavior of tantalum at room temperature. We find similar agreement when temperature is varied.

What is the model good for? With the increased power of modern computers, companies like automobile manufacturers can now simulate the forming and performance of key structural components. However, computer simulations are only as good as the underlying models used to describe the behavior of materials under conditions that are often severe (for example, crashes). Physically based models more realistically describe material properties, yield more meaningful results, and can be reliably extended beyond the scope of experimental data. Whereas the current Livermore model for the deformation of tantalum was conceived for bcc metals, it provides a framework for face-centered cubic metals as well.

## Modeling High Explosives

Energetic materials, which include high explosives, are widely used in both military and civilian applications. Livermore has studied high explosives for decades because they are crucial to the performance of nuclear weapons. In the area of stockpile stewardship, we studied how shock dynamics change in older, degraded materials. In another recent project, we developed a candidate bunker-busting munition for the Air Force following their experiences in the Gulf War. In the civilian sector, the Bureau of Mines needs to evaluate explosives for mining operations. To better assess environmental concerns, we need to know what reaction products are generated following a detonation.

Typical energetic materials are made of large, floppy molecules with more than 20 atoms, and they can undergo a variety of chemical reactions. Over time, such molecules can degrade and the crystals become more porous, making them dangerous to handle. At the atomistic level, we are simulating how the propagation of a shock wave through high explosives is affected by the degree of degradation. On a macroscopic scale, we can model the performance of existing and novel energetic materials.

As one example of new work on the atomistic scale, we are applying MD simulations to study how the shock properties of the widely used explosive triaminotrinitrobenzene (TATB) change as a function of its degradation and increased porosity. By using this advanced capability, we can assess how an explosion is initiated on a molecular level in aged material found in weapons stockpiles.

As shown in Figure 5, we simulate crystals of about 10,000 TATB molecules and apply a shock wave (a simulated pressure impulse) to crystals with different degrees of defects. We found that the shock wave in degraded material travels much more slowly and spreads out over a much wider area than in pure TATB. At the molecular level, the collapse of voids leads to hot spots in degraded (porous) TATB, and the temperature behind the shock front becomes higher and much more nonuniform.

To understand how molecules like those in TATB react on a much larger scale, we have developed the CHEETAH computer code, a phenomenological thermochemical model to predict the performance of explosives.[4] In contrast to our MD simulations, this more mature modeling effort looks at macroscopic events at lengths of centimeters to meters. The code is empirically based and is derived from more than 40 years of experiments on high explosives at LLNL.

CHEETAH models the interactions (for example, the electrical potentials) of a mix of molecules between them to predict a variety of outcomes, such as those shown in Figure 6. If we think of explosives as a bucket of hot chemical soup, CHEETAH acts like a thermometer and pressure gauge. It predicts the reaction products and the detonation properties, such as pressure, velocity, and energy. The code allows us to vary the recipe (chemistry) and the starting conditions to optimize the properties we want, such as the best early- or late-time energy. The value of CHEETAH is that it predicts the performance of a given amount of high explosives to within a few percent. With libraries of about
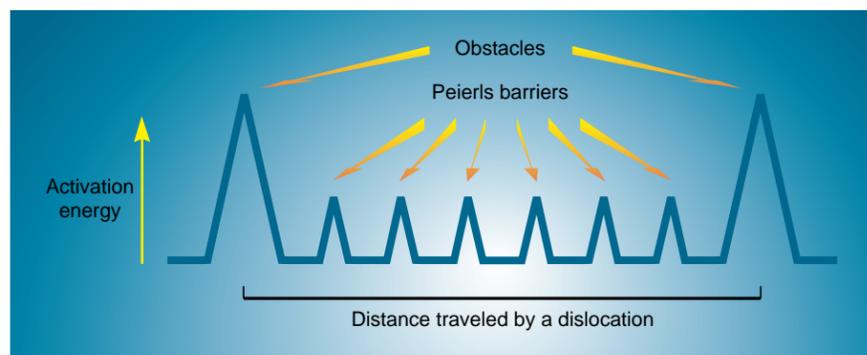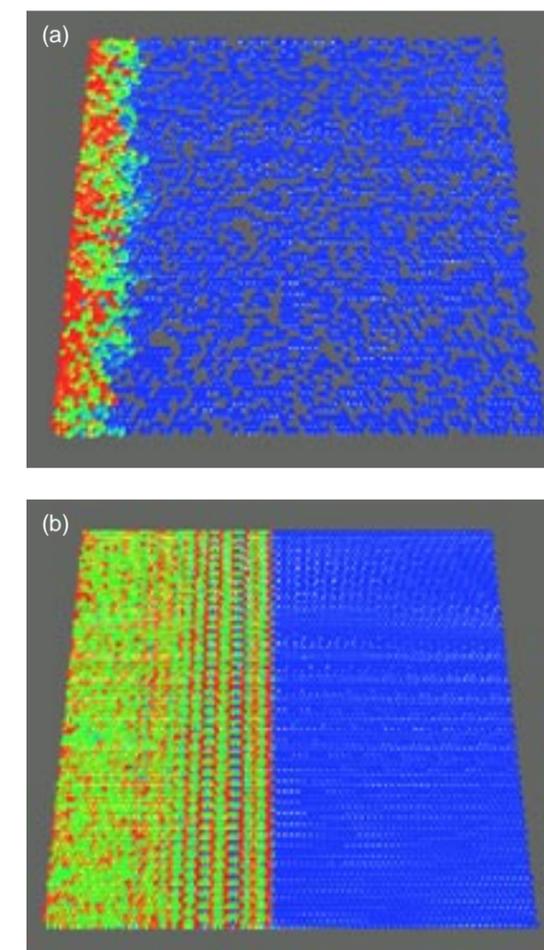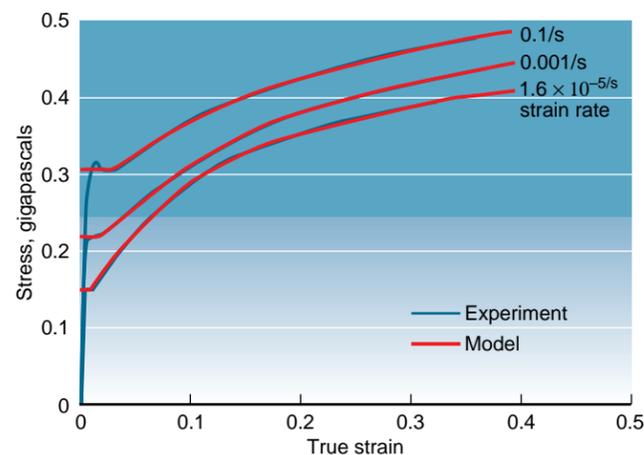


**Figure 5.** "Snapshots" of molecular dynamics simulations for (a) pure and (b) degraded TATB. The molecules are shaded according to their kinetic energy as a shock front passes through the lattice, with red corresponding to higher temperatures and purple to lower temperatures. In contrast to a sharp, smooth shock front in pure material, porous TATB produces a broader and less uniform shock front with hot spots.

100 reactants and 6,000 products, the program is now used by more than 80 research teams in industry, academia, and the international scientific community, including England, Canada, Japan, Sweden, and France.

The code is both physically simple and user friendly, and it can guide applications ranging from rocket and gun propellants to the formulation of new explosives with improved performance.
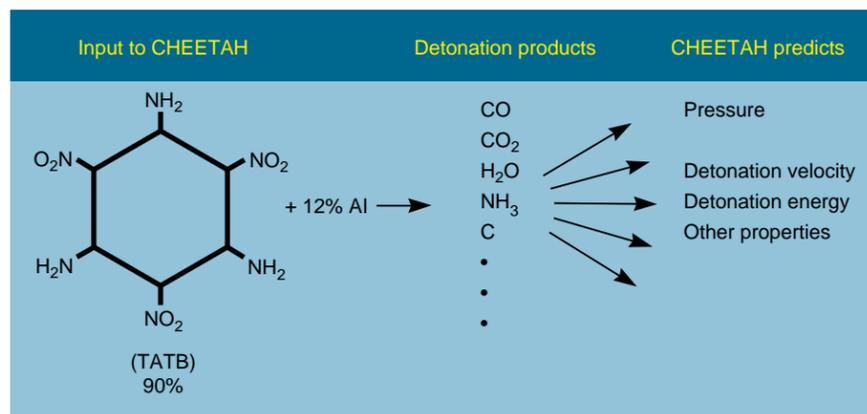


| Input to CHEETAH | Detonation products | CHEETAH predicts |
| --- | --- | --- |

NH2, O2N, NO2, H2N, NH2, NO2 (TATB) 90%

+ 12% Al →

CO, CO2, H2O, NH3, C

Pressure
Detonation velocity
Detonation energy
Other properties

**Figure 6.** To predict the performance of explosives, CHEETAH starts with one or more base reactants, such as TATB and metallic aluminum. It then solves thermodynamic equations to predict the detonation products and their properties, such as temperature and volume. From these values, CHEETAH predicts the detonation properties, including pressure, velocity, and energy.
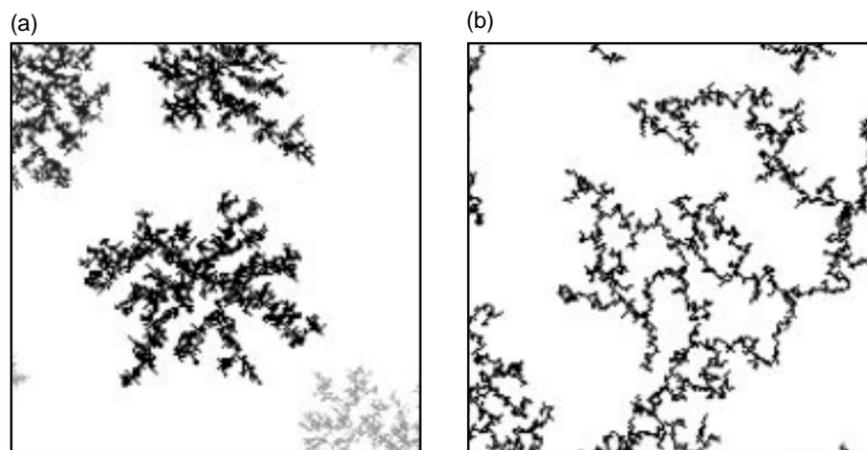
(a)                    (b)



**Figure 7.** We model aerogel structures by varying the number of starting particles and the rules by which they move and adhere to one another. Compared to (a) clusters grown from fixed seeds, (b) cluster–cluster aggregates more accurately mimic real aerogels.

## Transport Through Aerogels

Aerogels have exceptional strength and enormous surface area and are among the lightest solids known.[5] Some varieties are 100 times less dense than water. LLNL first studied aerogels for a national defense application, but their use is being proposed as electrical, thermal, and sound insulators; optics, space, and catalyst devices; capacitive deionization units for water purification; aerocapacitors for energy storage; and various novelties and toys. Many aerogel applications remain relevant to Laboratory programs focused on national defense, the environment, and energy. Their use as filters and catalyst supports take advantage of their tremendous surface area.

At the microscopic scale, these highly unconventional solids are made of "beads" that are some tens of nanometers in size. At an intermediate length scale (in the range of micrometers), groups of beads are clustered to form an open network with large and small voids or pores in the network. To understand how molecules flow through an aerogel, as they would in a filter, we need accurate structural models and flow codes for highly irregularly shaped networks.

Developing these models was a considerable challenge because the absence of any characteristic pore size in an aerogel complicates the treatment of fluid flow. We have replicated the structure of aerogels at the intermediate scale by simulating the growth of clusters.[6]

In the models, particles on the order of 10 nanometers wide represent the beads. These particles or "walkers" randomly move through a three-dimensional lattice and stick to each other. Both the number of walkers and the sticking rules are varied in different simulations. For example, if walkers only cluster around a set of fixed particles, then structures like those in Figure 7a are created. Alternatively, if walkers adhere to each other and the clusters continue to diffuse, then we generate structures like those in Figure 7b, called cluster–cluster aggregates.

When we make the structures more like those in Figure 7b, they act more like a simple, random distribution of obstacles, and they more accurately mimic the structure and behavior of real aerogels. A commonly measured quantity for flow through porous materials is permeability. In comparisons of calculated permeabilities based on our models, the cluster–cluster aggregates closely match the observed experimental behavior for the flow of a gas through aerogels.

Figure 8 shows a puff of smoke flowing through one of our modeled aerogels. This visualization, developed by the Livermore Computer Center graphics laboratory, clearly shows that the flow patterns are dominated by the largest pores. Such results reinforce the view that our approach successfully models these highly irregular and unconventional solids.

## Work to Come

What does the future hold for theory and modeling of materials properties at LLNL? To accomplish our stockpile stewardship mission, we must improve our ability to predict how the structures of metals, high explosives, and polymers change with time or vary with manufacturing methods. Then, we need to assess the effects of these changes under the extreme conditions relevant to weapons performance. For this purpose, we need robust models that can be used reliably. We are collaborating with Laboratory colleagues in the Physics and Space Technology and Engineering Directorates, as well as with researchers at many universities, to develop the required approaches.
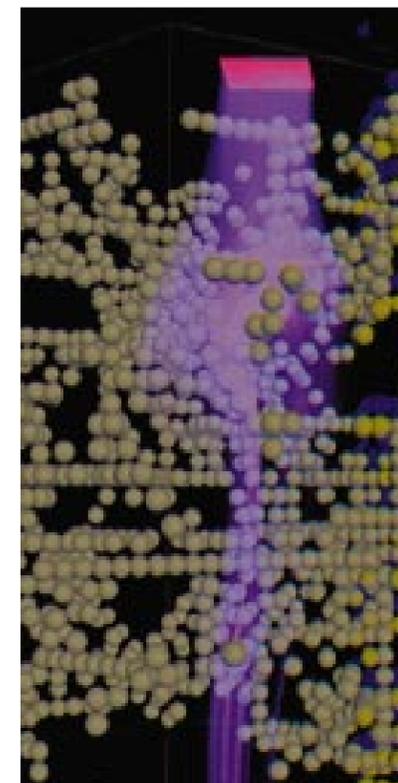


**Figure 8.** A puff of smoke flowing through an aerogel shows that the flow patterns are dominated by the largest pores.

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### About the Scientist

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