

Computational materials: Multi-scale modeling and simulation of nanostructured materials

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Abstract

The paper provides details on the current approach to multi-scale modeling and simulation of advanced materials for structural applications. Examples are given that illustrate the suggested approaches to predicting the behavior and influencing the design of nanostructured materials such as high-performance polymers, composites, and nanotube-reinforced polymers. Primary simulation and measurement methods applicable to multi-scale modeling are outlined. Key challenges including verification and validation are highlighted and discussed.

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1. Introduction

“I have not failed. I’ve just found 10,000 ways that don’t work” – Thomas Alva Edison (1847–1931).

Each distinct age in the development of humankind has been associated with advances in materials technology. Some historians have linked key technological and societal events with the materials technology that was prevalent during the “stone age,” “bronze age,” and so forth. The description of our current age and culture will be up to future historians, but the last 350 years have seen many advances in materials technology that have helped shape our world today. Much of this groundbreaking work (Table 1) was because of perseverant research scientists and engineers finding solutions after long periods of experimentation and development.

Within the last 20 years, many research institutions have recognized the need for a more systematic approach to new materials development that employs a multi-scale modeling approach. This approach was one that would combine interdisciplinary research, new advances in computational modeling and simulation, and critical laboratory experiments to rapidly reduce the time from concept to end product. The general consensus is that this new paradigm by which all future materials research would be conducted and has come to be known simply as “Computational Materials.”

Traditionally, research institutions have relied on a discipline-oriented approach to material development and design with new materials. It is recognized, however, that within the scope of materials and structures research, the breadth of length and time scales may range more than 12 orders of magnitude, and different scientific and engineering disciplines are involved at each level. To help address this wide-ranging interdisciplinary research, Computational Materials programs have been formulated with the specific goal of exploiting the

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Table 1
Significant events in materials development over the last 350 years

| |
|--|
| 1665 – Robert Hooke ... material microstructure |
| 1808 – John Dalton ... atomic theory |
| 1824 – Portland cement |
| 1839 – Vulcanization |
| 1856 – Large-scale steel production |
| 1869 – Mendeleev and Meyer ... Periodic Table of the Chemical Elements |
| 1886 – Aluminum |
| 1900 – Max Planck ... quantum mechanics |
| 1909 – Bakelite |
| 1921 – A.A. Griffith ... fracture strength |
| 1928 – Staudinger... polymers (small molecules that link to form chains) |
| 1955 – Synthetic diamond |
| 1970 – Optical fibers |
| 1985 – First university initiatives attempt computational materials design |
| 1985 – Bucky balls (C ₆₀) discovered at Rice University |
| 1991 – Carbon nanotubes discovered by Sumio Iijima |

tremendous physical and mechanical properties of new nano-materials by understanding materials at atomic, molecular, and supramolecular levels.

Computational Materials draws from physics and chemistry, but focuses on constitutive descriptions of materials that are useful in formulating macroscopic models of material performance. The objective of this paper is to describe in some detail how convergent technologies have facilitated multiscale modeling of novel nanostructured materials and to outline the Computational Materials approach for materials and structures research. In particular, the paper discusses how the Computational Materials approach utilizes multi-scale analysis methods, as illustrated in Fig. 1 and critical experiments or measurements, illustrated in Fig. 2, to establish the technology for the scale-up of nanostructured materials into engineering level, multifunctional materials for advanced applications such as next generation aircraft and spacecraft.

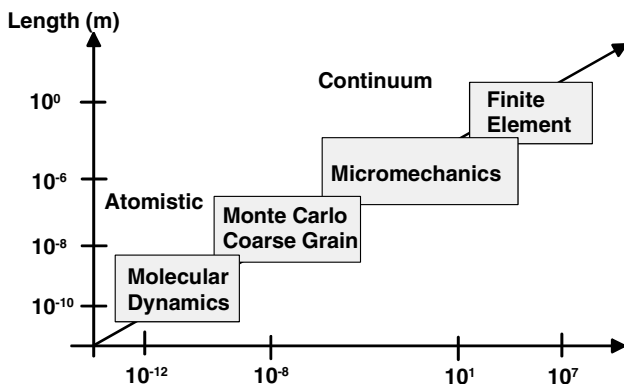


Fig. 1. Range of length and time scales of the key simulation methods.

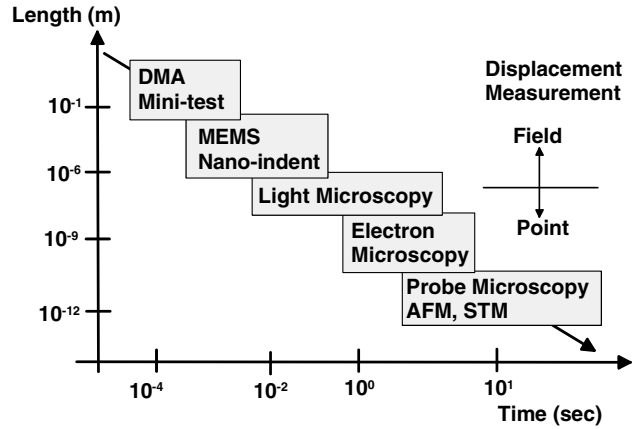


Fig. 2. Range of length and time scales associated with key measurement methods.

The benefits of the Computational Materials approach are threefold. First, it encourages a reduced reliance on costly trial and error, or serendipity, of the “Edisonian” approach to materials research. Second, it increases the confidence that new materials will possess the desired properties when scaled up from the laboratory level, so that lead-time for the introduction of new technologies is reduced. Third, the Computational Materials approach lowers the likelihood of conservative or compromised designs that might have resulted from reliance on less-than-perfect materials.

The paper is organized as follows. Key challenges are discussed, contributions from convergent technologies: measurement science, and information technology, are presented, details of the primary simulation methods are outlined, and the issues of method verification and validation are explained.

2. Key challenges

For aerospace applications, the most notable design challenges are directly related to enhancing the performance of advanced aircraft and spacecraft by increasing: size per mass, strength per mass, function per mass and power, and intelligence per mass and power. In terms of multi-scale modeling and the application of advanced nanostructured materials, these challenges translate into more specific requirements that include high-strength-per-mass smart materials for vehicles and large space structures, materials with designed-in mechanical/thermal/electrical properties, materials for high-efficiency energy conversion, and materials with embedded sensing/compensating systems for reliability and safety.

3. Computational materials

In order to address these goals and challenges, Computational Materials programs have developed schemes

for spanning both the length and time scales associated with analyses that describe material behavior. Schematically, this approach is illustrated in Fig. 3. The starting point is a quantum description of materials; this is carried forward to an atomistic scale for initial model development. Models at this scale are based on molecular mechanics or molecular dynamics. At the next scale, the models can incorporate micro-scale features and simplified constitutive relationships. Further progress up the scale leads to the meso or in-between levels that rely on combinations of micromechanics and well-established theories such as elasticity. The last step towards engineering-level performance is to move from mechanics of materials to structural mechanics by using methods that rely on empirical data, constitutive models, and fundamental mechanics. The central part of this hierarchical scheme, connections between the nano and micro scales, are examined in greater detail subsequently.

4. Nanostructured materials

From a “bottom-up” perspective, the multi-scale approach should consider the intrinsic attributes of the constituent materials for the system of study. Much of the current work focuses on the use of nanostructured materials. The origins of focused research into nanostructured materials can be traced back to a seminal lecture given by Richard Feynman [1] in 1959. In this lecture, he proposed an approach to “the problem of manipulating and controlling things on a small scale.” The scale he referred to was not the microscopic scale that was familiar to scientists of the day but the unexplored atomistic scale. Over the subsequent years, this idea was refined and eventually resulted in the announcement of the National Nanotechnology Initiative [2] in 2000. It is ironic that in Feynman’s lecture he conjectured that “in the year 2000, when they look

back at this age, they will wonder why it was not until the year 1960 that anybody began seriously to move in this direction.”

The recent history of “nano” science and engineering includes investigations into a variety of material systems and applications [3]. Table 1 highlights the discoveries of “buckyballs” (the C₆₀ family) in 1985 [4] and carbon nanotubes in 1991 [5]. The nanostructured materials based on carbon nanotubes and related carbon structures are of current interest for much of the materials community. Although at the time of their discoveries, other materials with well-defined nanoscopic structure were known, investigators were intrigued to find that these new forms of carbon could be viewed as either individual molecules or as potential structural materials [6]. This realization in turn energized a whole new culture of nanotechnology research accompanied by worldwide efforts to synthesize nano-materials and to use them to create multifunctional composite materials. More broadly then, nanotechnology presents the vision of working at the molecular level, atom by atom, to create large structures with fundamentally new molecular organization. With regards to aerospace, the objectives within the National Nanotechnology Initiative include advances in ultralight, ultrastrong, space durable materials for very large space structures (telescopes, antennae, solar sails), spacecraft electronics for greater autonomy and on-board decision-making, micro systems based on biological principles, utilization of in situ resources to create complex structures in space, and biologically inspired architectures for long duration missions (Table 2).

5. Convergent technologies

The growth of Computational Materials research, with its emphasis on the concepts of nanotechnology and a hierarchical, multi-scale modeling approach, has

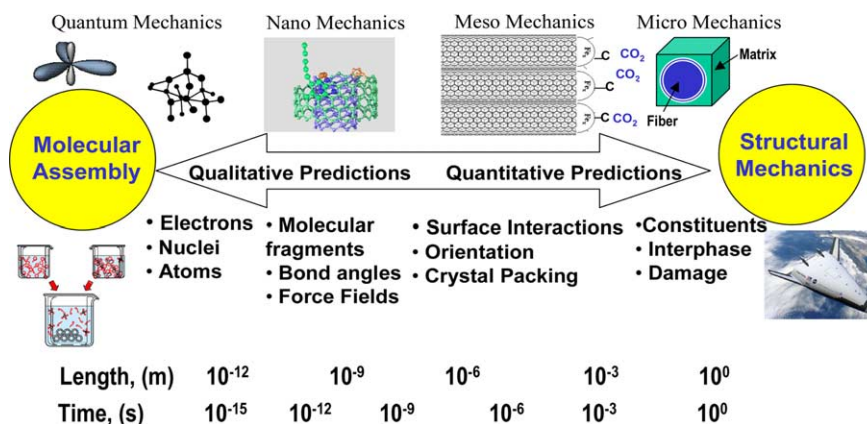


Fig. 3. Schematic illustration of relationships between time and length scales for the multi-scale simulation methodology.

Table 2
Typical spatial resolution of devices used for material characterization and testing

| Device | Spatial resolution (nm) |
|-------------------|-------------------------|
| AFM | .001 |
| TEM | .2 |
| SEM | 5 |
| Light microscope | 200 |
| MEMS/nanoindenter | 250 |

relied to some extent on inspiration and advances in two technology areas: measurement science, and information technology. The convergence of these key technologies may provide the means for Computational Materials to eventually solve some of the most fundamental problems in materials science and engineering.

5.1. Measurement science

Microscopy has consistently been a primary source of information on the fundamental structure of materials. Prior to the 1940s, microscopy was limited in resolution by the wavelength of visible light (approximately 10^{-6} – 10^{-7} m) and the associated optics systems. The practical limitations of light microscopes are $500\times$ to $1000\times$ magnification and a resolution of $0.2\ \mu\text{m}$. Obviously, discerning the intrinsic structure of nano-scale materials is impossible at this resolution.

The discovery of the Transmission Electron Microscope (TEM) occurred in the early 1940s and the first commercial electron microscopes became available around 1965. The Scanning Electron Microscope (SEM) is a microscope that uses electrons rather than light to form an image by scanning the beam across the specimen. The typical SEM has a magnification range from $15\times$ to $200,000\times$ and a resolution of 5 nm.

Beginning with the scanning tunneling microscope (STM) in 1981, experimentalists developed new techniques and devices for discerning the most basic unit of materials, the atom. Instruments that use variations of the principles of the STM are often called scanning probe microscopes (SPM). All of these microscopes work by measuring a local property – such as height, optical absorption, or magnetism – with a probe or “tip” placed very close to the sample. The small probe-sample separation (on the order of the instrument’s resolution) makes possible for the first time imaging and manipulation of materials at the level of individual atoms. A successor to the STM, atomic force microscopy (AFM), works by measuring attractive or repulsive forces between the tip and the sample, and converting the basic displacement information of this tip into pictures of atoms on or in surfaces. The AFM can work with the tip touching the sample (contact mode), or the tip can tap across the surface (tapping mode). Other SPM’s include the lateral-force microscope (LFM) to measure surface microfriction,

magnetic force microscopes (MFM) to detect the orientation of magnetic domains, and a force-modulation microscope (FMM) to image differences in elastic moduli on the micro-scale. A very recent adaptation of the SPM probes the differences in chemical forces across a surface at the molecular scale and has been called the chemical force microscope (CFM). These developments opened the door for significant advances in material characterization.

The light microscope and electron microscope are strictly imaging devices, while the probe microscopes have some utility as imaging devices and in manipulation or characterization of materials. However, to date, the accuracy and repeatability of basic force/displacement measurements taken using probe microscopy has been a subject of debate. Because of this uncertainty, it appears that accurate, quantitative material testing is currently limited to devices that resolve only down to the micro-scale (10^{-6} m). Examples of commercial devices that operate at this resolution are nanoindentors and mini-scale test devices built by using micro-electro-mechanical-systems (MEMS). These devices can be constructed with a high degree of repeatability and will operate under a range of environmental conditions. For example, the nanoindenter is a high-precision instrument for the determination of the localized mechanical properties of thin films, coatings and substrates. An indenter tip, normal to the sample surface, with a known geometry, is driven into the sample by applying an increasing load up to some preset value. The load is then gradually decreased until partial or complete relaxation of the sample has occurred. The load and displacement are recorded continuously throughout this process from which the mechanical properties such as hardness, Young’s modulus, and viscoelastic constants can be calculated. A typical nanoindenter has a depth resolution 0.02 nm, a maximum indentation depth of 500,000 nm, and maximum load of 500 mN with a resolution of 50 nN.

5.2. Information technology

The final technology element that has helped drive the advance in Computational Materials is the revolution in Information Technology (IT). In part, the IT revolution has been facilitated by the rapid increase in processing speed and power available to both desktop and mainframe computers. To illustrate this growth, one can consider Moore’s Law, a prediction that forecasted processing speed to double every 18 months. The observation was made in 1965 by Gordon Moore, co-founder of Intel, and was based on the fact that the number of transistors per square inch on integrated circuits had doubled every year since the integrated circuit was invented. To date, this forecast has held true and most experts, including Moore himself, expect Moore’s Law to hold for at least another two decades. These increases in processing speed have in turn helped drive the

availability of software that can solve the complex problems associated with computational chemistry and continuum mechanics with increased accuracy.

6. Structure–property relationships

In order to apply modeling and computer simulation to enhance the development of nanostructured materials systems, it is necessary to consider the structure–property relationships. These relationships relate the intrinsic structure of the material to the desired engineering-level property or performance. A list of these structure–property relationships for polymers and polymer/nanotube composites is given in Table 3. This table breaks down the structure according to scale and includes structure that can be directly influenced by material-synthesis methods. This table is by no means an exhaustive list but it does describe the principal structure–property elements in use by Computational Materials programs [7]. The simulation methods that address these structure–property relationships and are used to establish the multi-scale modeling are molecular statics and dynamics, coarse graining, micromechanics, and finite elements. Before outlining the simulation methods, a few key terms require definition. A model is the simplified part of a real structure. A theory is the framework by which physical results can be predicted. A simulation is a numerical solution. An experiment is performed to establish the relationship between several physically connected parameters. A measurement is the physical features observed in an experiment.

7. Simulation methods

7.1. Atomistic, molecular methods

The multi-scale approach taken by the Computational Materials Program is a formulation of a set of

integrated predictive models that bridge the time and length scales associated with material behavior from the nano through the meso scale. At the atomistic or molecular level, the reliance is on molecular mechanics, molecular dynamics, and coarse-grained simulation. Molecular models encompassing thousands and perhaps millions of atoms can be solved by these methods and used to predict fundamental, molecular level material behavior. The methods are both static and dynamic. For example, molecular mechanics can establish the minimum-energy structure statically and molecular dynamics can resolve the nanosecond-scale evolution of a molecule or molecular assembly. These approaches can model both bonded and nonbonded forces (e.g., Van der Waals and electrostatic), but are not parameterized for bond cleavage.

The molecular dynamics (MD) method was first introduced by Alder and Wainwright in the late 1950s to study the interactions of hard spheres [8,9]. Many important insights concerning the behavior of simple liquids emerged from their studies. The next major advance was in 1964, when Rahman carried out the first simulation by using a realistic potential for liquid argon [10].

Rahman's simulation size was 864 argon atoms represented by the Lennard–Jones potential function.

$$U_{LJ} = 4\epsilon \left(\frac{\sigma^{12}}{r^{12}} - \frac{\sigma^6}{r^6} \right). \quad (1)$$

The study reported several physical properties of argon calculated from the MD simulation. The radial distribution $g(r)$

$$g(r) = \int 4\pi r^2 \rho(r) dr \quad (2)$$

and its Fourier transform known as the structure factor $s(k)$. The simulation data reproduced the $g(r)$ calculated from X-ray data. The self-diffusion coefficient, D , is calculated in two ways using the Einstein relation

$$2Dt = \frac{1}{3} \langle |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \rangle, \quad (3)$$

Table 3
Structure–property relationships for polymer and polymer/carbon nanotube materials

| Structure | | | Property |
|-----------------------------|------------------------------|------------------------|----------------------------------|
| Molecular | | Meso | Macro |
| Nano | Micro | Milli | |
| Inter-molecular interaction | Molecular weight | Volume ratio, fraction | Strength |
| Bond rotation | Cross-link density | Orientation | Modulus |
| Bond angle | Crystallinity | Dispersion | Glass transition temperature |
| Bond strength | Polymer/nanotube interaction | Packing | Coefficient of thermal expansion |
| Chemical sequence | | | Viscosity |
| Nanotube diameter | | | Toughness |
| Nanotube length | | | Dielectric |
| Nanotube aspect ratio | | | Density |
| Nanotube chirality | | | Conductivity |
| | | | Plasticity |

which depends on the mean square displacement of the particle i , and alternatively, by using the velocity auto-correlation function

$$D = \frac{1}{3} \int_0^\infty \langle \mathbf{v}_i(t) \cdot \mathbf{v}_i(0) \rangle dt. \quad (4)$$

These simulations and their results provide a typical example of MD simulation results: structural information, transport phenomena, and time dependence of physical properties. The simulation results could be average quantities at a thermodynamic state point or the development of a structure-based property in time. In a non-equilibrium simulation, where the system is subjected to a temporary perturbation, the response of the material can be analyzed. The connections to measurable quantities are made through thermodynamics and statistical mechanics.

In the current literature, one routinely finds molecular dynamics simulations of organic and inorganic material systems addressing a variety of issues including the thermodynamics of biological processes, polymer chemistry and crystal structure [11,12]. The number of simulation techniques has greatly expanded; there exist now many specialized techniques for particular problems, including mixed quantum mechanical–classical simulations [13]. In classical MD, the particle movement in the simulation is driven by the forces on each particle which is described by a set of functions, the ‘force field’, used to describe how the particles interact. In quantum MD, the particles move according to the ab initio derived forces [13]. A variation of this approach is to use the ab initio derived forces in small areas of the system to provide a very detailed description of a specific area the physical system.

Molecular dynamics simulation techniques are widely used to help interpret experimental results from X-ray crystallography and nuclear magnetic resonance spectroscopy. Recent examples of atomistic simulations of carbon nanotube behavior at the nano-scale include [14,15].

Large-scale MD simulations of a few million atoms have addressed metallic and nanocrystalline materials [16]. A billion atom system was reported for SiC fibers in Si₃N₄ [17]. An example of a computationally intensive simulation is polymer MD. Polymer systems are typically not as large in system size as metal simulations, but they are more complex because of the multi-body interactions within the polymer chain and the electrostatic interactions. Polymer simulations are further complicated when time-dependent behavior is of interest. The chain relaxation processes are very slow compared to the nanosecond time frame more typically accessible using MD. For example, the theory for viscoelastic properties is available [18], but the practice is very limited by the requirement to accurately represent the time frame of the material processes [19].

Molecular dynamics simulations generate information at the nano-level, including atomic positions and velocities. The conversion of this information to macroscopic observables such as pressure, energy, heat capacities, etc., requires statistical mechanics. An experiment is usually made on a macroscopic sample that contains an extremely large number of atoms or molecules, representing an enormous number of conformations. In statistical mechanics, averages corresponding to experimental measurements are defined in terms of ensemble averages. For example, the average potential energy of the system is defined as

$$V = \frac{1}{M} \sum_{i=1}^M V_i, \quad (5)$$

where M is the number of configurations in the molecular dynamics trajectory and V_i is the potential energy of each configuration. Similarly, the average kinetic energy is given by

$$K = \frac{1}{M} \sum_{j=1}^M \left\{ \sum_{i=1}^N \frac{m_i}{2} v_i \cdot v_i \right\}_j, \quad (6)$$

where M is the number of configurations in the simulation, N is the number of atoms in the system, m_i is the mass of the particle i and v_i is the velocity of particle i . To ensure a proper average, a molecular dynamics simulation must account for a large number of representative conformations.

By using Newton’s second law to calculate a trajectory, one only needs the initial positions of the atoms, an initial distribution of velocities and the acceleration, which is determined by the gradient of the potential energy function. The equations of motion are deterministic; i.e., the positions and the velocities at time zero determine the positions and velocities at all other times, t . In some systems, the initial positions can be obtained from experimentally determined structures.

In a molecular dynamics simulation, the time dependent behavior of the molecular system is obtained by integrating Newton’s equations of motion. The result of the simulation is a time series of conformations or the path followed by each atom. Most molecular dynamics simulations are performed under conditions of constant number of atoms, volume, and energy (N, V, E) or constant number of atoms, temperature, and pressure (N, T, P) to better simulate experimental conditions. The basic steps in the MD simulation are given as follows.

1. Establish initial coordinates.
2. Minimize the structure.
3. Assign initial velocities.
4. Establish dynamics of the thermal conditions.
5. Perform equilibration dynamics.

6. Rescale the velocities and check if the temperature is correct.
7. Perform dynamic analysis of trajectories.

Current generation force fields (or potential energy functions) provide a reasonably good compromise between accuracy and computational efficiency. They are often found empirically and calibrated to experimental results (e.g., X-ray crystallography) and quantum mechanical calculations of small model compounds. The development of parameter sets that define these force fields may require extensive optimization and is an area of continuing research. One of the most important limitations imposed on a force field is that no drastic changes in electronic structure are allowed, i.e., no events like bond making or breaking can be modeled.

The most time consuming part of a molecular dynamics simulation is the calculation of the nonbonded terms in the potential energy function, e.g., the electrostatic and van der Waals forces. In principle, the non-bonded energy terms between every pair of atoms should be evaluated. This requirement would imply that the number of computations increases as the square of the number of atoms for a pair-wise model. To speed up the computation, the interactions between two atoms separated by a distance greater than a pre-defined distance, the cutoff distance, are ignored.

Coarse-graining the MD simulation increases the timescale accessible by about two orders of magnitude. This method, discussed in detail in the next section, involves reducing the number of contributors to the molecular forces, usually by grouping the atoms.

MD simulations are by their nature mechanical, because the particles are driven to move by the forces acting on them. In an MD simulation, the force, velocity, and position of each atom are known for each configuration as the simulation trajectory evolves in time. From this information, elastic mechanical constitutive properties can be calculated by using MD.

One basic use of MD in the determination of mechanical properties is to use it for generation of representa-

tive volume elements (RVE) of the material. The RVE should contain any structural information not readily available from computational mechanics. The MD simulation includes all the atomistic degrees of freedom and can be parameterized for a description of surface to surface interactions within the material system. This application of MD has recently been developed to study polymer nanocomposites. In these material systems there are at least two components, the nanostructured inclusion and the polymer. Because there are two components the details of how the components, interact affect the mechanical behavior. Assumptions such as perfect bonding between the components or arbitrary placement of atoms are avoided. Instead, a representative structure based on a well-parameterized molecular force field is generated. Information from the force fields can then be used at other levels to describe the atomistic interactions.

For example, the RVEs of a system of crystalline polyethylene were generated for a functionalized and non-functionalized single wall carbon nanotube in crystalline polyethylene [20]. The functionalized carbon nanotube was crosslinked into the crystalline polyethylene matrix by six covalent cross-links of two CH₂ (methylene) units each, see Fig. 4. The point of having both of these structures was to work out the mechanical consequences of having nanotubes chemically bonded (functionalized) into the polymer versus only interacting via van der Waals interactions (represented by the Lennard–Jones potential). The many-body bond-order potential derived by Brenner [21] was used to generate these structures. This potential was preferred for the structure generation over molecular mechanics type potential because it is parameterized to describe the chemical covalent bonding in hydrocarbon systems. Instead of inputting the atoms bonded, the bond type and force constants, this potential takes the coordinates given and determines which atoms are chemically bonded based on the coordination. It is parameterized from both empirical and first principal calculations to represent especially carbons of differing hybridization. As such it is capable of making a reason-

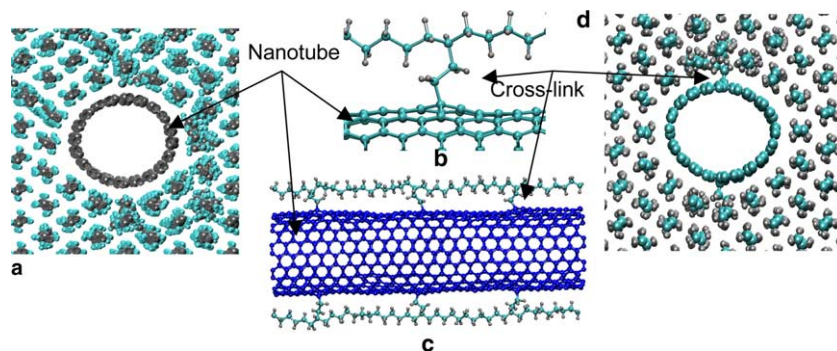


Fig. 4. Nonfunctionalized polyethylene nanotube RVE (b) the cross-link, (c) arrangement of cross-links in (d) the functionalized polyethylene nanotube RVE.

able prediction of both the bond length and local geometry of the chemical bonds in the system. In the polyethylene nanotube structures, the most uncharacterized bond is the covalent bond between the nanotube carbon and the carbon of the first methylene unit. The many-body bond-order potential is capable of assigning this bond and a suitable bond length, geometry, as well as incorporating its effects of the rest of the nanotube atoms without additional user assumptions.

Once an RVE of the material is obtained from MD, it may then be used for the computation of mechanical properties. Of particular interest for the above example was the effect of the nanotube functionalization on the material elastic constants. Without pursuing any further MD simulations, the molecular structural information of the two molecular structures was converted into material elastic constants.

Hooke's law assumes a linear relationship between stress and strain:

$$\sigma = \mathbf{C}\varepsilon, \quad (7)$$

where σ is the stress, ε strain, and \mathbf{C} the stiffness tensor. The energy associated with the linear response to strain U is

$$U = \frac{1}{2} \mathbf{C}\varepsilon^2. \quad (8)$$

In an MD simulation, the configurational energy, which is the potential energy of the simulation, changes as the material is deformed. Therefore, the energy of deformation of the linearly elastic solid can be equated to the energy of deformation of the molecular structure. The energy of deformation of the molecular structure can in turn be calculated by approximating the molecular interaction by a molecular mechanics force field with energy contributions from the bonds stretching and resistance to angular motion:

$$U^m = \sum_a K_a^\rho (\rho_a - P_a)^2 + \sum_a K_a^\theta (\theta_a - \Theta_a)^2, \quad (9)$$

where the terms P_a and Θ_a refer to the undeformed interatomic distance of bond number a and the undeformed bond-angle number a , respectively. The quantities ρ_a and θ_a are the distance and bond-angle after stretching and angle variance, respectively. The symbols K_a^ρ and K_a^θ represent the force constants associated with the stretching and angle variance of bond and bond-angle number a , respectively. The individual energy contributions are summed over the total number of corresponding interactions in the molecular model. To account for the van der Waals forces between the nanotube and the polymer, the Lennard–Jones interactions can be calculated for neighbors. Using this approach, along with the effective continuum model, described in a subsequent section, the effect of the functionalization was found to result in approximately a 10% decrease

in the C_{11} constant. Similarly, related decreases were found in most of the C_{ij} with axial components compared with increases of 20–40% in most of the transverse elastic constants [20].

MD simulations can also be performed on the RVEs to obtain the elastic constants directly. For this sort of calculation the energy of deformation can be calculated directly as a displacement field is applied to the molecular structure. The energy deformation is then equivalent to the difference in configurational energy of the molecular structure in the strained and unstrained states. Some authors prefer to compare configurational energies which have been minimized from equilibrium structures in the strained and unstrained conditions [22].

An alternative is to compare configurational energies which are averages of thermodynamic state points in the stressed and unstressed conditions. An example of this technique was used to calculate the nonlinear elastic constants of cross-linked carbon nanotubes. In these materials, depicted in Fig. 5, the nanotubes are covalently bonded to short organic molecules and each molecule can cross-link two nanotubes. The RVEs were generated with MD for a nanotube bundle, two materials in which the nanotubes were cross-linked with differing amounts of the cross-linking agent, and the organic cross-linking material without nanotubes. The force field used was AMBER, which is a molecular mechanics force field. It includes bond stretches, angular motion, dihedral angles and Lennard–Jones pair interactions. In this case, the parameters for the covalent bond to the nanotube from the cross-linkers were input. The chemical bond between nanotube and the cross-linker was treated as sp^3 (C–C single bond), as were the chemical bonds to this nanotube carbon atom within the nanotube.

In this study a modification was made to the constitutive equation to make it non-linear. The energies of deformation of the nanotube materials as a function of strain were then fit to the non-linear constitutive equation. Altogether nine displacement fields assuming orthotropic symmetry of the system were applied to the molecular dynamics simulations, and the average configurational energy was calculated for each displacement. Subsequently, the average change in configurational energy was then used to calculate the elastic constants of the orthotropic RVE.

In calculating the elastic constants above, the strain energy is used for the elastic constant. However, it is also possible to calculate the stress, sometimes known as the virial stress:

$$\sigma_{ij} = -\frac{1}{V} \sum_x \left(M^x v_i^x v_j^x + \sum_\beta F_{i^\alpha}^{\alpha\beta} r_j^{\alpha\beta} \right), \quad (10)$$

where V is the system volume, M is the mass of particle, v is the particle velocity, F is the force between particles

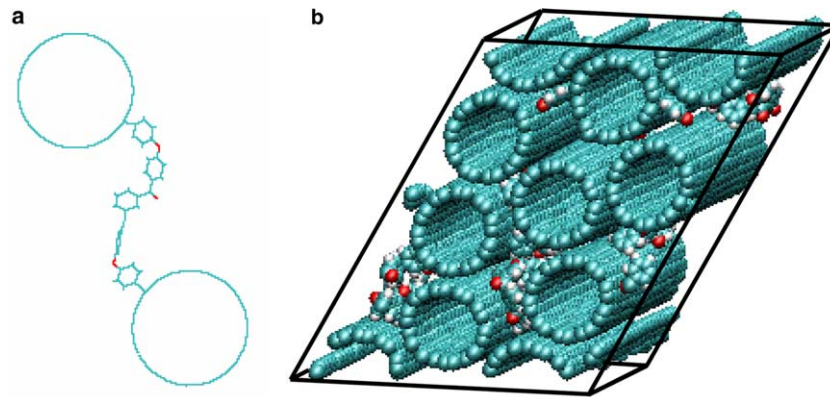


Fig. 5. (a) Cross-linked nanotubes and (b) RVE.

a and b , and i, j are the Cartesian coordinate directions. While there has been recent debate on whether virial stress is valid as engineering stress [23], it has been the standard way to calculate stress in MD simulations [24]. If the system is also deformed with a displacement similar to the above, the stress–strain curve may be calculated. In MD, these results come with the caveat that the strain rates are ballistic on the order of 0.01 per picosecond or 10^{10} per second.

This method was used to calculate the stress strain curves of amorphous polyethylene-nanotube composites [25]. The molecular system consisted of polyethylene chains of more than 1000 CH_2 units with each unit modeled by a united atom potential, and a carbon nanotube modeled with the many body bond order potential developed by Brenner. The nanotube was either periodically replicated through the system, or was short (aspect ratio 1:4) and capped. The stress strain curves were calculated for both the direction along the nanotube axis and in the transverse direction.

7.2. Coarse grain methods

Although molecular dynamics methods provide the kind of detail necessary to resolve molecular structure and localized interactions, this fidelity comes with a price. Namely, both the size and time scales of the model are limited by numerical and computational boundaries. To help overcome these limitations, coarse-grained methods are available that represent molecular chains as simpler models. A comparison to MD has shown up to four orders of magnitude decrease in CPU time through the use of the simpler models [26]. Although the coarse-grain models lack the atomistic detail of MD, they do preserve many of the important aspects of the chemical structure and allow for simulation of material behavior above the nano-scale [27,28]. The connection to the more detailed atomistic model can be made directly through an atomistic-to-coarse-grain mapping procedure that when reversed allows one to

model well-equilibrated atomistic structures by performing this equilibration by using the coarse-grain model. This mapping and reverse mapping helps to overcome the time-scale upper limits of MD simulations.

Several approaches to coarse-graining have been proposed and include both continuous and lattice models. The continuous models seem to be preferable for dynamic problems such as might occur when considering dynamic changes in volume [27]. As outlined in Kremer [27], the systematic development of the coarse-grain model requires three principal steps.

1. Determine the degree of coarse-graining and the geometry of the model.
2. Choose the form of the intra- and interchain potentials.
3. Optimize the free parameters, especially for the non-bonded interactions.

Coarse-grain models are often implemented by Monte Carlo (MC) simulations to provide a timely solution. The MC method is used to simulate stochastic events and provide statistical approaches to numerical integration [29]. As given by Raabe [30], there are three characteristic steps in the MC simulation that are given as follows.

1. Translate the physical problem into an analogous probabilistic or statistical model.
2. Solve the probabilistic model by a numerical sampling experiment.
3. Analyze the resultant data by using statistical methods.

Monte Carlo simulation methods are roughly grouped into four categories: weighted and non-weighted sampling methods, lattice type, spin model, and energy operator. As a specific example, we consider coarse grain modeling of polymers. Polymers are long chain molecules possessing structural detail across a

wide range of length scales (10^{-10} – 10^{-6} m). At the smaller length scale, are the details associated with the chemical structure of the monomer. These include number and arrangement of atoms, bond lengths and angles. At the larger length scale is the conformation of the polymer due to the characteristic of a long chain molecule. Associated with this range of length scales is a corresponding range of time scales. The relevant time scales range from bond length vibrations (10^{-13} s) to conformational rearrangements ($>10^{-4}$ s). Due to this range of length and time scales, a variety of approaches have been used to model polymers. In order to study the universal conformational features of long chains molecules, simplified coarse-grained models have been developed. In recent years, efforts have been made to bridge the gap between coarse grain and fully atomistic simulation types. These bridging methods attempt to address the problem of simulation across a range of scales through various mapping and reverse-mapping techniques. Extensive reviews of these various techniques are presented elsewhere [31,32].

The primary application for coarse grain polymer modeling involves studying processes which occur on longer time scales than is possible to study with atomistic simulations. Although careful consideration must be made in evaluating the interpretation of time step, direct comparison of coarse-grained and atomistic time scales has been made with several multi-scale modeling approaches [33,34].

Another application of coarse grain to atomistic modeling is the generation of an equilibrated atomistic simulation. Molecular dynamics [35] simulation is typically used to equilibrate atomistic models of small molecules. Due to the long relaxation times of polymer conformations, however, the time scale for equilibration can be prohibitive with atomistic models of polymers. Multi-scale modeling techniques can be used to address this issue. A schematic for this process is shown in Fig. 6 with a representative polymer chain shown with a periodic boundary cell. The atomistic model at position A is mapped to a coarse-grained model at position B. This is equilibrated with a computationally faster Monte Carlo (MC) simulation to position C. The reverse-mapping to position D recovers the atomistic model. The slow molecular dynamics simulation ($A \rightarrow D$) is circumvented with the multi-scale mapping/reverse mapping procedure ($A \rightarrow B \rightarrow C \rightarrow D$).

Several approaches have been developed for coarse-graining atomistic polymer models. Here the details involved in coarse-graining a polyimide monomer are presented [36,37]. The chemical structure of the BPDA 1,3,4-APB monomer (3,3',4,4'-biphenyltetracarboxylic dianhydride 1,3-bis(4-aminophenoxy)benzene) is shown in Fig. 7, superimposed with a depiction of the coarse-grained representation. The coarse-grained model is constructed as a series of linked vectors following the

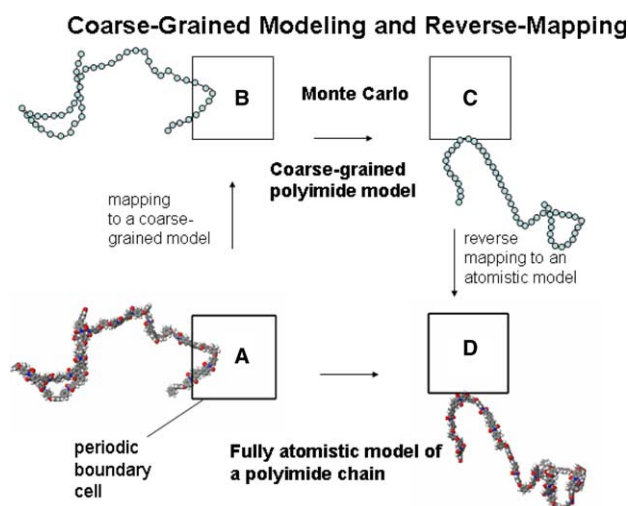


Fig. 6. Schematic illustrating the procedure for coarse-graining and reverse-mapping.

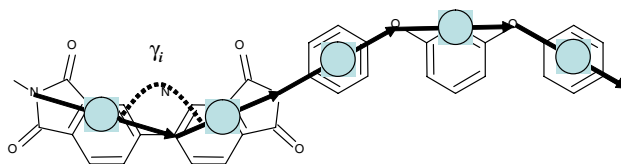


Fig. 7. For mapping between atomistic and coarse-grained models, the monomer is shown in atomistic chemical representation superimposed with the coarse-grained description.

backbone of the polymer chain. Beads are placed at the midpoints of these vectors as centers of interaction to approximate the forces between sets of atoms which are grouped together under the coarse-graining scheme.

Fig. 8 shows some typical data from a coarse-grained polymer simulation. Coarse-grained bulk simulations of three polyimide isomers of BPDA APB were performed at 650 K for chains with 10 repeat units [36,37]. The mean squared displacements of the centers of mass for each simulation are plotted as a function of dynamic MC step. These three polymers show considerable differentiation in their dynamical properties. Such data can be useful in studying the relative rates of diffusion.

Following the procedure outlined in Fig. 6, equilibrated atomistic polymer models can be obtained. A variety of properties can be calculated from atomistic models. Fig. 9 shows the pair correlation functions $g(r)$ for three polyimide isomer (BPDA APB) simulations. The differentiation reveals varying chain packing behavior between the isomer and provides insight into phase properties. Temperature dependence of density can be calculated from constant pressure molecular dynamics simulations.

Molecular modeling has been used to calculate mechanical properties of polymers and nano-structured materials [38]. These can be obtained as a function of temperature. Elastic constants (Lamé constants λ and

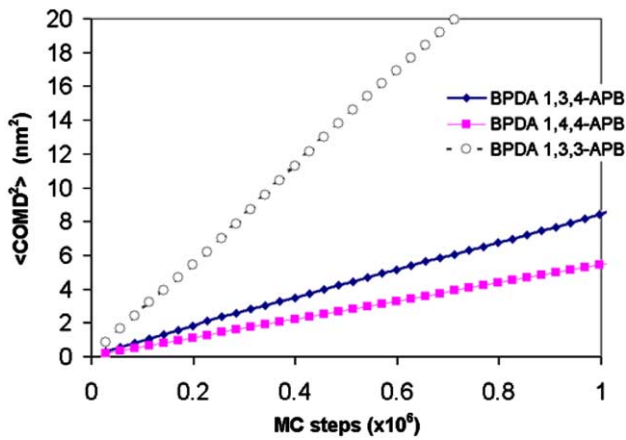


Fig. 8. The mean square displacements of the centers of mass ($\langle \text{COMD}^2 \rangle$) for the three bulk coarse-grained simulations.

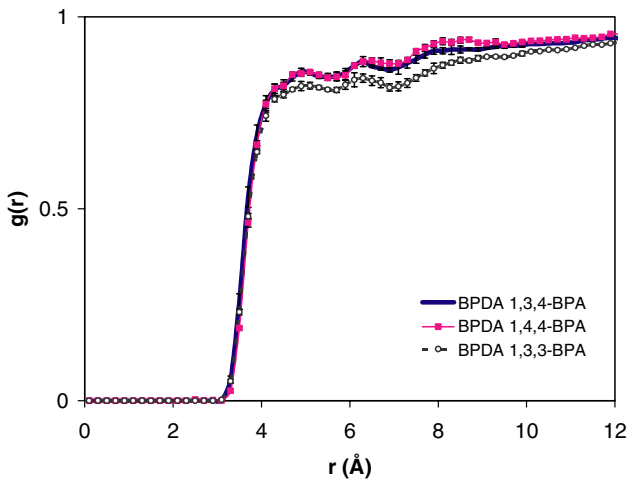


Fig. 9. The intermolecular pair correlation function, $g(r)$, for all carbon atoms from the bulk atomistic polyimide simulations.

μ , Young's modulus E , Poisson's ratio ν , and bulk modulus B) calculated from atomistic models of a polymer, BPDA 1,3,4-APB which was equilibrated from the method indicated in Fig. 6 are given in Fig. 10.

8. Continuum methods

With proper understanding of the molecular structure and nature of materials the behavior of collections of molecules and atoms can be homogenized. At the continuum level the observed macroscopic behavior is explained by disregarding the discrete atomistic and molecular structure and assuming that the material is continuously distributed throughout its volume. The continuum material is assumed to have an average density and can be subjected to body forces such as gravity and surface forces such as the contact between two bodies.

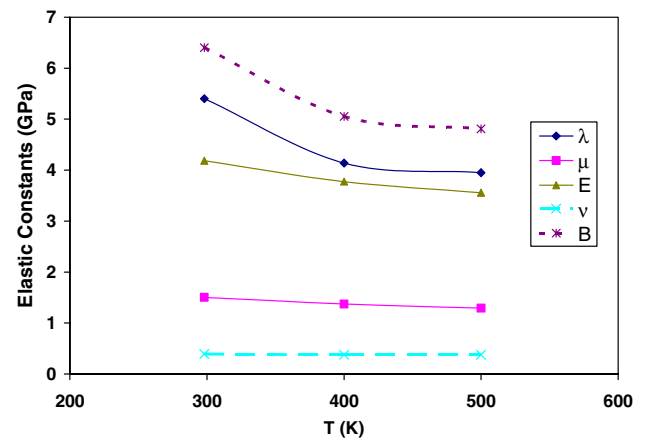


Fig. 10. Mechanical properties as a function of temperature as calculated from molecular dynamics simulations for BPDA-1,3,4-BPA. (Lamé constants λ and μ , Young's modulus E , Poisson's ratio ν , bulk modulus B).

The continuum can be assumed to obey several fundamental laws. The first, continuity, is derived from the conservation of mass. The second, equilibrium, is derived from momentum considerations and Newton's second law. The third, the moment of momentum principle, is based on the model that the time rate of change of angular momentum with respect to an arbitrary point is equal to the resultant moment. The next two laws, conservation of energy and entropy are based on the first and second laws of thermodynamics, respectively. These laws provide the basis for the continuum model and must be coupled with the appropriate constitutive equations and equations of state to provide all the equations necessary for solving a continuum problem. The state of the continuum system is described by several thermodynamic and kinematic state variables. The equations of state provide the relationships between the non-independent state variables.

The continuum method relates the deformation of a continuous medium to the external forces acting on the medium and the resulting internal stress and strain. Computational approaches range from simple closed-form analytical expressions to micromechanics to complex structural mechanics calculations based on beam and shell theory. The continuum-mechanics methods rely on describing the geometry, (i.e., a physical model), and must have a constitutive relationship to achieve a solution [39]. For a displacement-based form of continuum solution, the principle of virtual work is assumed valid. In general, this is given as

$$\begin{aligned} \delta W &= \iiint_V \sigma_{ij} \delta \varepsilon_{ij} dV \\ &= \iiint_V P_j \delta u_j dV + \iint_S T_j \delta u_j dS + F_j \delta u_j, \end{aligned} \quad (11)$$

where W is the virtual work which is the work done by imaginary or virtual displacements, ε is the strain, σ is the stress, P is the body force, u is the virtual displacement.

ment, T is the traction and F is the point force. The symbol δ is the variational operator designating the virtual quantity [40]. For a continuum system, a necessary and sufficient condition for equilibrium is that the virtual work done by sum of the external forces and internal forces vanish for any virtual displacement [40].

8.1. Micromechanics

One approach to the homogenization of a multi-constituent material is through the combination of the continuum method and a micromechanics model to provide a transition from the microscale to the macroscale. Micromechanics assumes small-deformation continuum mechanics as outlined in the preceding section. Continuum mechanics, in general, assumes uniform material properties within the boundaries of the problem. At the microscale, this assumption of uniformity may not hold and hence the micromechanics method is used to express the continuum quantities associated with an infinitesimal material element in terms of the parameters that characterize the structure and properties of the micro-constituents of the element [41].

A central theme of micromechanics models is the development of a representative volume element (RVE) that is a statistical representation of the local continuum properties. In this sense, the RVE may include material boundaries, voids, and defects apparent at the microscale. The RVE is constructed to ensure that the length scale is consistent with the smallest constituent that has a first-order effect on the macroscopic behavior. The RVE is then used in a repeating or periodic nature in the full-scale model. The approach to the micromechanics solution therefore requires a RVE and a suitable averaging technique. As given in [41], the volume average of a typical, spatially variable, integrable quantity $T(x)$ is

$$\langle T \rangle \equiv \frac{1}{V} \int_V T(x) dV, \quad (12)$$

where V is the volume of the RVE. Then, the unweighted volume average stress and strain are given by

$$\bar{\sigma} \equiv \langle \sigma \rangle \quad \text{and} \quad \bar{\varepsilon} \equiv \langle \varepsilon \rangle, \quad (13)$$

respectively. The principle of virtual work is assumed to be valid. The micromechanics method can account for interfaces between constituents, discontinuities, and coupled mechanical and non-mechanical properties.

8.2. Finite element methods

Finite element methods (FEM) have a long history of development for a wide variety of applications including problems in mechanical, biological, and geological systems. The FEM goal is to provide a numerical, approximate solution to initial-value and boundary-value

problems including time-dependent processes. The method uses a variational technique for solving the differential equations wherein the continuous problem described by the differential equation is cast into the equivalent variation form and the solution is found to be a linear combination of approximation functions [42,30]. In the FEM, the physical shape of the domain of interest is broken into simple subdomains (elements) that are interconnected and fill the entire domain without overlaps. A displacement-based form of the FEM starts with the principle of virtual work for a continuum described above. The following steps outline the FEM approach:

1. Replace the continuum domain with an assemblage of subdomains.
2. Select the appropriate constitutive laws.
3. Select the interpolation functions necessary to map the element topology.
4. Describe the problem by using the variational principle and divide the system level integral into subintegrals over the elements.
5. Replace continuum state variables by interpolation functions.
6. Assemble element equations.
7. Assemble global system equations.
8. Solve global system of equations, taking into account the prescribed boundary conditions.
9. Calculate the state equation values from state variables.

9. Effective continuum

The Effective Continuum approach for connecting atomistic models to continuum models uses relevant input from the atomistic simulations and carries forward the critical information to represent the continuum with the intrinsic nano-scale features incorporated into the model. The design of large-scale engineering structures requires a complete knowledge of the bulk-level behavior and properties of a material. For structural analysis, the bulk-level material behavior is described or predicted using continuum-based approaches, such as the micromechanical and finite element methods described above. Continuum mechanical parameters, such as Young's modulus or stress, are classically defined with the assumption that the material is a mathematical continuum [43]. However, a set of atoms in a molecular modeling simulation, which possess a structure that is in thermodynamic equilibrium, clearly does not resemble a mathematical continuum, but a discrete lattice structure. Therefore, the direct application of continuum-mechanics analyses for molecular models is problematic unless steps are taken to secure their equivalency.

Establishing an effective-continuum model for a discrete structure is the only way to reliably describe the behavior of the discrete structure in terms of continuum mechanics-based parameters. Ideally, the behavior of the effective continuum closely resembles that of the atomistic structure under any set of boundary conditions. Early attempts at establishing effective continuum models include those developed for simple crystalline materials [44,45] and aerospace lattice structures [46–51]. Many of these studies incorporate a generalized theory of elasticity which allows displacement and rotational degrees of freedom of infinitesimal material points [52], and/or the concept of energy equivalence of the lattice and effective continuum models.

The prediction of mechanical properties of crystalline materials, such as metals with dislocation defects and grain boundaries, using a combination of atomistic and finite element models has been established with the *Quasicontinuum*, [53–58] approach. With this method, the deformation of a RVE of individual atoms is mapped into a finite element model such that the nodes of the finite element model deform in an identical manner as the corresponding points in the molecular model. In addition, the energies of deformation for the atomic and finite element models are the same for identical loading conditions. This process is captured with the *Cauchy–Born rule*, which hypothesizes that an atomic crystal, which is represented by a continuum, will deform according to the overall continuum deformation gradient. Therefore, the strain energy density at a continuum point can be determined from the energy of the atomistic model. The deformation gradient can be determined using

$$F_{ij} = \frac{\partial x_i}{\partial X_j}, \quad (14)$$

where x_i and X_j are the components of the spatial and material coordinates. The energy of deformation from the atomic model is computed from an atomic potential; such as the Embedded Atom Method potential [59];

$$U_{\text{total}} = \sum_i U(\rho_i) + \frac{1}{2} \sum_{ij} \phi(R_{ij}), \quad (15)$$

where U is the embedding energy term, ρ is the local electronic density of atom i , and ϕ is the pair potential energy between atoms i and j that are separated by R_{ij} ; or the Brenner potential; which is given by [21]

$$U_{\text{total}} = \sum_i \sum_{j(>i)} [U_R(R_{ij}) - B_{ij}U_A(R_{ij})], \quad (16)$$

where $U_R(R_{ij})$ and $U_A(R_{ij})$ are repulsive and attractive terms, respectively, and B_{ij} represents a many-body coupling between the bond from atom i to atom j and the local environment of atom i . The resulting Cauchy stress tensor of the continuum at atom i can be calculated using

$$\boldsymbol{\sigma} = \frac{1}{2V} \sum_j \frac{\partial U_{\text{total}}}{\partial R_{ij}} \frac{\mathbf{x}^j \otimes \mathbf{x}^j}{R_{ij}}, \quad (17)$$

where V is the volume of the unit cell and \mathbf{x}^j is the coordinate vector of atom j . The coordinate vectors correspond to lattice vectors in the crystal. This approach has been used to simulate dislocation motion, interactions among grain boundaries, nanoindentation of crystalline materials, and fracture of crystals [16,17].

Similar approaches [60–65] have also been employed which either map the deformation of atoms from atomistic simulations onto a finite element model (or non-classical elastic model) or incorporate a *handshake* region between the atomistic and finite element models. Nakano et al. [63] simulated projectile impact onto a silicon crystal. The MAAD (macroscopic, atomistic, ab initio dynamics) approach [60,61] was used to study brittle crack propagation in silicon. The Bridging Scale method [64] was developed to overcome issues of time scale with simultaneous simulations of molecular and continuum models. This approach has been used to model various atomic lattice structures and carbon nanotubes. A bridging domain method [65] was developed that overlaps continuum and molecular domains where the Hamiltonian function is a linear combination of the two models. The atomic-scale finite element method (AFEM) [62] was developed and applied to carbon nanotubes. As an example, this method is described in more detail. In the AFEM, the finite element stiffness matrix and non-equilibrium force vector are, respectively,

$$\mathbf{K} = \frac{\partial U_{\text{total}}}{\partial \mathbf{x} \partial \mathbf{x}} \Big|_{\mathbf{x}=\mathbf{x}^{(0)}}, \quad (18)$$

$$\mathbf{P} = \bar{\mathbf{F}} - \frac{\partial U_{\text{total}}}{\partial \mathbf{x}} \Big|_{\mathbf{x}=\mathbf{x}^{(0)}}, \quad (19)$$

where U_{total} is the energy from Eq. (16), $\mathbf{x}^{(0)}$ is the initial guess of coordinate vector \mathbf{x} , and $\bar{\mathbf{F}}$ is the applied external force vector. For the case of a carbon nanotube (Fig. 11), a special element type was developed using Eqs. (18) and (19) whose stiffness matrix and non-equilibrium force vector are, respectively,

$$\mathbf{K}^{\text{element}} = \begin{bmatrix} \left(\frac{\partial^2 U_{\text{total}}}{\partial \mathbf{x}_1 \partial \mathbf{x}_1} \right)_{3 \times 3} & \left(\frac{1}{2} \frac{\partial^2 U_{\text{total}}}{\partial \mathbf{x}_1 \partial \mathbf{x}_r} \right)_{3 \times 27} \\ \left(\frac{1}{2} \frac{\partial^2 U_{\text{total}}}{\partial \mathbf{x}_r \partial \mathbf{x}_1} \right)_{27 \times 3} & (0)_{27 \times 27} \end{bmatrix}, \quad (20)$$

$$\mathbf{P}^{\text{element}} = \begin{bmatrix} \left(\bar{\mathbf{F}}_1 - \frac{\partial U_{\text{total}}}{\partial \mathbf{x}_1} \right)_{3 \times 1} \\ (0)_{27 \times 1} \end{bmatrix}, \quad (21)$$

where i ranges from 2 to 10 and corresponds to the atoms in the RVE of the carbon nanotube structure (Fig. 11) and $\bar{\mathbf{F}}_1$ is the external applied force on atom 1. While the above-mentioned effective-continuum models accurately predict the mechanical behavior of some

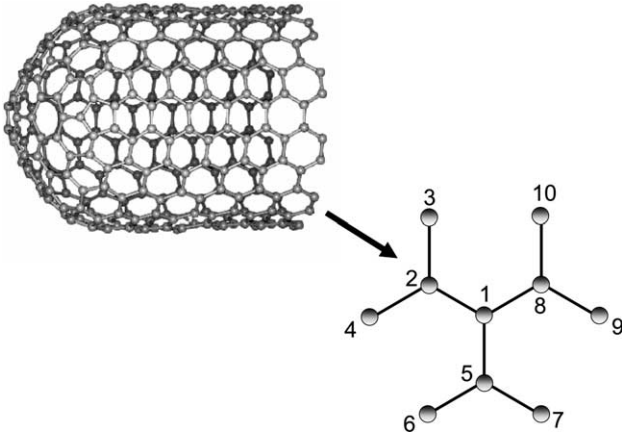


Fig. 11. Schematic of a carbon nanotube and the nanotube RVE.

atomistic systems, it has only been employed for crystalline materials and carbon nanotubes.

The molecular structural mechanics method was developed to model the mechanical behavior of carbon nanotubes and carbon-nanotube composites [66–70]. In this technique, a discrete finite element analysis is conducted in which each element represents a series of atomic interactions described by a force field. For example, a single element models bond stretching, bond-angle bending, and bond-angle torsion between carbon atoms in the carbon nanotube. The resulting axial, bending, and torsional element properties are, respectively,

$$\frac{EA}{L} = K_r, \quad \frac{EI}{L} = K_\theta, \quad \frac{GJ}{L} = K_\tau, \quad (22)$$

where E is the Young's modulus; I is the moment of inertia; L is the element length; J is the polar moment of inertia; G is the shear modulus; and K_r , K_θ , and K_τ are the force constants associated with bond stretching, bond-angle bending, and bond-angle torsion, respectively. In this manner, a molecular mechanics simulation is conducted in a more simplified finite element framework. As an example, the predicted Young's modulus and shear modulus for a multi-walled carbon nanotube is about 1.0 and 0.4 TPa, respectively [67]. For carbon-nanotube composites, the polymer surrounding the nanotube is assumed to be continuous, and is modeled with solid finite elements.

For the modeling of large amorphous, organic-based materials in general; such as polymers, carbon nanotubes, and polymer nanocomposites; the equivalent-continuum modeling approach has been developed [20,38,71–73]. This method consists of three steps: Establishing a RVE of the molecular and effective-continuum model, establishing a constitutive relationship for the effective-continuum model, and equating the potential energies of deformation for identical boundary conditions. This model recognizes that at the nanometer length scale the constituent materials such as polymers and carbon nanotubes closely resemble an atomic lattice structure composed of discrete ele-

ments rather than a continuum. Therefore, an equivalent-continuum model of the RVE is developed to facilitate bulk constitutive modeling of the composite. For the nanotube/polymer composite, a constitutive model is thus desired that will take into account the discrete nature of the atomic interactions at the nanometer length scale and the interfacial characteristics of the nanotube and surrounding polymer matrix. To formulate this constitutive model, the first step is to obtain an atomistic model of the equilibrium molecular structure of the constituents by using molecular dynamics. The total potential energy of deformation of the molecular model is computed directly from the force field [75] which has the following form

$$U_{\text{total}} = \sum U_{\text{stretch}} + \sum U_{\text{bend}} + \sum U_{\text{torsion}} + \sum U_{\text{interaction}} + \sum U_{\text{nb}}, \quad (23)$$

where the summations are taken over the corresponding atomic interactions in the RVE; U_{stretch} , U_{bend} , and U_{torsion} are the energies associated with bond stretching, bond-angle bending, and bond-angle torsions, respectively; $U_{\text{interaction}}$ consist of energies associated with force field cross-interactions; and U_{nb} are the energies associated with non-bonded atomic interactions, such as van der Waals, hydrogen, and electrostatic bonding. For example, the specific energy terms for bond stretching, and angle bending are

$$U^m = \sum_a K_a^p (\rho_a - P_a)^2 + \sum_a K_a^\theta (\theta_a - \Theta_a)^2, \quad (24)$$

where the terms P_a and Θ_a refer to the undeformed interatomic distance of bond number a and the undeformed bond-angle number a , respectively. The quantities ρ_a and θ_a are the distance and bond-angle after stretching and angle variance, respectively. The symbols K_a^p and K_a^θ represent the force constants associated with the stretching and angle variance of bond and bond-angle number a , respectively. The individual energy contributions are summed over the total number of corresponding interactions in the molecular model.

In the second step, an equivalent-continuum model is developed in which the mechanical properties are determined based on energetic contributions that describe the bonded and non-bonded interactions of the atoms in the molecular model and reflect the local nanostructure. The transition from molecular model to continuum is facilitated by the selection of a RVE. The RVE is several nanometers in extent and thus consists of an assemblage of many atoms. As depicted schematically in Fig. 12, a pin-jointed truss model that uses truss elements to represent the chemical bonds in the lattice structure may represent the RVE. The total mechanical strain energy of the truss model may take the form

$$E^t = \sum_b \sum_a \frac{A_a^b Y_a^b}{2R_a^b} (r_a^b - R_a^b)^2, \quad (25)$$

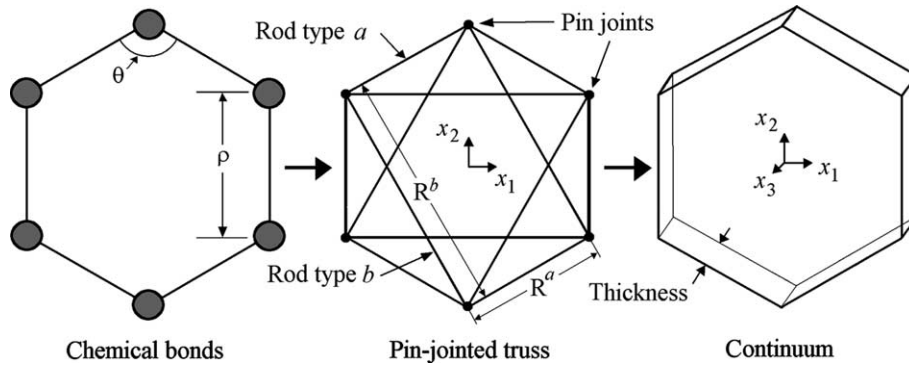


Fig. 12. Representative volume elements for the chemical, truss, and continuum models where θ , ρ , and R are dimensions.

where the term $r_a^b - R_a^b$ is the stretching of rod a of truss member type b , where R_a^b and r_a^b are the undeformed and deformed lengths of the truss elements, respectively. This truss-model representation can then be modeled directly by using the FEM [20].

To develop the correspondence between the molecular and equivalent-continuum models, the total strain energies for the two models are calculated under identical loading conditions. The effective mechanical properties, or the effective geometry, of the equivalent-continuum is determined by the requirement that the strain energies be equal. The equivalent-continuum RVE can be used in a micromechanical analysis to determine the bulk constitutive properties of the composite [20].

The potential energy of the equivalent-continuum model is derived from thermodynamic potentials in a finite-deformation framework, e.g., the Saint–Venant Kirchhoff model,

$$U_{\text{total}}(\mathbf{E}) = \frac{\lambda}{2}(\text{tr}\mathbf{E})^2 + \mu\text{tr}(\mathbf{E}^2), \quad (26)$$

where \mathbf{E} is the Lagrangian strain tensor, λ and μ are Lamé constants, $\text{tr}\mathbf{E}$ is the trace of the tensor \mathbf{E} , and $\text{tr}(\mathbf{E}^2)$ is the trace of tensor \mathbf{E}^2 . The Lagrangian strain tensor is determined from

$$\mathbf{E} = \frac{1}{2}(\mathbf{F}^T\mathbf{F} - \mathbf{I}), \quad (27)$$

where \mathbf{F} is the deformation gradient in Eq. (14) the superscript T indicates a tensor transpose, and \mathbf{I} is the identity tensor. The potential energy of the equivalent-continuum model is used to determine the equivalent-continuum constitutive equation

$$\mathbf{S} = \frac{\partial U(\mathbf{E})}{\partial \mathbf{E}}, \quad (28)$$

where \mathbf{S} is the Second-Piola Kirchhoff stress tensor. Substitution of Eq. (26) into (28) results in

$$\mathbf{S} = \lambda\text{tr}(\mathbf{E})\mathbf{I} + 2\mu\mathbf{E}. \quad (29)$$

The material parameters in Eq. (29) are determined by equating Eqs. (23) and (26) under identical boundary conditions. This modeling approach has been used to predict the mechanical properties of carbon nanotubes, polymers, nanotube/polymer composites, and nanoparticle/polymer composites. As an example, the RVEs of the molecular and equivalent-continuum models of a polyimide are shown in Fig. 13 [74]. The predicted Young's moduli and shear moduli of the polyimide are shown in Table 4 for the OPLS-AA [75,76] and MM3 [77] force fields. For comparison purposes, the experimentally determined Young's and shear moduli are included in Table 4. The data indicates a strong relationship between force field and predicted elastic properties.

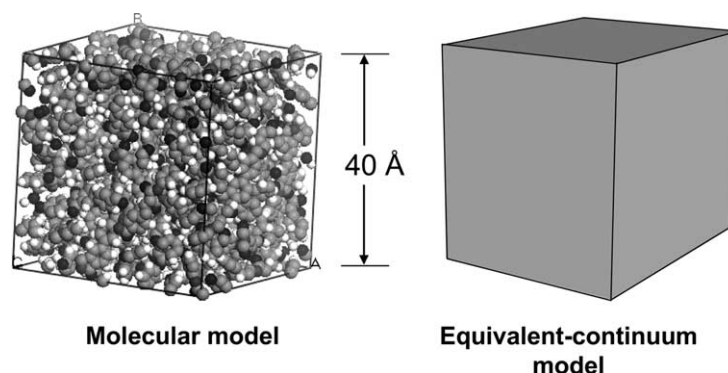


Fig. 13. Molecular and equivalent-continuum model of a polyimide.

Table 4
Predicted elastic properties of a polyimide [76]

| Method | Young's modulus (GPa) | Shear modulus (GPa) |
|----------------------------------|-----------------------|---------------------|
| Simulation (OPLS-AA force field) | 2.7 | 0.9 |
| Simulation (MM3 force field) | 5.9 | 2.1 |
| Experiment | 3.6 | 1.3 |

10. Modeling – summary

The multi-scale, computational materials modeling approach illustrates one of the primary challenges associated with hierarchical modeling of materials; namely, the accurate prediction of physical/chemical properties and behavior from nanoscale to macroscale without loss of intrinsic structural information. The time and length scales associated with the simulation methods described in the preceding sections have been illustrated in Fig. 1, with each method placed according to the upper range of its resolution. As one moves across a scale, overlaps on both time and length resolution occur, but the overall trend is consistent.

It is recognized that at each level of homogenization or scale-up, the risk of losing the key structural information increases. The way to provide an accurate check and balance against these losses is to establish verification of analysis methods and validation of simulations at both the atomic and bulk scales.

11. Verification and validation

To gain confidence in a model and to evaluate the utility of the simulation, both verification and validation need to be addressed. The American Society of Mechanical Engineers (ASME) has recently taken on this task in a Standards committee that was formed in September of 2001 on “Verification and Validation in Computational Solid Mechanics.” This committee defined verification as the “process of determining that a model implementation accurately represents the developer’s conceptual description of the model and the solution to the model.” Essentially, this is a mathematics issue that checks whether the modeler is solving the equations correctly. Validation was defined as the “process of determining the degree to which a model is an accurate representation of the physical world from the perspective of the intended uses of the model.” Therefore, validation is a physics issue that checks whether the analyst is solving the right equations.

Of course, the issues of verification and validation are not unique to Computational Materials and have been a continuous source of discussion. In a 1967 lecture on the interaction of theory and experiments, Drucker [78] stated that the purpose of experiment is to “guide the development of theory by providing the fundamental

basis for an understanding of the real world.” On the topic of scale, Drucker goes on to state that the continuum models could be used at the microscale but that “unless they are modified drastically, they cannot contain the information provided by experimental observation.” He also warns “observations made on the free surface do not necessarily indicate what is happening throughout the bulk of the material.” In a more recent paper, Knauss [79] provides the definitions and relationships among measurements, experiments, models and theory. He states “the method consists in observing physical fact(s) and formulating an analytical framework for them to produce a scheme or theory by which other physical results can be predicted” and warns against “theories or models that are ultimately no more than a demonstration of computational feasibility, without adding any really new understanding of the underlying science.” On the topic of scale, Knauss notes that at the nanoscale “there will be a continuing need to simulate such large molecular structures through assumptions that need physical examination, i.e., experimentation at the nanoscale.”

Schematically, these ideas, the processes of verification and validation and the relationship to measurements and experiments are illustrated in Fig. 14. Although the process of verification and validation is somewhat circular, the entry point into this process is clearly through experiments that help determine the validity of theory and assumptions while also helping to quantify the state variables associated with the problem.

It is therefore necessary that the Computational Materials approach must use experimental data to establish the range of performance of a material and to validate predicted behavior. Even at the atomistic level, methods such as molecular dynamics require careful parameterization (fit) to empirical data.

Therein, perhaps, lays the biggest challenge to Computational Materials: validation of methods across the complete range of length and time scales. To achieve this validation requires advances in measurement sciences as well as advances in theory and models, coupled with integrated, interdisciplinary research. It is imperative

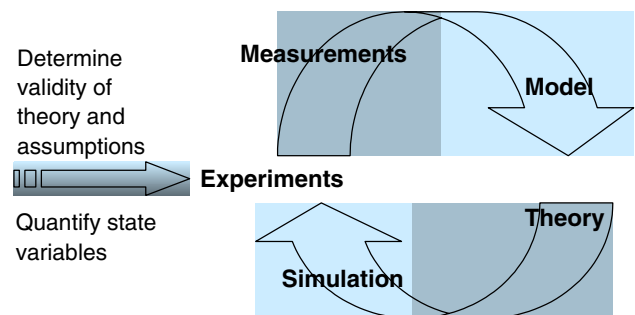


Fig. 14. Illustration of the circular relationship between the necessary elements of a successful multi-scale modeling approach.

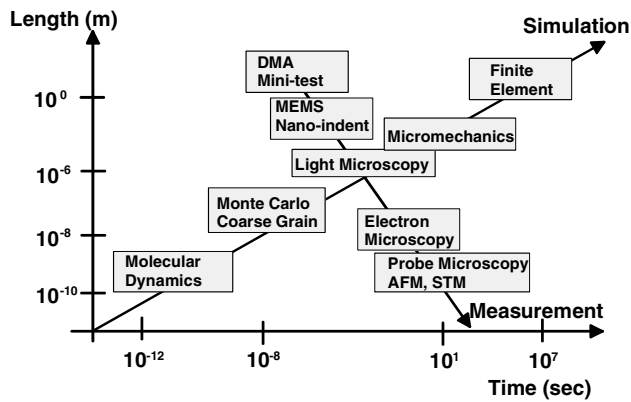


Fig. 15. Intersection of simulation and measurement methods highlighting the challenges for validation of multi-scale modeling methods.

that research laboratories maintain a focused effort to develop new programs that provide for the simultaneous growth of all the critical elements that are required for validation of multi-scale methods.

11.1. Spatial resolution of measurement devices

The spatial resolution of the previously described measurement devices is an important consideration for Computational Materials. A numerical comparison of typical spatial resolution is provided in Table 2.

However, to correctly address the requirements of characterizing nanostructured materials, the time-scale limits must also be taken into consideration. To put these limits in perspective, Fig. 2 illustrates how the primary measurement devices used in a Computational Materials program compare on a time versus length-scale plot. In this Figure, each device is placed according to the upper range of its resolution. As one moves across a scale, overlaps on both time and length resolution occurs, but the overall trend is consistent. An important break point on this plot occurs at the wavelength of light. At lengths greater than this break point, most displacement measurements are field quantities while below this break point displacement measurements are point quantities.

Overlaying Figs. 1 and 2 onto a single plot provides a comparison between the spatial and time scales of measurement and simulation. This comparison plot is shown in Fig. 15. Although this comparison is somewhat subjective, the obvious result is that direct validation of molecular-scale simulation methods, such as MD, are difficult because of the limited time-scale range of the measurement methods such as electron and probe microscopy.

12. Concluding remarks

Computational Materials research that relies on multi-scale modeling has the potential to significantly reduce development costs of new nanostructured materials for

demanding structural applications by bringing physical and microstructural information into the realm of the design engineer. The intent is to assist the material developer by providing a rational approach to material development and concurrently assist the structural designer by providing an integrated analysis tool that incorporates fundamental material behavior. The approach is to draw upon advances in measurement sciences and information technology to develop multi-scale simulation methods that are validated by critical experiments across a wide range of time and length scales. Currently, key structure–property relationships are being addressed by effective continuum methods that include molecular dynamics, coarse grain simulation, micromechanics, and finite element methods. Advances to date include constitutive relationships and effective-continuum representations of polymers and polymer/nanotube composite materials. Critical issues that remain unresolved include seamless transfer of data between the nano-to-meso-scale models and experimentally validating simulations of atomistic behavior.

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References

- [1] Feynman R. There's plenty of room at the bottom. Pasadena: American Physical Society; 1959.
- [2] National nanotechnology initiative: the initiative and its implementation plan, National Science and Technology Council, Committee on Technology, Subcommittee on Nanoscale Science, Engineering and Technology; 2000.
- [3] Edelman AS, Cammarata RC, editors. Nanomaterials: synthesis, properties and applications. Bristol: Institute of Physics; 1996.
- [4] Kroto HW et al. C60 Buckminsterfullerene. Nature 1985;318:162.
- [5] Iijima S. Helical microtubes of graphitic carbon. Nature 1991;354:56.
- [6] Harris PJF. Carbon nanotubes and related structures. Cambridge: Cambridge University Press; 1999.
- [7] Hinkley JA, Devern JF. Crystallization of stretched polyimides: a structure–property study. NASA Langley Research Center, NASA/TM-2002-211418; 2002.
- [8] Alder BJ, Wainwright TE. Phase transition for a hard sphere system. J Chem Phys 1957;27:1208–11.
- [9] Alder BJ, Wainwright TE. Studies in molecular dynamics. I. General method. J Chem Phys 1959;31:459–66.
- [10] Rahman A. Correlations in the motion of atoms in liquid argon. Phys Rev 1964;136(2A):405–11.
- [11] Young JA, Farmer BL, Hinkley JA. Molecular modeling of the poling of piezoelectric polyimides. Polymer 1999;40(10):2787.
- [12] Young JA, Hinkley JA, Farmer BL. Molecular simulations of the imidization of adsorbed polyamic acid. Macromolecules 2000;33:4936.

- [13] Car R, Parrinello M. Unified approach for molecular dynamics and density functional theory. *Phys Rev Lett* 1985;55:2471.
- [14] Frankland SJV et al. Molecular simulation of the influence of chemical cross-links on the shear strength of carbon nanotube–polymer interfaces. *J Phys Chem B* 2002;106(12):3046–8.
- [15] Saether E, Pipes RB, Frankland SJV. Transverse mechanical properties of single-walled carbon nanotube crystals. Part I. Determination of elastic moduli. *Compos Sci Technol* 2003;63:1543–50.
- [16] Wolf D. Deformation of nanocrystalline materials by molecular dynamics simulation: relationship to experiments. *Acta Mater* 2005;53:1–40.
- [17] Rountree CL et al. Atomistic aspects of crack propagation in brittle materials. *Annu Rev Mater Res* 2002;32:377–400.
- [18] Zwanzig R. Time correlation function and transport coefficients in statistical mechanics. *Annu Rev Phys Chem* 1965;16:67–102.
- [19] Smith GD et al. A molecular dynamics simulation study of the viscoelastic properties of polymer nanocomposites. *J Chem Phys* 2002;117:9478–89.
- [20] Odegard GM, Frankland SJV, Gates TS. The effect of chemical functionalization on mechanical properties of nanotube/polymer composites. In: 44th AIAA/ASME/ASCE/AHS Structures, structural dynamics, and materials conference, Norfolk, VA; 2003.
- [21] Brenner DW. Empirical potential for hydrocarbons for use in simulating the chemical vapor deposition of diamond films. *Phys Rev B* 1990;42:9458–71.
- [22] Theodorou DN, Suter UW. Atomistic modeling of mechanical properties of polymeric glasses. *Macromolecules* 1986;19(1): 139–54.
- [23] Zhou M. A new look at the atomic level virial stress: on continuum-molecular system equivalence. *Proc R Soc Lond Ser A* 2003;459:2347–92.
- [24] Haile JM. *Molecular dynamics simulations: elementary methods*. New York: John Wiley & Sons, Inc.; 1992.
- [25] Frankland SJV et al. The stress–strain behavior of polymer–nanotube composites from molecular dynamics simulation. *Compos Sci Technol* 2003;63(11):1655–61.
- [26] Lopez CF et al. Computer simulation studies of biomembranes using a coarse grain model. *Comput Phys Commun* 2002;147:1–6.
- [27] Kremer K, Muller-Plathe F. Multiscale problems in polymer science: simulation approaches. *Mater Res Soc Bull* 2001(March): 205–14.
- [28] Hinkley JA, Young JA. Monte Carlo simulation of endlinking oligomers, NASA Langley Research Center, NASA/TM-1998-207649; 1998.
- [29] Binder K, editor. *Monte Carlo and molecular dynamics simulations in polymer science*. New York: Oxford University Press; 1995.
- [30] Raabe D. *Computational materials science*. Weinheim: Wiley-VCH; 1998.
- [31] Baschnagel J et al. Bridging the gap between atomistic and coarse-grained models of polymers: status and perspectives. *Adv Polym Sci* 2000;152:41–156.
- [32] Müller-Plathe F. Coarse-graining in polymer simulation: from the atomistic to the mesoscopic and back. *Chem Phys Chem* 2002;3(9):754–69.
- [33] Doruker P, Mattice WL. A second generation of mapping/reverse mapping of coarse-grained and fully atomistic models of polymer melts. *Macromol Theory Simul* 1999;8(5):463–78.
- [34] Tschop W et al. Simulation of polymer melts. I. Coarse-graining procedure for polycarbonates. *Acta Polym* 1998;49(2–3):61–74.
- [35] Allen MP, Tildesley DJ. *Computer simulation of liquids*. New York: O.U. Press; 1987.
- [36] Clancy TC. Multi-scale modeling of polyimides. *Polymer* 2004;45:707–10.
- [37] Clancy TC, Hinkley J. Coarse-grained and atomistic modeling of polyimides. National Aeronautics and Space Administration, NASA/TM-2004-213030; 2004.
- [38] Odegard GM, Clancy TC, Gates TS. Modeling the mechanical properties of nanoparticle/polymer composites. *Polymer* 2005;46(2):553–62.
- [39] Mase GE. *Theory and problems of continuum mechanics*. Schaum's outline series. New York: McGraw-Hill; 1970.
- [40] Yang TY. *Finite element structural analysis*. Englewood Cliffs: Prentice-Hall; 1986.
- [41] Nemat-Nasser S, Hori M. *Micromechanics: overall properties of heterogeneous materials*. 2nd ed. Amsterdam: Elsevier; 1999.
- [42] Reddy JN. *An introduction to the finite element method*. New York: McGraw-Hill; 1984.
- [43] Fung YC. *Foundations of solid mechanics*. Englewood Cliffs (NJ): Prentice-Hall, Inc; 1965.
- [44] Born M, Huang K. *Dynamical theory of crystal lattices*. London: Oxford University Press; 1954.
- [45] Kittel C. *Introduction to solid state physics*. 4th ed. New York: Wiley; 1971.
- [46] Dow JO, Huyer SA. Continuum models of space station structures. *J Aerospace Eng* 1989;2(4):220–38.
- [47] Lee U. Equivalent continuum models of large plate-like lattice structures. *Int J Solids Struct* 1994;31(4):457–67.
- [48] Noor AK. Continuum modeling for repetitive lattice structures. *Appl Mech Rev* 1988;41(7):285–96.
- [49] Noor AK, Anderson MS, Greene WH. Continuum models for beam- and platelike lattice structures. *AIAA J* 1978;16(12): 1219–28.
- [50] Sun CT, Kim BJ, Bogdanoff JL. On the derivation of equivalent simple models for beam and plate-like structures in dynamic analysis. In: 22nd AIAA/ASME/ASCE/AHS structures, structural dynamics & materials conference. Atlanta: American Institute of Aeronautics and Astronautics; 1981.
- [51] Sun CT, Leibbe SW. Global–local approach to solving vibration of large truss structures. *AIAA J* 1990;28(2):303–8.
- [52] Eringen AC. Linear theory of micropolar elasticity. *J Math Mech* 1966;15(6):909–23.
- [53] Miller R et al. Quasicontinuum simulation of fracture at the atomic scale. *Model Simul Mater Sci Eng* 1998;6(5):607–38.
- [54] Shenoy VB et al. Quasicontinuum models of interfacial structure and deformation. *Phys Rev Lett* 1998;80(4):742–5.
- [55] Shenoy VB et al. An adaptive finite element approach to atomic-scale mechanics – the quasicontinuum method. *J Mech Phys Solids* 1999;47(3):611–42.
- [56] Tadmor EB, Ortiz M, Phillips R. Quasicontinuum analysis of defects in solids. *Philos Mag A* 1996;73(6):1529–93.
- [57] Tadmor EB, Phillips R, Ortiz M. Mixed atomistic and continuum models of deformation in solids. *Langmuir* 1996;12(19): 4529–34.
- [58] Tadmor EB, Phillips R, Ortiz M. Hierarchical modeling in the mechanics of materials. *Int J Solids Struct* 2000;37(1–2):379–89.
- [59] Daw MS, Baskes MI. Semiempirical, quantum mechanical calculation of hydrogen embrittlement in metals. *Phys Rev Lett* 1983;50(17):1285–8.
- [60] Abraham FF et al. Spanning the continuum to quantum length scales in a dynamic simulation of brittle fracture. *Europhys Lett* 1998;44(6):783–7.
- [61] Broughton JQ et al. Concurrent coupling of length scales: methodology and application. *Phys Rev B* 1999;60(4):2391–403.
- [62] Liu B et al. The atomic-scale finite element method. *Comput Meth Appl Mech Eng* 2004;193(17–20):1849–64.
- [63] Nakano A et al. Multiscale simulation of nanosystems. *Comput Sci Eng* 2001;3(4):56–66.
- [64] Wagner GJ, Liu WK. Coupling of atomistic and continuum simulations using a bridging scale decomposition. *J Comput Phys* 2003;190(1):249–74.
- [65] Xiao SP, Belytschko T. A bridging domain method for coupling continua with molecular dynamics. *Comput Meth Appl Mech Eng* 2004;193(17–20):1645–69.

- [66] Li CY, Chou TW. A structural mechanics approach for the analysis of carbon nanotubes. *Int J Solids Struct* 2003;40(10):2487–99.
- [67] Li CY, Chou TW. Elastic moduli of multi-walled carbon nanotubes and the effects of van der Waals forces. *Compos Sci Technol* 2003;63(11):1517–24.
- [68] Li CY, Chou TW. Multiscale modeling of carbon nanotube reinforced polymer composites. *J Nanosci Nanotechnol* 2003;3(5):423–30.
- [69] Li CY, Chou TW. Modeling of elastic buckling of carbon nanotubes by molecular structural mechanics approach. *Mech Mater* 2004;36(11):1047–55.
- [70] Li CY, Chou TW. Strain and pressure sensing using single-walled carbon nanotubes. *Nanotechnology* 2004;15(11):1493–6.
- [71] Odegard GM, et al. Modeling and characterization of a graphite nanoplatelet/epoxy composite. In: SEM X international congress and exposition on experimental and applied mechanics, Costa Mesa, CA; 2004.
- [72] Odegard GM et al. Equivalent-continuum modeling of nano-structured materials. *Compos Sci Technol* 2002;62(14):1869–80.
- [73] Odegard GM et al. Constitutive modeling of nanotube-reinforced polymer composites. *Compos Sci Technol* 2003;63(11):1671–87.
- [74] Odegard GM, Clancy TC, Gates TS. Prediction of mechanical properties of polymers with various force fields. In: 46th AIAA/ASME/ASCE/AHS/ASC structures, structural dynamics, and materials conference, Austin, TX; 2005.
- [75] Jorgensen WL, Maxwell DS, Tirado-Rives J. Development and testing of the OPLS all-atom force field on conformational energetics and properties of organic liquids. *J Am Chem Soc* 1996;117:11225–36.
- [76] Kaminsky GA et al. Evaluation and reparametrization of the OPLS-AA force field for proteins via comparison with accurate quantum chemical calculations on peptides. *J Phys Chem B* 2001;105:6474–87.
- [77] Allinger NL, Yuh YH, Lii JH. Molecular mechanics. The MM3 force field for hydrocarbons. *J Am Chem Soc* 1989;111:8551–66.
- [78] Drucker DC. Thoughts on the present and future interrelation theoretical and experimental mechanics. *Exp Mech* 1968.
- [79] Knauss WG. Perspectives in experimental solid mechanics. *Int J Solids Struct* 2000;37:251–66.