TECHNICAL DISCUSSION

MOLECULAR DYNAMICS SIMULATION OF THERMAL TRANSPORT IN SOLIDS

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Novel nanometer-scale solid-phase materials such as buckyballs and buckytubes, highly nanoporous and ultrathin films, and quantum wires and dots are becoming increasingly important in modern technology. Thin solid films currently are key components in integrated-circuit transistors, quantum-well lasers, and microelectromechanical systems (MEMS). The favorable optical, thermophysical, mechanical and/or electrical properties exhibited by quantum dots, quantum wires, porous thin films, and buckytubes may play a critical role in many future applications such as thermoelectric materials and optical computing devices. Operating temperatures have a significant impact on device and material performance in the above applications. For example, heating adversely affects the operation of vertical-cavity surface-emitting lasers and edge-emitting lasers, and temperature strongly influences the optical properties of semiconductor materials. For the best design of devices and novel materials in temperature-sensitive applications, an understanding of thermal transport is of paramount importance. The molecular dynamics computational technique will be an important tool for the analysis of thermal transport in such applications.

Molecular dynamics (MD) is a computational method that simulates the real behavior of materials and calculates physical properties of these materials by simultaneously solving the equations of motion for a system of atoms interacting with a given potential. The computational work on anharmonic one-dimensional chains of atoms by Fermi et al. [1] in the 1950s was the earliest contribution to the field of MD. This pioneering research was followed by other critical MD studies, including Alder and Wainwright's analysis [2] of two- and three-dimensional systems of hard spheres, Gibson et al.'s simulation [3] of radiation damage, and Rahman's much-cited study [4] of a small cluster of atoms. A lack of sufficient

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computational power limited these and other early simulations to systems with a very small number of atoms.

In the past two decades, however, the number of MD studies has skyrocketed due to rapid developments in computer speed and memory. It is now possible, using parallel computation, to model systems on the order of a million atoms. However, this is still very small, since 1 million atoms is a cube 100 atoms on a side, which is on the order of tens of nanometers! Bulk materials are simulated by using periodic boundary conditions, in which the actual simulation cell of a small number of atoms is essentially repeated infinitely in all directions. This method often yields values for physical properties that are surprisingly close to experimental results, but artifically excludes phonons in solids that have wavelengths larger than the simulation cell size [5].

APPLICATION TO REAL MATERIALS

The limitations of MD in simulating bulk materials can be turned to advantage for novel nanometer-scale materials. It is well known from measurements on thin films that such materials display markedly lower thermal conductivities than their bulk counterparts. Other types of nanostructured materials are also expected to exhibit reduced thermal conductivity when their characteristic dimensions become small. Several approaches exist to predict the thermal conductivity for materials in which heat conduction by lattice vibrations is dominant. These approaches, which are based on the transport of phonons, include the Monte Carlo computational technique and the Boltzmann transport equation. Such methods, however, do not easily handle the nonuniformly distributed impurities, voids, cracks, and dislocations found in real thin films or the complex geometries present in novel materials. Irregularities can create localized, fractal, or other types of vibrational modes in a material, calling into question the assumption of pure phonon transport, which is implicit in the above approaches. Another advantage of MD is its strong physical basis. Intermolecular interaction potentials are the basis of MD simulations, not random numbers or questionable relaxation times.

Numerous articles on topics such as crack initiation and propagation, density of states in microcrystalline and glassy materials, and the effect of intricate nanostructures on thermal conductivity show that MD is well suited for the study of nanoscale phenomena in solid-phase materials. It is a needed supplement to experimental measurements, which can be extremely difficult at such length scales. Additionally, MD provides a way to ascertain the behavior of materials at time scales that are often hard to access with experiments. Only time scales on the order of nanoseconds and shorter can be treated in a reasonable time by MD simulations, because the finite-difference schemes used in such simulations require small time steps for energy conservation. The transient heat conduction work of Volz et al. [6] is a good example of short-time-scale MD studies in the literature.

ARGON-TYPE MODEL

Frequent topics of MD studies in the literature are fluid flow, phase change, mass diffusion, and the chemistry of fluids composed of large, complex molecules.

Typical properties calculated in these studies include energy, viscosity, and mass diffusion coefficient. Of all the materials simulated with MD in the above studies, argon-type fluid systems are overwhelmingly the most well explored and characterized. Argon is a good choice for such simulations because the widely accepted Lennard-Jones 12-6 (LJ) potential matches liquid-phase experimental data for argon well, and has meaningful physical constants as parameters. Additionally, its simple form, with only two-body terms, requires much less computation time than more complex potentials involving three-body and higher terms [7]. A rigorous quantum mechanical approach is currently not feasible for systems of more than a few atoms because such a method is too numerically intensive, although the efforts of many workers are now being directed toward this problem [8].

Several MD studies have explored the thermal conductivity of bulk argon-type fluids. Nonequilibrium MD [9] work by several groups demonstrates that the use of LJ potentials in MD simulations gives good agreement with experimental thermal conductivity data for bulk argon. Fewer researchers have used MD to address the vibrational and thermophysical properties of nanoscale and nanostructured solid materials. Kotake and Wakuri's recent study [10] of size effects on thermal transport in a two-dimensional solid system subjected to a constant flux is one important example of this work. Such work has shown that an argon-type potential yields results that correspond well qualitatively with experimental data for several types of nanoscale materials. These results support Kristensen et al.'s [11] postulation that the fundamental vibrational, structural, and melting properties of many materials are not strongly dependent on the interaction potential and can be suitably modeled by an argon-type potential.

Although argon is not a technologically relevant material, it is a good choice for initial MD studies. This is due not only to the fact that the results can be benchmarked against the large body of existing work on argon-type systems, but also because the argon model, as discussed above, should reveal fundamental phenomena for a wide variety of materials in a computationally economical manner. Also, impurities, pores, defects, and other types of complicated structures can be easily handled by the model. To get the most quantitatively accurate results for a given material, a potential specific to that material should be used, but for predicting qualitative trends, the argon model is a sensible choice.

COMPUTATIONAL PROCEDURE

For bulk equilibrium calculations, MD results are more accurate as the size of the computational domain (simulation cell) increases, because more long-wavelength phonon modes can be sustained. Increases in size, however, cause a considerable increase in computation time. To balance the needs for accuracy and for reasonable computation time, the simulation cell size must be chosen carefully. The first part of the computational procedure consists of assigning initial positions and velocities to atoms and calculating the initial forces on the atoms using the derivative of the interaction potential. The difference equations of motion are then used to advance the atomic positions, velocities, and forces at each time step. Quantities of interest such as energy and temperature are then calculated and time-averaged for the duration of the simulation.

The calculation of nonequilibrium quantities such as thermal conductivity is more difficult than calculation of equilibrium quantities. It is possible to compute thermal conductivity from an analysis of fluctuations of a system at equilibrium, but this method generally requires much more computation time than direct nonequilibrium simulations. In direct thermal conductivity simulations, the nonequilibrium condition can be generated either by introducing additional forces into the atomic equations of motion or by enforcing hot and cold regions in the simulation cell to induce a temperature gradient physically. The thermal conductivity is found using a simple ratio of heat flux to temperature gradient.

CONCLUDING REMARKS

Molecular dynamics is a valuable tool for analyzing thermal transport in solids at micro- and nanoscales. The primary advantages of this technique are its adaptability to complex nanostructures, its ability to capture short-time-scale behavior, and its strong physical basis. An important disadvantage is the suppression of long-wavelength phonons by the periodic boundary conditions. Other disadvantages include the size limitation of the computational domain and the long simulation times required to model systems with sizes greater than a few nanometers. Future work should be done to apply this versatile, conceptually simple technique to microscale problems for which other experimental and analytical approaches are difficult. MD is especially suited to study the thermophysical properties of more complex microstructures such as doped and nanoporous thin films and materials with voids, cracks, dislocations, or other complex geometries.

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