Computational Nanomechanics and Thermal Transport in Nanotubes and Nanowires

Deepak Srivastava1, *, Maxim A. Makeev1, Madhu Menon2, and Mohamed Osman3

1 Advanced Aerospace Materials and Devices Group, UARC, NASA Ames Research Center, Moffett Field, CA 94035-1000, USA
2 Department of Physics and Center for Computational Sciences, University of Kentucky, Lexington, KY 40506, USA
3 School of Electrical Engineering and Computer Science, Washington State University, Pullman, WA 99164-2752, USA

Representative results of computer simulation and/or modeling studies of the nanomechanical and thermal transport properties of an individual carbon nanotube, silicon nanowire, and silicon carbide nanowire systems have been reviewed and compared with available experimental observations. The investigated nanomechanical properties include different elastic moduli of carbon nanotubes, silicon nanowires, and silicon carbide nanowires, all obtained within their elastic limits. Moreover, atomistic mechanisms of elastic to plastic transition under external stresses and yielding of carbon nanotubes under experimentally feasible temperature and strain rate conditions are discussed in detail. The simulation and/or modeling results on thermal properties, presented in this work, include vibrational modes, thermal conductivity and heat pulse transport through single carbon nanotubes, and thermal conductivity of silicon nanowires.

Keywords:

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1. INTRODUCTION

The science and technology of nanometer-scale materials, nanostructure-based devices, and their applications in functionally graded materials, molecular electronics, quantum computers, sensors, actuators, and molecular machines form the realm of modern Nanotechnology. At a few nanometer length scales, the devices and systems sizes are downscaled to reach the limit of tens to hundreds of atoms, where new physical and chemical phenomena are observed. This form the basis for development of new generations of advanced materials and devices, based on building blocks made of nano-structured materials. A true breakthrough in Nanotechnology has been spurred by the discovery of atomically precise nanometer-scale materials, such as fullerences, in the middle of 1980s, carbon nanotubes (CNTs), in the early 1990s, and silicon and compound semiconductor nanowires, in the late 1990s. The CNTs can be thought of as sheets of carbon atoms rolled up into tubular structures, such that the atoms at the seams are connected in a flawless manner according to the rules of chemical bonding. The nanowires, on the other hand, are solid crystalline, one-dimensional structures with approximately cylindrical geometry. For small diameter nanotubes or nanowires, the typical materials defect densities are expected to be very low and surface to volume ratio to be very high. Consequently, unique structural, mechanical, and chemical properties have been observed, which have led to proposals for applications of these materials in a variety of areas of modern technology. In this review paper, we focus primarily on the structural, mechanical,
and thermal transport behavior of CNTs as well as silicon and silicon carbide nanowires.

A single sheet of carbon atoms, rolled up into a tubular structure, is called a single-wall carbon nanotube (SWCNT), and a rolled-up stack of multiple sheets of carbon atoms results in multi-wall carbon nanotubes (MWCNT). Since the discovery of multi-wall carbon nanotubes in the year 1991 by Iijima and subsequent synthesis of single-wall carbon nanotubes by Iijima and Bethune, numerous experimental and theoretical studies

Deepak Srivastava has been a Lead Scientist and Manager of computational materials design and nanotechnology related activities at NASA Ames Center for Nanotechnology for last ten years. In recent years he has given more than 100 invited talks on computational materials design, nanotechnology, and aerospace and defense related materials applications in USA and abroad. His recent award and honors include winner of Feynman Prize in Nanotechnology (Theory) in 1997, Veridian Medal Paper (1999), The Eric Reissener Medal (2002), and CSC Award for Technical Excellence (2003). Dr. Srivastava has served as Associate Editor of two peer reviewed nanotechnology and computational materials sciences related journals and sits on the editorial boards of two other journals. Dr. Srivastava co-founded and served as CTO of a computational materials design company Junius Tech, which was acquired by a nanomaterials rational design and fabrication company—Nanostellar in the automotive catalysis sector. At Nanostellar he served as a technical advisor for two years helping to build and advice the technical team, investigate future new product and technology areas, and technology development consulting on a regular basis. Since the beginning of 2007, Dr. Srivastava has also become the CTO of Nanoexa, a clean energy company focused on quantum simulation based design, performance optimization, and product development for the next generation of Li-Ion battery and Solar PV materials, devices and applications.

Maxim A. Makeev

Madhu Menon

Mohamed Osman

of their electronic, chemical, and mechanical properties have been undertaken.\textsuperscript{4,5} Carbon nanotubes possess very good mechanical strength (stiffness) and the other elastic characteristics, electronic properties ranging from semiconductors to metals, high electronic sensitivity to chemical adsorbates and mechanical strains, and very large aspect and surface to volume ratios. Given their superb properties, CNTs have been proposed for application as reinforcing fibers in functionally graded lightweight composite materials, components of molecular electronic devices, chemical and mechanical sensors and actuators, metrology probe tips, and gas and energy storage materials.\textsuperscript{6} Concurrently, the field of low-dimensional silicon and silicon carbide based semiconductor structures has also become very attractive due to its tremendous potential towards development of next generations of electronic, sensing and thermo-electric devices applications. Single crystal nanowires of a variety of individual elements and compound semiconductors have been grown and investigated in experiments for electronic, optoelectronic, and thermo-electric applications.

The tools for computational studies of nanomechanics and thermal properties of nanostructured materials cover a wide range of the multiple length- and time-scales simulation techniques.\textsuperscript{7} For instance, simulations of the atomic-level structure and nanomechanics, in the large strain (elastic to plastic transition) regime, are performed using quantum mechanical and reactive molecular dynamics methods, whereas the thermal transport characteristics are performed using non-reactive classical molecular dynamics. The mechanics of large diameter and length nanotubes and nanowires can be studied with mesoscale dynamics methods, which are in the preliminary stages of development. In this review, we focus our attention only on the simulation methods that are relevant to the simulations of the mechanical and thermal properties of nanotubes and nanowires. The remainder of the manuscript is organized as follows. In Sections 2 and 3, we describe the basic atomic-scale structural characteristics and simulation methods underlying investigations of the mechanical and thermal transport properties. The focus of Section 4 of the manuscript is on nanomechanics of CNTs, in both elastic and plastic regimes of deformation. In Section 5, the elastic properties of Si and SiC nanowires are discussed, in the elastic response and plastic failure regimes. Section 6 is devoted to a detailed discussion of simulation studies of thermal transport characteristics in the equilibrium and non-equilibrium heat pulse transport conditions. A brief summary of the presented results, conclusions, and outlook is given in Section 7.

2. STRUCTURE OF CARBON NANOTUBES AND SILICON NANOWIRES

A SWCNT is best described as a rolled-up tubular shell of a graphene made of hexagonal rings (in a sheet) of carbon atoms.\textsuperscript{4,5} The two ends of the tubular shell are capped by dome-shaped half-fullerene-like structures. The natural curvature of the sidewalls is due to the rolling of the sheets into the tubular structure, whereas the curvature in the end caps is due to the presence of topological defects, i.e., pentagonal rings in the otherwise hexagonal structure of the underlying lattice. The role of the pentagonal ring defects is to give a positive (convex) curvature to the surface, which helps in closing of the tube at the two ends. A multi-wall nanotube is a rolled-up stack of graphene sheets into concentric geometry SWCNTs, with the two ends, again, either capped by half-fullerenes or kept open. A nomenclature \((n, m)\), used to identify each single-wall nanotube in the literature, refers to integer indices of two graphene unit lattice vectors corresponding to the chiral vector of a nanotube, as illustrated in Figure 1(a). Chirality vectors determine the directions along which the graphene sheets are rolled to form tubular shell structures and perpendicular to the tube axis vectors, as explained in Refs. [4-6]. The nanotubes of type \((n, n)\) are commonly called armchair nanotubes because of

![Fig. 1. Schematic showing: (a) rolling directions for armchair-type (AA) and zigzag-type (ZZ) CNTs. In the figure, \(a_1\) and \(a_2\) are the unit vectors of the graphene sheet lattice; (b) atomic structure of a \((5, 5)\) armchair CNT; (c) the structure of a \((10, 0)\) zigzag CNT.](image-url)
the \[ /\_\_ /\_ \] arrangement of C–C bonds perpendicular to the tube axis, and have a symmetry along the axis with a short unit cell (0.25 nm) that can be repeated to make the entire section of a long nanotube. The atomic structure of a (5, 5) CNT is shown in Figure 1(b). The nanotubes of type \((n, 0)\) are known as zigzag nanotubes because of the \(/\_\_ /\_ \) arrangement of C–C bonds, perpendicular to the tube axis, and also have a short unit cell (0.43 nm) along the axis. The atomic-level structure of a (10, 0) CNT is shown in Figure 1(c), as an example. All the remaining nanotubes are divided into chiral and helical nanotubes and have longer unit cell sizes along the tube axis. Details of the symmetry properties of the nanotubes of different chiralities are explained in detail in Refs. [4–6].

Unlike carbon nanotubes, the silicon nanowires can be considered as high aspect ratio solid cylindrical structures. The large diameter silicon nanowires derive their structures from the basic diamond lattice structure of bulk silicon. For thin nanowires, as the diameter decreases to within few nanometers, the surface to volume ratio becomes very large, and it is expected that the surface reconstruction may exert inward stress on the structure, such that the single crystalline tetrahedral structure may not be the most stable one. Experimentally produced silicon nanowires, however, come in various diameters and are usually covered with thin oxide layers. It is only recently that experimentalists have succeeded in removing the oxide layers and terminating the surface with hydrogen. Although it is well established by now that most of the Si nanowires consist of a single crystalline core, it is not clear if the crystalline core is that of bulk Si or may have other arrangement of atoms in the structure. Based on computer simulation

![Fig. 2. Atomic structures of small-diameter Si nanowires: (a) tetrahedral; (b) clathrate with Si$_{14}$ basis; (c) clathrate with Si$_{16}$ basis; (d) polycrystalline with pentagonal cross-section.](image-url)
studies, some possible structures for Si nanowires have been predicted recently.\(^9,10\) Thus, in the studies, reported on in Refs. [11–13], nanowires were found to consist of fullerene-like cages. In particular, the Si nanowire structures, proposed by Menon and Richter,\(^9\) have four-fold coordinated cores and three-fold-coordinated surfaces with one of the most stable reconstructions of bulk silicon surface. Such reconstructions are of great importance since they provide a considerable reduction in the surface energy that can be relatively high for quasi-one-dimensional structures, especially in the small diameter regime. Recently, Zhao et al.\(^{11}\) have compared the energetics of formation of silicon nanowires with crystalline and polycrystalline cores and suggested that, for very thin (1–6 nm diameter) nanowires, polycrystalline structure with pentagonal cross-section may have lower energy than the single crystal structures observed in experiments.

In the absence of any direct experimental evidence for the structure of thin nanowires, it can be assumed that there exist several competing structures with energy and stability close to each other. Although the diamond structure (tetrahedral) is established to be the most stable form of the bulk Si, the clathrate or cage-like forms are very close in energies to the diamond structure. In the case of small-diameter silicon nanowires, the possibility exists that relatively larger contributions of surface energies could tilt the balance in favor of either the clathrate or the polycrystalline forms. It is on these grounds that precise knowledge of atomic structure of nanowires would be a very useful in determining their mechanical, thermal, electronic and optoelectronics properties. To this end, a number of atomistic simulations (including first-principles calculations and classical molecular dynamics) have been recently performed to predict the structure of small-size nanowires.

A thorough energetic analysis of a wide variety of silicon nanowires including tetrahedral, cage like clathrate type, and polycrystalline structures has been performed incorporating a careful consideration of the corresponding surface reconstructions. All model structures were fully relaxed without any symmetry constraints using the generalized tight-binding molecular dynamics scheme.\(^11\) A total of 65 silicon nanowires were considered. All investigated nanowires had crystalline cores consisting of four-fold-coordinated atoms and three-fold-coordinated surface atoms. The nanowires belonged to four different categories, as shown in Figure 2. Their diameters ranged from 1 nm to 5 nm. The cage-like silicon nanowires were carved out from silicon clathrate structures consisting of a face centered cubic (fcc) lattice with a 34-atom basis as well as a simple cubic (sc) lattice with a 46-atom basis. Both these forms are known to be the most stable clathrate forms of silicon.\(^14\) The tetrahedral nanowires have been found to be the most stable among all the others and, surprisingly, the polycrystalline forms of nanowires (which have the smallest surface to bulk ratio) were found to be the least stable. Furthermore, the cage-like nanowires with clathrate-type core structures have been found to possess greater thermal stability than the tetrahedral nanowires of the same diameters.\(^15\)

3. SIMULATION METHODS

The development of multi-scale simulation approaches is vital for realistic studies of nanostructured materials and based thereupon devices. In recent years, a number of simulation methods covering multi-length and/or multi-time scales have been designed for the structure, dynamics, chemical, thermal and electronic characterization of nanotubes and nanowires. In this section, we briefly describe the emerged simulation methods that are most relevant to studies of the mechanical and thermal properties of carbon nanotubes as well as silicon and silicon carbide nanowires.

3.1. Multi-Scale Simulations for Nanomechanics

In the early days, the structural, mechanical and thermal properties of bulk condensed matter systems have been studied using analytical approximation methods for infinitely extended material systems. Computer simulations of the finite model systems have become more common only recently because powerful computer, necessary to simulate nano-scale systems in full complexity, have came to the scene. One of the commonly used atomistic simulation technique is classical molecular dynamics (MD), which now-a-days allows for modeling of the systems of atoms as large as several billions, thus covering the characteristic for nanostructures length-scales. Classical MD method is based upon numerical solution (in the finite difference approximation) of the Newtonian equations of motion for each atom or molecule in the system under consideration. Except when dealing with very light atoms and very low temperatures, the use of classical MD method is well justified. In MD simulations, the dynamic evolution of the system is governed by the set of Newton’s classical equations of motion, \(d^2 \mathbf{R}_i/dt^2 = F_i = -dV/d\mathbf{R}_i\), which are derived from the classical Hamiltonian of the system, \(H = \sum \mathbf{P}_i^2/2m + V(\mathbf{R}_i)\). The atomic forces are derived as analytic derivatives of the interaction energy functions, \(F_i(\mathbf{R}_i) = -dV/d\mathbf{R}_i\), and are used to construct Newton’s classical equations of motion, which are second order ordinary differential equations. In its global structure, a general MD code typically implements an algorithm to find a numerical solution of a set of coupled first-order ordinary differential equations given by the Hamiltonian formulation of Newton’s second law.\(^16\) The equations of motion are numerically integrated forward in finite time steps using an \(n\)-order predictor-corrector scheme (normally, \(n = 2\) or \(3\)).
The MD code for carbon-based systems involves analytic many-body force field functions, such as Tersoff-Brenner potentials, for C—C and C—H interactions. The Tersoff-Brenner potential is especially suited for carbon-based systems, such as diamond, graphite, fullerenes and nanotubes, and has been previously used in a wide variety of simulation scenarios with obtained results being in a good agreement with experimental observations. The structures and mechanical properties of silicon nanowires have been simulated with Stillinger-Weber potential for Si—Si interactions. Currently, there are no universal analytic many-body force field functions that work for all materials in all possible scenarios. A major distinguishing feature of the Tersoff-Brenner potential for carbon-based systems (including SiC) and Stillinger-Weber potential, for silicon based systems, is that short-range bonded interactions in the Tersoff-Brenner potential are reactive, so that chemical bonds can form and break during the course of a simulation. Therefore, compared to some other molecular dynamics codes, the neighbor list, describing the environment of each atom, includes only few atoms and needs to be updated more frequently. The computational cost of the many-body bonded interactions is relatively high compared to the cost of similar methods with non-reactive interactions with simpler functional forms. As a result, the overall computational costs of both short-range interactions and long-range, non-bonding van der Waals (e.g., Lennard-Jones potential) interactions are roughly comparable. For large-scale atomistic modeling (10^3–10^6 atoms), multiple processors are used for MD simulations, and the MD codes are generally parallelized.

In recent years, several accurate quantum molecular dynamics (QMD) schemes have been developed in which the forces between atoms are computed at each time step via quantum mechanical calculations within the Born-Oppenheimer approximation. The dynamics of ionic positions is still governed by Newtonian (or Hamiltonian mechanics) and described by molecular dynamics. In the most general approach of fully quantum mechanical description of materials, atoms are described as a collection of quantum mechanical particles, nuclei and electrons, governed by the Schrödinger equation, $\hat{H}\Phi([R_0, r]) = E_\omega \Phi([R_0, r])$, with the full quantum many-body Hamiltonian operator $H = \sum \phi_i^2/2M_i + \sum Z_i e^2/|R_i - r| + \sum \phi_i^2/2m_i + \sum e^2/r - \sum Z_i e^2/|R_i - r|$, where $R$ and $r$ are nuclei and electron coordinates. Using the Born-Oppenheimer approximation, the electronic degrees of freedom are assumed to follow adiabatically the corresponding nuclear positions and the nuclear coordinates become thus classical variables. With this approximation, the full quantum many-body problem is reduced to a quantum many-electron problem $\hat{H}[\mathbf{r}]\Psi[\mathbf{r}] = E_\omega \Psi[\mathbf{r}]$, where $\hat{H} = \sum \phi_i/2M_i + \mathbf{V}[\mathbf{R}]$. In the intermediate regimes, for up to few thousand atoms, the tight-binding molecular dynamics (TBMD) approach provides a very good accuracy for both structural and mechanical characteristics predictions. The computational efficiency of the tight-binding method derives from the fact that the quantum Hamiltonian of the system can be parameterized. Furthermore, the electronic structure information can easily be extracted from the tight-binding Hamiltonian, which, in addition, also contains the effects of angular torques in a natural way. In a generalized non-orthogonal TBMD scheme, Menon and Subbaswamy have used minimal number of adjustable parameters to develop a transferable scheme applicable to clusters as well as bulk systems containing Si, C, B, N and H. The main advantage of this approach is that it can be used to find a minimum energy configuration of a nanoscale system under consideration without symmetry constraints applied. The nanomechanics of carbon nanotubes, silicon and silicon carbide nanowires, to be described later, is a multi-scale problem that has been investigated with both atomistic and tight-binding molecular dynamics methods. The main advantage of atomistic MD methods is that these can be used to simulate structures with hundreds of thousands of atoms on a regular basis. The key results of atomistic MD methods, however, are generally subsequently validated with more accurate quantum tight-binding molecular dynamics methods. For larger systems (e.g., consisting of bundles of nanotubes or nanowires and multi-wall nanotubes), even the atomistic MD methods may become excessively computationally extensive and run over weeks on parallel high-performance computing resources. However, a bridge to mechanics of larger size systems is feasible through continuum mechanics based approaches, but such approaches generally neglect all atomic- and molecular-level information that could primarily determine the much-promised novel application capabilities of nanomaterials.

In the intermediate “mesoscopic” (few hundred nanometer) length-scale regime, therefore, CNTs and their derived materials are generally “too large” to be simulated with quantum or atomistic approaches on the regular basis and are “too small” for the direct applicability or even accuracy of the methods based on continuum mechanics. It turns out that currently there are no mesoscopic structure and dynamics methods well suited for nanotubes or nanowires. There have been some attempts to find equivalence between the large-scale “structural mechanics” that is based on beams and struts and the atomic scale “molecular mechanics” based on atoms and bonds, respectively. A preliminary hybrid approach, “molecular structural mechanics,” has been developed. So far it has been applied only for static structural simulations, and it is not clear how much computational efficiency is achieved, when individual atoms and molecules are replaced in the alternative scheme by equivalent but individual struts and beams.
dynamics, and mechanics of nanotubes. The cylindrical shaped nanotube or nanowire is broken into smaller cylindrical segments which interact with each other via a mesoscopic force-field (MFF) function. The form of the MFF function allows for all feasible stress-strain distribution in dynamically distorted or strained cylindrical geometries representing nanotubes or nanowires. In the spirit of full-scale MD simulations for atomistic dynamics of the same systems, the MFF function describing the internal energy of nanotubes has terms representing: (a) stretching interactions determined by the axial deformation of the segments; (b) bending interaction determined by the local transverse curvature; (c) internal breathing function determined by the local radii of each segment; (d) a torsion interaction determined by the torsion angular deformation of the segment; (e) and coupling terms between the stretching-bending; (f) stretching-bending interactions that describe coupling between stretching of two segments adjacent to radial contraction and the local curvature at the segment. The functional forms of different terms are chosen based on the results of experimental investigations and/or atomic-level simulations. In particular, data on the vibrational dynamics of the low-frequency modes of the nanotubes (longitudinal stretching, radial breathing, transverse flexion, and torsional twist) and nanowires, as well as the data on the mechanical response of an individual tube to external loading can be used to find the force constants in the mesoscopic force-field function that controls the dynamics of the system. Analytical functions can be used at small deformations, whereas tabulated values of energies and forces are used to describe complex behavior at large deformations. Both low and high frequency vibrational modes of the carbon nanotubes have been incorporated in this formalism. The model was applied to study free bending vibrations of a model 395 Å long (10,10) SWCNT with initial radii of curvature ≈500 Å. A comparison of temporal strain energy evolution, obtained using MD simulations and MFF approach, is given in Figures 3(a) and (b). To further illustrate the applicability of the method to vibrational mode calculations, in Figures 3(c) and (d), a comparison between the mesoscale MFF dynamics and full atomistic scale MD simulation of the edge of a bent CNT is given. The nanotube was bent in both of these simulations in a similar way, and the velocity of one of the end as a function of time shows an overall good agreement not only for the low frequency phonon modes but also for the high frequency modes. The differences come in for the very high-frequency atomic vibrations, which naturally cannot be incorporated in the coarse-grained mesoscopic dynamics method. Once fully developed in the near future, such approaches will allow for micron-size simulations of the nanotube, nanowire, and composite material systems as well as mechanical systems based on these nanostructures.

3.2. Molecular Dynamics Simulations for Thermal Transport

The simulation studies of thermal transport in nanotubes and nanowires are in the early stages of development. A general review of the recent advances in understanding of the thermal transport properties of carbon nanotubes is succinctly described in Ref. [26]. In the following, we briefly overview the MD-based simulation methods employed for the purposes of thermal conductivity studies in nanotubes and nanowires. The MD simulations of thermal transport are based on the assumption that, at room temperature, the electronic contribution to the overall thermal conductivity is small and the thermal transport occurs mainly through the phonon driven mechanisms. To obtain a simple qualitative understanding of the temperature dependence of thermal conductivity, thermal conductivity is expressed as \( \kappa = (1/3)Cv_\lambda \), where \( C \) is the lattice heat capacity, \( v \) is the average phonon velocity, and \( \lambda \) is the mean free path of the phonons in the system under consideration. In non-metallic crystalline systems, \( v \) is approximately equal to the sound velocity, and, at low temperatures, \( \lambda \) is large but is limited by the surface and boundary scattering events, whereas, at high temperatures, \( \lambda \) is limited by the Umklapp scattering processes. The thermal conductivity as a function of temperature, thus, generally shows a peaking behavior (see below).

The MD simulation approaches to thermal conductivity problem can be divided into two main categories: (1) equilibrium MD methods, which use Green-Kubo formula, and (2) non-equilibrium MD methods, based on forcing temperature gradients (explicitly or implicitly) on the system. A detailed comparison of different MD-based approaches to the thermal conductivity studies, their advantages and shortcomings is given in Ref. [28]. The equilibrium MD approach uses heat current fluctuations to calculate the thermal conductivity via the fluctuation-dissipation theorem. The MD trajectories in the phase space are used to compute the autocorrelation function of the heat flux at a given temperature, which is related to the thermal conductivity by the Green-Kubo formula, given by \( \kappa = V/k_B T^2 \sum_{ij} \langle J_i(0)J_j(t) \rangle dt \), where \( T \) is the system temperature, \( J_i(t) \) is the \( i \)-component of the heat flux, \( k_B \) is the Boltzmann constant, and \( V \) is the volume of the sample under investigation. For nanotubes and nanowires, the \( z \)-axis can be assumed parallel to the tube or wire axis, and in general the heat flux \( J_z \) is given by \( J_z(t) = \sum_i \dot{e}_i + (1/2) \sum_{i,j} \dot{r}_{ij} \langle F_{ij}^z \cdot \bar{r} \rangle \), where \( \dot{e}_i \) is the total energy of the system under consideration that includes the many body potential energy contributions discussed above. The advantage of this approach is that simulations are done under equilibrium conditions at any given temperature without imposing any driving forces, such as temperature gradient or fictitious force as in the non-equilibrium MD approach. Unfortunately, as the upper limit of the integration indicates, very long simulation times (5 × 10^7 to
5 × 10⁶ time steps) are required to ensure the convergence of the flux–flux autocorrelation function. Recent examples of equilibrium MD simulations of thermal conductivity in silicon-based materials and in carbon nanotubes have been described in Refs. [28] and [29], respectively.

The non-equilibrium MD approach involves applying a temperature gradient across the system under investigation, as in experimental conditions, via either a fictitious velocity exchange term[10,11] or a velocity scaling method[32–34] which results in an internal heat flux to counter the effects of the imposed temperature gradient or the external force on the system. It turns out that for covalently bonded materials, such as carbon nanotubes or silicon nanowires, the velocity exchange approach may not be suitable for computing thermal conductivity.[25] Here, we briefly describe only the velocity scaling approach introduced recently for carbon nanotube based systems.[32–34] The velocity scaling procedure involves imposing a temperature gradient by setting the temperature at the hot slab to \( T_H + \Delta T \) and that of the cold slab to \( T_C - \Delta T \), where \( T_E \) is the equilibrium temperature. The temperatures are maintained at these values throughout the simulations by scaling the velocities of each atom \( i \) in the cold and hot slabs from initial value of \( v_i \) to final \( v_i' \) at each time step. The amounts of added (or subtracted) kinetic energy to the slab of interest are:

\[
\Delta E = \left( \frac{1}{2} \right) \sum_{i=1}^{N_i} m_i (v_i'^2 - v_i^2),
\]

where \( N_i \) is the number of atoms in the slab. The energy flux, \( J_E \), is then given by:

\[
J_E = \langle \Delta E \rangle / 2\Delta t \kappa = -\kappa (2\Delta T / (L/2)),
\]

where \( \langle \Delta E \rangle \) is the average energy per time step, \( \Delta t \), \( \kappa \) is the thermal conductivity, \( L \) is the length of the simulation region, and \( 2\Delta T \) is the temperature difference between the cold and hot slabs in the system. Details of the simulations are described elsewhere.[26,32–34] It should be noted that, within this framework of this method, one has to take into account

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Fig. 3. Strain energy density (per atom) distribution of free bending vibrations of a 395 Å long (10,10) SWCNT with the initial radius of curvature of 500 Å, obtained via: (a) MD simulations with Tersoff-Brenner potential; (b) mesoscopic MFF model. The strain energy density is color-coded: light blue color corresponds to zero energy density and red color corresponds to 0.002 eV/atom. Also shown in the figure is velocity of an end part the SWCNT as a function of time, obtained via: (c) MD simulations with Tersoff-Brenner potential; (d) mesoscopic MFF model. Reprinted with permission from [25], L. Zhigilei et al., Phys. Rev. B 71, 165417 (2005). © 2005.
size effects and make sure the length of simulation box is greater than the mean free path of the phonons, and the system remains in the linear response region. In many cases one can simulate only very small sample sizes and the imposed temperature gradients can lead to deviations from linear response. To account for these effects, simulations are usually done for samples of different length and, then, extrapolated to determine thermal conductivity for a sample infinite length or micron scale.

4. COMPUTATIONAL NANOMECHANICS OF NANOTUBES AND NANOWIRES

The earliest atomistic simulations of mechanical properties of carbon nanotubes have predicted unusually large Young’s modulus [of up to 5 Tera Pascal (TPa)] or 5 times larger than the modulus of diamond, and elastic limits of up to 20–30% strain before failure. These predictions led to the proposition of using nanotubes as super-strong reinforcing fibers with few orders of magnitude higher strength and stiffness than those of any other material discovered so far. Subsequently, more accurate simulation studies employing TBMD methods and ab initio density functional total energy calculations with realistic strain rate, temperature dependence, and nanotube sizes have provided more realistic values of ≈1 TPa for the Young’s modulus and 5–10% elastic limit for the tensile strain before failure. The experimental and simulation-based studies of the nanomechanics of silicon and silicon carbide nanowires are very few and rather recent. In this section, we focus on the mechanical properties of individual single- and multi-wall carbon nanotubes, plastic behavior of nanotubes under realistic strain rates and temperatures.

4.1. Elastic Moduli of Carbon Nanotubes

The moduli of the carbon nanotubes measure the strength and stiffness against small uniaxial tensile and compressive strains or non-axial bending and torsion strains. Contributions to the superb mechanical characteristics of carbon nanotubes come mainly from the strength of the in-plane covalent \(C=C\) bonds in graphene sheet and facile, out-of-plane deformations of the structure. Using the Tersoff and Tersoff-Brenner potentials, Robertson et al. showed that the elastic energy of a SWCNT scales as \(1/R_y\), where \(R\) is the radius of the tube. This is similar to the results deduced from the continuum elastic theory. For uniaxial strains, \(k_{xy}\), the Young’s modulus of a SWCNT is defined as \(Y = (1/V)(\partial^2 E/\partial x^2)\), where \(E\) is the strain energy and \(V\) is the volume of the nanotube. Initial computational studies using the Tersoff-Brenner potential reported the value of Young’s modulus to be as high as \(\approx 5.5\) TPa. This was mainly due to a very small value of CNT wall thickness (≈0.06 nm) used in this study. In many recent studies, the values of the Young’s modulus have been reduced slightly, so that they are close to the experimental values.
Table I. Summary of Young’s modulus values of carbon nanotubes from theoretical studies is given. In the table, $Y$ is Young’s modulus and $h$ is the wall thickness used in different studies.

<table>
<thead>
<tr>
<th>Method</th>
<th>Molecular dynamics with Tersoff-Brenner force field</th>
<th>Empirical force constant model</th>
<th>Non-orthogonal tight-binding</th>
<th>$Ab\ initio\ DFT^{41}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$h$</td>
<td>0.06 nm</td>
<td>0.34 nm</td>
<td>0.34 nm</td>
<td>0.34 nm</td>
</tr>
<tr>
<td>$Y$</td>
<td>SWCNT: 5.5 TPa</td>
<td>SWCNT: 0.97 TPa</td>
<td>SWCNT: 1.2 TPa</td>
<td>SWCNT: 0.8 TPa</td>
</tr>
</tbody>
</table>

works, this discrepancy has been corrected, and the van der Waals radius of $C$ atoms, used to define the spatial extent of the atoms and the single wall thickness, comes to be $\approx 0.34$ nm. Using empirical force constant, ab initio DFT, and non-orthogonal TBMD-based descriptions of interatomic forces, the Young’s modulus of a single-wall nanotube is found to be about $0.1$ TPa. The Young’s modulus of a wide variety of carbon (and non-carbon) nanotubes as a function of tube diameter, obtained in Hernandez et al. study, is shown in Figure 4(a). In Ref. [41], the authors introduced a new measure of stiffness for a single-wall nanotube, $Y$, which is independent of shell thickness. This quantity relates to the Young’s modulus through the $Y = \frac{Y}{R} \Theta R$, expression, where $\Theta R$ is the CNT wall thickness. The main virtue of this approach to stiffness quantification is that it allows one to avoid usage of $\delta R$ value, which cannot be considered as a well-defined quantity for the nanometer-scale tubes. Another recent work by Harik examines the validity of continuum elasticity theory for nanomechanics and suggests that small and large diameter nanotubes need to be described with different approximations, such as solid rod model for small diameter nanotubes and the shell model for large-diameter nanotubes. The values of the axial Young’s modulus of SWCNTs, simulated with different techniques, in comparison with experimental values are listed in Tables I and II.

The bending stiffness of a SWCNT is defined as $(1/L)(dE/dC)$, where $E$ is the total strain energy, $L$ is the length, and $C$ is the curvature of the bent nanotube, which is related with the bending angle, $\theta$, as $C = \Theta / L$. From the elastic theory of bending of beams, the strain energy of a bent nanotube can be expressed as $E = 0.5\Theta^2 L / \Theta C^2 d$, where $Y$ the Young’s modulus of the SWCNT, and $h$ is the thickness of the wall. The integral is taken over the circumference of the nanotube, and $t$ is distance of atoms from the central line (or the bent axis) of the tube. From this expression, the bending stiffness $K$ is found to be equal to $Yh (\pi R^3)$, and scales as cubic of the radius of the tube. Results of the molecular dynamics simulations with the Tersoff-Brenner potential, plotted in Figure 4(b), show that force constant scales as $\sim R^2$, thus being in good agreement with scaling predicted by the continuum elasticity theory. The torsion stiffness of a SWCNT is defined as $K = (1/L)\left(\frac{d^2 E}{d\Theta^2}\right)$, where $E$ is the total strain energy and $\Theta$ is the torsion angle. The shear strain is related with torsion angle as $e = R\Theta / L$, where $R$ is the radius of tube and $L$ is its length. From continuum elasticity theory, the total strain energy of a cylinder can be written as $E = (1/2)G^* \int \int e^2 dV$, where $G$ is shear modulus of the tube. The torsion stiffness, thus, is related to $G$ as $K = (1/L)(d^2 E/d\Theta^2) = G(2\Theta h)R^3 / L^2$, where $h$ is the thickness of the wall of the nanotube. The torsional stiffness of several armchair-type and zigzag-type CNTs has been recently studied using Tersoff-Brenner potential. It was shown that the magnitude of torsional stiffness is about $0.1 eV A^{-1} rad^{-2}$, for $(5, 5)$ and $(10, 0)$ CNTs. The dependence of the force constant and torsion stiffness on the radius of tube is found to be $K \propto R^{10.1}$, for tube diameter greater than $0.8$ nm. The radius dependence of the torsion force constant is illustrated in Figure 4(c). This is also in good agreement with the predicted in the framework of continuum elasticity theory cubic dependence. The shear modulus of SWCNTs is found to be around $0.3$ TPa and is not strongly dependent on diameters for nanotube diameter greater than $0.8$ nm. For small diameter tubes, such as $(5, 5)$ nanotubes, the shear modulus deviates from the continuum elastic theory description.

The high strength of carbon nanotubes has been verified by several experimental studies. Thus, Treacy et al. investigated the Young’s modulus of MWCNTs by measuring the thermal vibrations and found $Y$ to be about $0.18 \pm 1.4$ TPa. Subsequent studies by Wong et al. performed on MWCNTs, reported the Young’s modulus of $1.28 \pm 0.59$ TPa. Furthermore, Krishnan et al. performed a study of stiffness of SWCNTs, and found an average Young’s modulus to be about $1.25$ TPa. This is close to the experimental results obtained by Salvetat et al., where $Y$ was found to be about $1$ TPa.

Table II. Summary of Young’s modulus values of carbon nanotubes from experimental studies is given. The definitions of $Y$ and $h$ are the same as in Table I.

<table>
<thead>
<tr>
<th>Method</th>
<th>Thermal vibrations</th>
<th>Restoring force of bending</th>
<th>Thermal vibrations</th>
<th>Deflection forces</th>
</tr>
</thead>
<tbody>
<tr>
<td>$h$</td>
<td>0.34 nm</td>
<td>0.34 nm</td>
<td>0.34 nm</td>
<td>0.34 nm</td>
</tr>
<tr>
<td>$Y$</td>
<td>SWCNT: 1.8 $\pm$ 1.4 TPa</td>
<td>SWCNT: 1.28 $\pm$ 0.59 TPa</td>
<td>SWCNT: 1.2 TPa</td>
<td>SWCNT: 1.0 TPa</td>
</tr>
</tbody>
</table>
4.2. Plastic Deformation and Yielding of Nanotubes

It is well established by now that subjected to large strains CNTs undergo two different kinds of structural changes. First, under uniaxial compression, nanotubes exhibit structural instabilities resulting in sideways buckling, but the deformed structure remains within the elastic limit. Second, under large strains, bonding rearrangements or transitions occur giving rise to permanent damage, plastic deformation or yielding of nanotubes. Thus, it was found that single-wall nanotubes might acquire a non-uniform “fins-like” structure under a large compressive strain. The structure is illustrated in Figure 5(a). The sideways displacement or buckling of tubes occurs for even larger strain and contributes towards the relief of strain energy from the “fins-like” structure, but the tubes remain super-elastic for more than 20% compressive strains. Experiments have observed sideways buckling feature in compressed multi-wall nanotubes in polymer composite materials. Yet another mode of plastic deformation of compressed thin nanotubes is also observed in the same experiments. In this mode, a tube remains essentially straight but the structure locally collapses. Using TBMD method, Srivastava et al. have found that, within Euler buckling length limitation, an (8,0) carbon nanotube locally collapses at 12% compressive strain, as shown in Figure 5(b). The local plastic collapse is due to a graphitic (sp²) to diamond-like (sp³) bonding transition at the location of the collapse and the release of excess strain in the remaining uncollapsed section. The released strain in the uncollapsed section drives the local collapse with a compressive pressure being as high as 150 GPa at the location of the collapse. The influence of changes in the chemical nature on the nanomechanics and the plastic behavior of nanotubes have been recently investigated by considering the structure and plasticity of boron-nitride (BN) nanotubes. The TBMD and ab initio total energy calculations show that, due to BN bond rotation effect, BN nanotubes, under similar conditions to equivalent carbon nanotubes, show anisotropic response to the uniaxial strains (i.e., the nanotube buckles anisotropically towards one end, when uniformly compressed at both ends).

For the case of tensile strain, Nardelli et al. studied the formation of Stone-Wales bond-rotation-induced defects as the cause for the plastic deformation of nanotubes. This mechanism is explained by formation of heptagon-pentagon pair defects in the wall of nanotubes, as illustrated in Figure 6. The formation energy of such defects is decreased with the applied strain and is also dependent on the diameter and chirality of the nanotube under consideration. At high temperatures, plastic flow of a material proceeds through the motion of defects, leading to eventual necking and breaking of nanotubes. Subsequently, Zhang et al. have studied the plastic deformations of SWCNTs, induced by the Stone-Wales dislocations, under tensile strain and found that the SW defects can facilitate the release of the strain energy in the system. It was noted that SW defects form more favorably on an armchair nanotube than on a zigzag ones because the rotation of the C—C bond can compensate for more tensile strain along the axis in the former case. The yielding of the nanotube, initiated by the formation of SW defects in the lattice, is sensitive to the existing temperature dependent strain in the nanotube and the rate at which the nanotube is loaded in simulations. This dependency and comparison with representative experimental studies are described next.

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Fig. 5. Shown in the figure is the illustration of the mechanism of local plastic collapse of the CNT structure, driven by graphitic-like to diamond-like bonding transition at the location of the collapse, while the CNT remains essentially straight. Reprinted with permission from [42], D. Srivastava et al., Phys. Rev. Lett. 83, 2973 (1999). © 1999.

Fig. 6. Shown in the figure is the configuration of a Stone-Wales defect that initiates the plastic collapse of a CNT under tensile strain. Reprinted with permission from [57], C. Y. Wei et al., Phys. Rev. B 67, 115407 (2003). © 2003.
4.3. Strain-Rate and Temperature Dependence of Yielding of Nanotubes

The breaking of carbon nanotubes under tension through the formation of SW defects is inherently a kinetic phenomenon and a more relevant quantity is the activation energy or barrier to the formation of the SW-type defects in the nanotubes under tension. The activation barriers have been investigated via the static total energy simulations, the TBMD, and _ab initio_ methods for in-plane rotation of the C—C bond, for both strained and unstrained carbon nanotube cases. The static in-plane activation barriers are found to be about 10 eV, in nanotubes with no strain, while the value drops to about 5–6 eV, for tensile strain magnitude in the range 5 to 10%.\(^{2,4}\) Using simple transition state theory, the breaking strain of SWCNTs under tensile stretching is predicted to be about 17%, which is smaller than the earlier predictions for breaking strain of about 30%, reported by the same group,\(^{15}\) but still much larger than the breaking strain observed in experiments on ropes or bundles of SWCNTs and on MWCNTs.\(^{34-36}\) The experimentally measured breaking (or yielding strain) of a rope or bundle of SWCNTs has been found to be about 5–6%,\(^{34,35}\) whereas similar measurements on MWCNTs show the breaking strain to be about 12% or lower.\(^{36}\)

In simulation studies, the yield strain was found to be very sensitive to both the strain rate and the kinetic temperature. At the strain rate of \(\approx 10^{-4}\) ps\(^{-1}\) the yield strain can vary between 15%, at low temperatures, and 5%, at high temperatures [see Fig. 7(a)]. Extensive MD simulations, performed over wide range of temperature variations, with strain rate changing by three orders of magnitude, have been carried out recently and revealed a complex dependence of the yield strain on the temperature and strain rate.\(^{54}\) For example, yield strain of a 6 nm long (10, 0) single-wall nanotube at several temperatures and strain rates varying between \(10^{-3}\) to \(10^{-5}\) ps\(^{-1}\) were simulated and are shown in Figure 7(b). The yield strain at low temperatures and slow strain rates are significantly higher than the yield strain for high temperatures and higher strain rates. Moreover, a linear behavior of the yield strain as a function of strain rate at a given temperature indicates that the tensile yielding is a kinetic (or activation barrier driven) process. A strain rate and temperature dependent model of yielding for SWCNTs, within the transition state theory (TST) based framework, has been derived, which gives the yield strain as \(e_y = \frac{E_y}{YV} + (kT/YV)\ln(Ne/nz_0)\), where the yield strain, \(e_y\), depends on the activation volume, \(V\), force constant, \(K\), temperature, \(T\), time-averaged dynamic activation energy, \(E_y\), the number of activation sites, \(N\), the intrinsic strain rate, \(\dot{\epsilon}_0\), and the strain rate, \(\dot{\epsilon}\). The tensile yielding or breaking of carbon nanotube is considered to be through a number \(N\) of successive SW defect formations. It turns out that some of the intrinsic parameters, such as dynamic activation energy, activation volume, and intrinsic strain rate can be fitted from the MD simulation data, as shown in Figure 7(b), while the remaining parameters such as the temperature, number of possible activation sites, and strain rates can be chosen to reflect the experimental reality. The room temperature yield strain of a 1 micrometer long (10, 10) carbon nanotube comes out to be about 9%, for a realistic and experimentally feasible strain rate of 1% per hour.\(^{57}\) This compares very well with the yielding strain of 6–12%, observed in experiments on bundles of SWCNTs and MWCNTs.\(^{54-56}\) The other details of the
model and MD simulation technique are described in Ref. [57]. It is worth noting that the main advantage of the above model is that one could directly compute the activation energy for yielding defect formation and get the yield strain from the above model. Within the simulation and experimental error bars, this model is in very good agreement with experimental observations reported up to date. Moreover, the model has been extended to MWCNTs [schematically shown in Fig. 8(a)], and predicts that the MWCNTs are stronger than the equivalent single-wall nanotubes by couple of percent of yield strain at experimentally feasible strain rate and temperatures, as shown in Figure 8(b).[58]

Fig. 8. The yielding strain of a multi-wall CNT through: (a) a model of a double wall CNT, where the contact is made only on the outermost wall; (b) The yielding strain of the double-wall (20,0)(10,0) CNT is shown as a function of strain rate (solid circle and solid line) and compared with (20,0) CNT (diamond and dashed line). Open circle, open triangle, and open square correspond to (8,0)(20,0), (12,0)(20,0), and (5,5)(10,10) MWCNT, respectively. The arrow in the left-hand-side marks the crossover point. The strain rate in the top axis corresponds to \( T = 2400 \text{ K} \), while the bottom axis corresponds to \( T = 300 \text{ K} \). The arrows at the top axis show strain rates of 1% per hour and 1% per year, respectively. The experimentally feasible strain rate and yielding strain is indicated with the elliptical area. Reprinted with permission from [58], C. Y. Wei et al., Appl. Phys. Lett. 82, 2512 (2003). © 2003.

5. NANOMECHANICS AND PLASTICITY OF NANOWIRES

5.1. Silicon Nanowires

Understanding the nanomechanical and thermal transport properties of silicon nanowires is important for their potential use in nanoscale electromechanical resonator, sensor, and thermal management devices. The nanomechanical properties of thick silicon nanowires (with diameter larger than 10–20 nm) are expected to be similar to the corresponding bulk silicon structures, which have been well reported over the years. In this subsection, the focus is on the nanomechanics of thin (diameter less than 10 nm) nanowires for which (a) the surface to volume ratio is expected to be large, and (b) there maybe more than one possible crystalline arrangement for the possible nanowire structure. Recently, the structure, stability, and nanomechanics of tetrahedral and cage-like silicon nanowires have been extensively investigated using molecular dynamics and energetics simulations, using Stillinger-Weber many-body potential[59] for the Si–Si interactions. The initial configurations of nanowires are obtained by carving out the corresponding structures from bulk silicon. The cage-like silicon nanowires are carved out from a Si clathrate structure consisting of a simple cubic (sc) lattice with 46-atom basis.[25] This is known to be one of the most stable clathrate forms for Si. The properties of all studied nanowires are summarized in Table III. The cohesive energy of this clathrate structure is found to be \( \approx 4.29 \text{ eV/atom} \), within the Stillinger-Weber approximation for interatomic potential. The properties of the nanowires are summarized in Table III. The value for the equivalent diamond-lattice structure nanowire, by comparison, is \( \approx 4.34 \text{ eV/atom} \). In the 3 to 5 nm diameter range, the energies of the formation of the tetrahedral (T) and cage-like (C) silicon nanowires should be comparable to each other.

For determining the mechanical properties, the T-type and C-type nanowires were loaded dynamically with uniaxial compression, tension, and bending stresses. Details of the simulation procedure are described elsewhere.[59] The changes in the total energy with respect to the energy of the initial strain free configurations provide the strain energy as a function of strain. The strain energy behavior is shown in Figure 9, in the case of tensile and compressive loading. The Young’s modulus for compression and tension, as defined in Ref. [36], was computed for small strains and listed in Table III. In all considered cases, we find that, for small axial strain, the Young’s modulus of T-type nanowire is about 5–6% more than the axial Young’s modulus of C-type nanowire. This is expected because, for nanowires of similar cross sections, the diamond T-type lattice structure is supposed to be the strongest and stiffest. However, the difference with respect to the more open-cage C-type nanowire structure is not large, when comparison is made for the normalized (modulus/density) values [59,16 vs. 47.75 in units
of GPa/(g cm\(^{-2}\)); see Table III. The onset of plasticity in the nanowire structures is defined by the formation of over-coordinated silicon atoms.

The microstructure evolution of Si nanowires under compressive loading is illustrated in Figure 10, for the C-type end T-type nanowires. The microstructures of T-type are shown for compressive strain values of 0.0%, 6.4%, 8.7%, 11.0%, and 20.93% (beginning of plastic collapse). The microstructures of C-type wires are shown for 0.0%, 7.96%, 8.67%, 9.03%, and 9.57% (beginning of plastic collapse), correspondingly. As can be observed in Figure 10, under uniaxial compression, the formation of fivefold-coordinated atoms occurs at \(\approx 4.16\%\) strain, in the middle region of the T-type nanowire. The formation of fivefold-coordinated atoms accelerates with the increase in applied compressive strain magnitude and, at \(\approx 5.8\%\) strain value, the appearance of atoms with coordination number greater than five is observed. At 17.0% strain value, all atoms (except those on the surface and atoms held fixed at both ends) have coordination in excess of four, and the buckling of the wire occurs at 20.93% strain. For compressive loading, the elastic limit is concurrent with the appearance of fivefold-coordinated atoms, and is found to occur at \(\approx 4.3\%\) strain. In the case of C-type nanowire, fivefold-coordinated atoms make their first appearance at \(\approx 7.96\%\) strain value. The elastic limit for the C-type nanowire is found to be \(\approx 8.05\%\). At larger strain values, the over-coordinated region rapidly expands inward from the surface. The buckling of C-type nanowire occurs at \(\approx 9.03\%\) strain. The microstructure evolutions of Si nanowires under compressive loadings are illustrated in Figure 10, for the C-type end T-type structures.

Under tensile strain, fivefold-coordinated atoms first appear at \(\approx 10.26\%\) strain value for the T-type nanowire. At \(\approx 11.5\%\) tensile strain, a second region of multi-coordinated atoms appears in the nanowire. Upon further stretching, buckling occurs, at \(\approx 11.92\%\) strain. Elastic limit coincides with the onset of multi-coordinated atoms for the T-type nanowire. For the C-type nanowire,
five-fold-coordinated atoms make their first appearance at \( \approx 9.03\% \) strain. The elastic limit is reached at \( \approx 11.8\% \) and buckling is observed at \( \approx 12.7\% \) strain magnitudes, respectively.

The total energy with respect to the energy of the initial strain-free configurations as a function of bending strain is shown in Figure 11, for the C-type and T-type nanowires. The bending stiffness, as defined in Ref. [36], was computed for small strain magnitudes and is listed in Table III. The coordination numbers of the nanowire atoms was monitored in the process of loading for both studied types of nanowire. An illustration of plastic deformation under bending in the C-type (lower panel) and T-type (upper panel) Si nanowires is given in Figure 12. The evolution of microstructure of the nanowires during loading can be described as follows. For T-type nanowire, the onset of fivefold-coordinated atoms occurs at bending angle \( \approx 0.21 \) rad. Fivefold-coordinated atoms appear almost symmetrically with respect to the ends of nanowire. In going from a bending angle of \( \approx 0.21 \) rad to \( \approx 0.25 \) rad, the total number of fivefold-coordinated atoms changes only slightly but they move from the ends of the nanowire towards its center. At the bending angle of \( \approx 0.26 \) rad, there is a significant increase in the number of fivefold-coordinated atoms. The buckling of the nanowire structure occurs at the bending angle of \( \approx 0.53 \) rad. The elastic limit is, thus, found to be at \( \approx 0.21 \) rad. For the C-type nanowire, both the onset of fivefold- and greater than fivefold-coordinated atoms occurs for the same value of the bending angle (\( \approx 0.57 \) rad). This is strikingly different from the case of the T-type nanowire. Another interesting difference, worth noting here, is that the undamaged regions remains almost perfectly regular despite changes in the bond lengths and the bond angles. At the bending angle of \( \approx 0.67 \) rad, fivefold-coordinated atoms make their first appearance in the contracted region of the wire. When buckling finally occurs, it happens symmetrically from both sides. Elastic limit for the C-type wire is reached at the bending angle of \( \approx 0.65 \) rad. This is more than three times the corresponding value for the T-type nanowire, indicating greater structural integrity for the C-type wire under bending strain. Since many practical applications of nanowires are based on their ability to restore to their original shape after loading, the important advantage of the C-type wire is evident.\(^{59} \)

The strain-rate effects may considerably alter the presented above pictures of the micro-mechanical response of nanowires and their failure under threshold loading. The influence of these effects on carbon nanotube systems has been discussed in the above. On the other hand, in the works reported to date on the semiconductor nanowire systems, the simulations have been performed in the adiabatic approximation. It is quite clear, however, that the issues of strain-rate dependence of the response properties must be addressed to obtain a complete picture of mechanical behavior of nanoscopic wire systems. This represents a future challenge to both the theory and experiment.

5.2. Silicon Carbide Nanowires

Silicon carbide nanometer-scale wires possess superior mechanical and thermal properties, which is why they are considered as potential building blocks for applications in the high-frequency and high-temperature electronic and micromechanical devices. In this subsection, we overview the results of recent studies of nanomechanical properties of silicon carbide nanometer-scale wires. The mechanical response characteristics of \([111]\)-oriented 3C-SiC nanowires with different diameters, ranging from \( \approx 0.89 \) nm to \( \approx 3.56 \) nm, were investigated via molecular dynamics simulations using the Tersoff interatomic potential.\(^{60} \) A detailed description of the methodology of
of tensile loading, the nanowires undergo homogenous elongation, for strains not exceeding \( \approx 18\% \). For larger strains, disintegration, closely resembling the brittle fracture, occurs in each of the considered diameter case. The regions, where the fracture occurs, remain localized to within two to three atomic planes. In the case of compression, the strain energy does not depend appreciably on the diameter of the nanowire, for \( \varepsilon_{zz} \leq -5\% \). In the limit of large strains, a size-dependent deformation behavior is observed, as illustrated in Figure 14. As can be seen in the figure, the nanowire with small diameter buckle under compression. The region experiencing a considerable atomic rearrangement is located around point “B.” In this region, a presence of low-coordinated atoms and broken bonds are observed. The region around point “A” is under large compressive stress. Consequently, atomic rearrangements in this region take place so that the local density can be reduced. As the diameter of the nanowire increases (at a fixed length), the buckling mode and the mechanism of strain relaxations both undergo changes. The mechanism of response of large diameter nanowire \( (d_w = 3.56 \text{ nm}) \), near the elastic limit, is illustrated in Figure 14. As can be observed in the figure, the nanowire preserves its original geometry; however, regions with increased defect number density and loss of crystalline structure develop near top and bottom of the nanowire. In the deformed regions, both under- and over-coordinated atoms are present. The observed size-dependence of the response can be interpreted in terms of the mechanism of Euler-type buckling. Indeed, the
modes of buckling are defined by both the length and diameter of the nanowire. The threshold stress for buckling instability development follows $\sim 1/IL^2$ dependence with nanowire length, and proportional to the moment of inertia, $I_a \sim d^4_w$. Consequently, the Euler buckling instability is expected to take place also for nanowires of large diameters, if their lengths are increased correspondingly. Indeed, the threshold strain for the Euler instability development, for nanowire with $d_w = 0.89$ nm, can be estimated as $\approx 0.2\%$. Thus, nearly in the whole region of strain variations, the nanowires undergo buckling and the transitions between different buckling modes are allowed. The buckling of the thinnest wire ($d_w = 0.89$ nm), illustrated in Figure 14, occurs at $\approx 1\%$ strain, which is much larger than the value predicted by the continuum elasticity theory. This can be understood as a failure of the continuum elasticity in the limit of small nanowire diameters. On the other hand, the nanowire with $d_w = 3.56$ nm is expected to buckle for the applied strains of $\approx 6.0\%$. Hence, during loading it reaches structural instability threshold before the buckling instability. It should be noted that the modes of buckling, we observed in the simulations (modes 1 through 3), are not the only possible. There exist an infinite number of buckling modes, depending on the applied strain and relation between geometrical parameters of the nanowire. Thus, the Euler buckling mode was observed also for the $d_w = 1.42$ nm nanowire. As described above, the Euler buckling has also been observed for carbon nanotubes under compressive strain (see Section 4.2). Based upon our study of SiC nanowires under compression, one can conclude that nano-mechanical properties of small diameter nanowires are comparable to those of carbon nanotubes of similar diameters. However, one important difference between the two cases is worth noting. In the case of SiC nanowires, the buckling causes the formation of plastic bonding rearrangements in certain local regions, whereas, in the case of carbon nanotubes, the elastic response behavior persists even under the non-linear Euler buckling of a CNT. The mechanical response under bending strain has been studied for the same set of nanowires as above. The loading was performed in steps with an angle increment being $\approx 0.3$ rad. The elastic energy of the loaded nanowires, $E_w$, was measured at each step of loading. Shown in Figure 15 is the strain energy of bended nanowires, plotted as a function of the bending angle, $\beta$. Similar to the cases of tension and compression, the loading curve is quadratic for small values of $\beta$ and, consequently, bending modulus can readily be deduced from simulation data using $\kappa = (N/L)(\partial^2 E_w/\partial \beta^2)$ relation, where $L$ is the length of SiC nanowire, $\beta$ is the bending angle, $E_w$ is the normalized per atom elastic energy, and $N$ is total number of atoms in the nanowire. As the scaling analysis shows, the bending rigidity vary with the nanowire diameter following a power law, $\kappa \sim d^2_w$, and the power-law exponent $\gamma \approx 3.52$. It is worth noting that this result is in good correspondence with the continuum elasticity theory based analysis, where $\sim d^4_w$ behavior was predicted. In the limit of small diameters, deviations from the above scaling behavior are observed. For instance, for nanowire with $d_w = 1.5$ nm, the bending rigidity is much larger as compared with one predicted by the scaling relation. For large bending strain magnitudes, non-linear effects in the stress-strain behavior become significant, leading to considerable deviations from the linear elasticity predictions. When the bending angle exceeds critical $\beta_c$, the strain energy behavior resembles that of the plastic flow; i.e., the strain energy becomes nearly constant function of the strain. This behavior holds for nanowires with relatively small diameters. For nanowires with $d_w$ exceeding $\approx 3.0$ nm, the onset of the structural instability manifests itself by changes in the transition to a slower rate of increase in the elastic energy. The angles at which this transition takes place are shown in Figure 15 by arrows. Similar transition was observed in the case of Si nanoscopic wires, discussed in Section 5.1. Further loading leads to a transition to the regime resembling the plastic flow as in the case of small diameter nanowires. As scaling analysis have shown, $\beta_c$ scales as a power law with the nanowire, $\beta_c \sim d^2_w$, and the power-law exponent $\xi \approx -1.0$. As in the case of silicon nanowires (see Section 5.1), the micro-structural analysis of nanowires during bending was performed by monitoring the number of nearest neighbors after each loading step. An atomically resolved configurations of two nanowires with $d_w = 0.89$ nm and $d_w = 3.56$ nm, approaching the limit of structural stability are presented in Figure 16. The structural rearrangements, taking place in the sub-critical regime of adiabatic bending, are similar for all considered nanowire diameters. In the limit of large bending angles, significant rearrangement of the nanowire atoms takes place in the region near center of each nanowire, as shown in Figure 16.
region is expected to bear largest local strains. The atoms around point “B” experience compressive strain of large magnitude, and corresponding local rearrangement of the atoms occurs as a means of partial stress relaxation. In the region around point “A,” large gradients of the tensile stress develop, which causes bond breaking, when loading reaches a certain (nanowire diameter dependent) magnitude. The region involved in the plastic deformation is rather small, being localized within several atomic planes around point “A.” Upon further loading, a complete failure of the nanowire occurs at this region. The failure in the over-critical regime of loading closely resembles brittle fracture. Note that, except for small volumes around point “A” and “B,” no plastic behavior was observed to develop during bending. This is different from the results obtained on Si nanowire systems (see Section 5.1). Similar to the case of silicon nanowires, the mechanical properties of silicon carbide nanoscopic systems have been studied in the adiabatic approximation. Thus, the issue of strain-rate dependence of micro-mechanical properties of SiC nanowires was not included into consideration. To further advance our understanding of the mechanical behavior of the nano-scale systems, a study of the strain-rate dependence of the mechanical response and failure must be performed.

6. COMPUTATIONAL THERMAL TRANSPORT IN NANOTUBES AND NANOWIRES

In the preceding sections, we discussed the elastic properties of carbon nanotubes and nanowires as well as mechanism and rate of the failure under applied external loads. In the following, the focus is on the vibrational and thermal properties of CNTs and Si nanowires. The zero-temperature phonon spectra (or dispersion relations) describe the energy and behavior of the possible vibrational modes of the system. The thermal transport can be computed either by summing over all contributions to the energy transport from an individual single-phonon or multi-phonon processes or directly by MD simulations. In MD simulations at a given temperature, all single- and multiple-phonon processes are excited in a natural way, and it is possible to enforce the thermal energy flux in the system from a hot region to a cold one. The focus of this section is not on the comparison and contrast among different methods, used to compute thermal energy transport under equilibrium and/or non-equilibrium conditions, but rather on the thermal transport through nanotube and nanowire based materials under different conditions.

6.1. Vibrational Phonon Modes in CNTs

The zero-temperature vibrational spectra of any newly discovered material are generally very useful for characterization purposes. The simulated spectra can be used to identify and assign the peaks in the resonance Raman experiments. The simulated spectra, in comparison with experiments, not only provide the basic and original characteristics of the nanomaterial under investigation but also the characteristic changes in the structural properties of the material as a function of the physical or chemical modifications. Given interatomic forces for a given material system, the vibrational (phonon) spectrum is obtained by constructing and diagonalizing dynamical matrix from position dependent interatomic force constants. The eigenvalues of the dynamical matrix give the frequency of vibrations, while the corresponding eigenvectors reflect the nature of the corresponding modes of the vibration for atoms within a unit cell. The accuracy of the computed phonon spectra at zero temperature obviously depend on the accuracy of the interatomic forces, used in constructing the dynamical matrix. Many studies on the zero temperature vibrational or phonon spectra of carbon nanotubes, using the ab initio density functional calculations, TBMD method, and harmonic spring constants satisfying Hooke’s law, have appeared in the literature. In Ref. [62], the frequencies of the low-lying vibrational modes of a (5,5) carbon nanotube, computed using different interatomic force field functions, are compared and deformations of the shape of the nanotube, corresponding to these low-lying vibrational modes, are described. The agreement between the experimental peaks and zero-temperature vibrational peaks is generally good, because only the configurations at or very close to equilibrium structures are investigated. On the
other hand, the dynamics of a carbon nanotube in thermal equilibrium at a non-zero temperature is rather sensitive to the choice of interatomic interaction potential including the anharmonic part, because the atomic displacements far from equilibrium positions are also sampled during the dynamical evolution of the system. The room-temperature \( T = 300 \text{ K} \) phonon density of states and vibrational amplitudes (radial breathing modes) have been computed recently.\textsuperscript{69} The spectra were simulated through Fourier transform of temperature dependent velocity autocorrelation functions, computed from MD trajectories using Tersoff-Brenner potential for C–C interactions.\textsuperscript{13–14} A good agreement with the zero-temperature phonon spectra, computed with higher accuracy \textit{ab initio} DFT and tight-binding methods,\textsuperscript{65–67} was obtained. Additionally, the line-width of the computed spectra provides temperature dependent life and correlation time of the phonon excitations involved. The spectra were also used to assign the low frequency Raman modes of carbon nanotube bundles (see Ref. [69] for further details).

6.2. Thermal Conductivity of CNTs

The field of thermal transport simulations in the systems of carbon nanotubes and CNT-based materials are in the early stages of development. To account for the ballistic nature of phonon transport in these systems and the quantized thermal conductance at low temperatures, an approach analogous to the Landauer theory of electronic transport was proposed recently.\textsuperscript{68} Within the framework of this approach, a single-wall nanotube is sandwiched between a hot and a cold heat bath, which gives rise to a thermal current in the system. The thermal current density was shown to be described by the Landauer-type formula, \( J_T = \sum_m \int_0^\infty \langle dq/2\pi \rangle \omega_m(q) v_m(q) \{ N(\omega_m, T) - N(\omega_m, T_{\text{cold}}) \} f_m(q) \), where \( m \) is the phonon mode, \( q \) is the phonon wave vector, \( \omega_m(q) \) is the phonon energy, \( v_m(q) = \partial \omega_m(q)/\partial q \) is the group velocity, \( N(\omega_m, T) \) is the Bose-Einstein phonon distribution function of the heat bath at temperature, \( T \), and \( f_m(q) \) is the transmission coefficient between the heat baths and the system. To arrive at an analytical solution for thermal conductance the following assumptions have been made: (a) an adiabatic control between the heat baths and the system, \( f_m(q) = 1 \); (b) linear response condition, \( \Delta T = T - T_{\text{cold}} \ll T \approx (T_{\text{hot}} + T_{\text{cold}})/2 \); and (c) the frequencies of the \( m \)th phonon dispersion are limited to a range between \( \omega_m^\text{min} \) and \( \omega_m^\text{max} \).\textsuperscript{70}

These assumptions lead to the thermal conductance, \( \kappa_{ph} \), given by

\[
\kappa_{ph} = \frac{I_T}{\Delta T} = \frac{k_B T}{2\pi h} \sum_m \left\{ \int_0^{\omega_m^\text{min}} dx \frac{x^2 e^x}{(e^x-1)^2} \right\} v_m^2 \phi(1, e^{-x}) + \left( x_m^\text{min}_m \right)^2 N(x_m^\text{min}_m)
\]

where \( x_m^\text{min}_m = \hbar \omega_m^\text{min}/k_B T \), \( \alpha \) denotes “min” or “max,” and \( \phi(y, s) = \sum_{n=1}^{\infty} (s^n/n^s) \) is the Appel function, which for a gapless (acoustic) mode, \( \omega_m^\text{min} = 0 \) \((s = 1)\), yields the Riemann’s zeta function. This mode contributes a universal quantum of \( \kappa_\alpha = \pi k_B^2 T/3\hbar \) to the thermal conductance.

There are four acoustic modes that are responsible for the quantization of thermal conductance in nanotubes at temperatures below the excitation of the lowest two optical modes with energy gap, \( \hbar \omega_m \), which is equal to 2.1 m\text{ eV} in the (10, 10) carbon nanotubes. A similar approach was used to calculate the thermal conductance of electrons. This model predicts values for ratio \( \kappa_e/\kappa_\alpha \) of the thermal conductance by electrons to that by phonons that ranges from 1, at \( T \) close to 0 K, to 0.1, at \( T = 350 \text{ K} \). However, the calculated ratios are an order of magnitude higher than the measured ratio,\textsuperscript{71} and show that at room temperature the electronic contribution to thermal conductivity can be neglected.

The thermal conductivity of carbon nanotubes at room and higher temperatures can be simulated through direct equilibrium or non-equilibrium MD-based approaches, as described briefly in the above. In the direct non-equilibrium MD simulation methods,\textsuperscript{32–34} appropriate heat baths are created at the two ends of a nanotube, thus resulting in a flux of thermal energy from the hot region of the tube to the cold, as schematically illustrated in Figure 17(a). The ratio of heat flux and the temperature

\[\text{Fig. 17.} \quad \text{(a) Simulation system of a nanotube is divided into} \ N \ \text{segments with hot region in the center segment and the cold region at the end segment. In a periodic boundary condition configuration cold regions at the segment 1 and} \ N \ \text{are connected with each other. (b) The simulated temperature gradient on (10, 10) carbon nanotube is shown at different mean temperatures. Reprinted with permission from [32]. M. A. Osman and D. Srivastava, Nanotechnology 12, 21 (2001). © 2001.} \]

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gradient in equilibrium condition is sufficient to compute the thermal conductivity at the simulation temperature. A typical equilibrium temperature distribution or thermal gradient in a nanotube is shown in Figure 17(b), for five different simulation temperatures. This temperature distribution yields two gradients, $\partial T / \partial z$, which are used to compute the thermal conductivities from left and right parts of the system, corresponding to the temperature distributions to left and right of the hot slab in the center of a periodic simulation, respectively. These are averaged to yield the room-temperature thermal conductivity, which shows less than 2% fluctuations around the average value of $\approx 1320$ W/mK during the final 20 ps of the simulation. The typical room temperature thermal conductivity of SWCNTs of 1 to 3 nm diameters is found to be $\approx 2500$ W/mK. The thermal conductivity as a function of temperature is shown Figures 18(a) and (b), for (5,5), (10,10), (15,15), and (10,0) SWCNTs. The thermal conductivity demonstrates a peaking behavior as a function of temperature. This is because, as the temperature is raised up from very low values, more and more phonons are excited and contribute towards the heat flow in the system. However, at higher temperatures, phonon-phonon scattering starts to dominate and streamline heat flow in the CNTs decreases causing a peak in thermal conductivity, in the intermediate temperature range. For all simulated types of CNTs (of 1 to 2 nm diameter) as a function of the tube diameter and chirality, it was found that the peak position is around room temperature and sensitive to the radius of the CNTs and not the chirality or the helicity. This means that the thermal transport in SWNTs occurs mainly through excitations of low-frequency radial phonon modes and the coupling of the radial modes with the axial or longitudinal phonons in the low frequency region. Additionally, the non-equilibrium MD-based simulations, employing periodic velocity exchange approach, predict higher thermal conductivities for zigzag SWCNTs as compared to armchair SWCNT, at low temperatures. The higher value was attributed to higher strain in the sigma bonds along the circumference in armchair SWNT as compared to zigzag SWCNT. The convergence of the thermal conductivity as a function of the length of a nanotube, however, is still an open issue for all direct MD simulation methods reported so far. A significant variation in the room temperature thermal conductivity of (10,10) CNT has been reported partly because some of the studies have used very small CNT lengths in the simulations. Preliminary investigations of the convergence with respect to the temperature gradient, $\partial T / \partial z$, across the CNT length have shown an inverse power-law dependence of the thermal conductivity on the thermal gradient. Rigorous, long time and length scale simulations are required to investigate the convergence behavior as a function of CNT length. It is noted, however, that only the absolute value of thermal conductivity changes and not the qualitative behavior of the relative peak heights and positions as a function of temperature.

The thermal conductivity measurements, performed in temperature range from 8 K to 350 K, on as grown and sintered SWCNT mat samples have shown that the thermal conductivity at room temperature ranges from to 2.3 W/m-K to 35 W/m-K for sintered and as grown mat samples, respectively. These values are very small compared to that of metals and graphite at room temperature due to the random orientation of nanotubes within the mat samples. The thermal conductivity of oriented multi-wall nanotube bundles was measured in temperature range from 10 to 300 K, with diameter distributions ranging from 20 to 40 nm. The measured thermal conductivity exhibits a smooth increase as a function of temperature, with maximum value of about 25 W/mK corresponding to room temperature. This measured value of $\kappa$ of multi-wall nanotubes at 300 K is about two orders of magnitudes lower than those of graphite and diamond at room temperature. This behavior was attributed to the imperfections introduced during the growth, which significantly reduce the mean free path length for phonons. Another experiment on multi-wall nanotube films, performed at $T = 300$ K, reported a value of about 200 W/mK. The measurement was performed using pulsed photothermal reflectance (PPR) technique and corrected for air gaps.

Fig. 18. The direct MD simulated thermal conductivity of carbon nanotubes as a function of temperature with: (a) a comparison between (5,5), (10,10) and (15,15) nanotubes, and (b) a comparison between a (5,5) and (10,0) nanotubes. Reprinted with permission from [32], M. A. Osman and D. Srivastava, Nanotechnology 12, 21 (2001). © 2001.
between nanotube bundles. The scattering from defects, inter-graphene layer and inter-tube coupling was thought to be responsible for the low measured thermal conductivity in these experiments. The thermal conductance of an individually suspended MWCNT was thus measured over the temperature range from 8 to 370 K.\textsuperscript{35} The MWCNT had $\approx 14$ nm diameter and a length of $\approx 2.5$ $\mu$m corresponding to the gap between the two suspended islands. The measured room temperature thermal conductivity exceeds 3000 W/mK, which is an order of magnitude higher than that reported in Ref. \cite{76}.

### 6.3. Heat Pulse Transport in CNTs

Another type of thermal transport is feasible and investigated when nanotubes are subjected to intense heat pulses.\textsuperscript{37-39} The application of strong heat pulses, generating several waves propagating at different speeds corresponding to different phonon modes, can provide information about individual modes and their contribution towards the overall heat transport.\textsuperscript{39} Heat pulse measurements in NaF at low temperatures revealed ballistic longitudinal acoustic (LA) and transverse acoustic (TA) phonon mode propagation as well as second-sound waves, at temperatures below 14 K.\textsuperscript{39} Therefore, heat pulse experiments provide quantitative information on transport by diffusion, ballistic phonons, and second-sound waves. The second-sound waves are not attenuated by the dissipative scattering processes, and, therefore, MD simulation technique is ideally suited for studies of such phenomenon, because the temperature, shape, and duration of heat pulses can be simulated in a controlled way in nanotubes. The speed of the leading edges of pulses arriving at the detector side is determined from the arrival time and the sample length and used to determine the ballistic phonon mode (LA or TA). The heat pulse duration was taken to be 1 ps during which the temperature was ramped up and down according to a desired shape. The first-sound or the leading waves move at higher speed but the shape of the wave changes and intensity also decays.\textsuperscript{39} The leading wave is followed by a second-sound wave that maintains its shape and intensity for the entire duration of the simulation. In Ref. \cite{80}, the propagation of both the first- and second-sound waves was investigated. In zigzag nanotubes, the leading wave are found to move at the sound velocity of LA phonons, whereas, in the armchair carbon nanotubes, the leading wave moves with a sound velocity of TA phonons.\textsuperscript{39} The main conclusion is that the leading stress waves under heat pulse conditions travel slower in armchair nanotubes as compared to that in zigzag nanotubes, which is consistent with the earlier thermal conductivity simulations that showed a higher thermal conductivity for a zigzag nanotube as compared to that of an equivalent armchair nanotube of the similar diameter.\textsuperscript{35, 34}

### 6.4. Thermal Conductivity of Silicon Nanowires

The electronic and thermal transport behavior of single-crystal and defected nanowires has been investigated recently for their possible use in thermal management in electronics and computing chips, and also in thermoelectric power generation and refrigeration applications.\textsuperscript{81} For thermo-electric applications, the thermoelectric figure of merit is defined, which is inversely proportional to the product of electrical resistivity and thermal conductivity at a given temperature. The bulk Si, Ge, and some other semiconductor materials have low thermal conductivity, which is expected to be lowered further for nanowires of small diameters. The thermal conductivity of silicon nanowires as a function of nanowire diameter has been investigated recently using both simulations and experiments. The atomic simulations of the thermal conductivity of silicon nanowires are based on the similar simulation techniques for bulk silicon,\textsuperscript{28} described in Section 3.

The direct MD simulations of thermal conductivity of silicon nanowires, based on simulations of thermal flux-flux correlation function within the Green-Kubo approach, have been carried out recently using Stillinger-Weber potential for Si–Si interatomic interactions.\textsuperscript{82} The silicon nanowires of square cross-sectional shape of different sizes were equilibrated to allow for surface reconstruction to occur in the MD simulations. The thermal conductivity simulations on the thus equilibrated nanowire structures were performed within the Green-Kubo equilibrium MD approach, discussed in the above. The thermal conductivity of the nanowire with cross-sectional dimensions varying between (1.61 $\mathrm{nm} \times 1.61 \mathrm{~nm}$) to (5.37 $\mathrm{nm} \times 5.37 \mathrm{~nm}$) was found to be between 1.2 and 3.5 W/mK, respectively, at room temperature. The simulated thermal conductivity, thus, is found to be about two orders magnitude smaller than the corresponding experimental value for bulk silicon at room temperature. Such low thermal conductivity for thin nanowires of square cross-sectional area can be attributed to large surface reconstruction induced phonon scattering. As discussed in Section 2, the square shape, however, is highly unlikely for silicon nanowires with such a small cross-sectional area. The atomistic simulations, using the direct equilibrium or non-equilibrium MD approach, therefore, are needed for realistic silicon nanowire structures and cross-sections.

Second approach, based on quasi-classical approximation to the quantum thermal conductivity (the Boltzmann Transport Equation (BTE) formalism within diffusive limit), has been applied to study the thermal conductivity of silicon nanowires with diameters varying in the range of 37–100 nm.\textsuperscript{83} The BTE approach is a quasi-classical formulation of the heat transport in the materials system as opposed to the quantum formulation based on Landauer equation, discussed in the above. The advantage of the numerical solution of BTE-based approach is that the anharmonic effects can be included...
in consideration. The limitation of the BTE-based method is that contributions to the thermal conductivity due to quantum interference effects among different phonon processes are not included. Only bulk silicon thermal transport characteristics have been used to parameterize BTE model for the thermal conductivity of silicon nanowires, and a good agreement with experimentally reported values for silicon nanowires with diameter as small as 30 nm has been achieved.\textsuperscript{18} At room temperature, this method reports thermal conductivity varying between 15–40 W/mK, for silicon nanowires diameter varying between 39–132 nm, respectively. These values are an order of magnitude larger than the values reported above from MD simulation based investigations for thin silicon nanowires of diameter 1–5 nm. It is not clear, however, if the reported difference is solely due to the differences in the diameter of nanowires or due to the methods used to compute thermal conductivity in the two cases. In the larger diameter range of 30–150 nm the computed using BTE thermal conductivity values are in good agreement with the reported experimental values.\textsuperscript{14} The direct MD simulations of the thermal conductivity of silicon nanowires of small diameter as a function of diameter, lattice structure and realistic surface reconstruction are currently in progress and expected to quantify the effect of surface scattering on the thermal conductivity of non-oxidized thin silicon nanowires.

7. SUMMARY AND OUTLOOK

The above discussion of the computational nanomechanics and thermal transport studies of nanotubes and nanowires, performed in recent years, provides a narrow window on a broad nanoscience applications area, based on nanotubes and nanowires. From technology development and applications perspective, the simulations of the mechanical and thermal characterization of carbon nanotubes in composite materials, silicon nanowires in thermo-electric-power generation and cooling, and silicon carbide nanowires in high-frequency and high-temperature applications are vigorously pursued recently. The thrust of the discussion in this review, however, has been kept focused on discussion of individual nanotubes and nanowires. Similarly, no attempt has been made to include the simulations of electronic and chemical characterization in the description, even though they are important from the technology development perspective in the molecular electronics and chemical-bio sensor areas. It is clearly beyond the scope of this review to cover all the possible areas and applications in which significant progress has been made through computer modeling and simulation based approaches. In the future, as better multi-scale simulation algorithms for nanomechanics and thermal transport are developed, it may be possible to perform system-level simulations of the structural reinforcement and thermal management capabilities of nanotubes in polymer and ceramic matrices, and compound or doped semiconductor nanowires for thermoelectrics or optoelectronics applications.

Acknowledgments: Part of this work (D. S. and M. A. M.) is supported by NASA contract NAS2-03144 to UARC at Ames Research Center. M. M. gratefully acknowledges support from DOE (DE-FG02-00ER45817) and US-ARO (W911NF-05-1-0372). The authors gratefully acknowledge their colleagues, collaborators, students and postdocs, who have contributed to the work, described and reviewed in this manuscript. In particular, authors are very thankful to C. Andersen (University of Minnesota), D. W. Brenner (North Carolina State University), I. Ponomareva (University of Arkansas), K. J. Cho (Stanford University), A. Cummings (Washington State University), N. Mingo, (UARC, NASA Ames Research Center), E. G. Noya (University of Santiago, Spain), R. Ruoff (Northwestern University), K. Tamme (University of Minnesota), C. Y. Wei (Elorot Corporation, NASA Ames Research Center), and L. Zhigilei (University of Virginia) for their contribution to many papers quoted in this review.

References and Notes

43. V. M. Harik, Solid State Commun. 120, 331 (2001).

Received: 9 March 2007. Accepted: 12 May 2007.