

Computational Nano-mechanics and Multi-scale Simulation

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Abstract: This article provides a review of the computational nanomechanics, from the *ab initio* methods to classical molecular dynamics simulations, and multi-temporal and spatial scale simulations. The recent improvements and developments are briefly discussed. Their applications in nanomechanics and nanotubes are also summarized.

1 Introduction

Due to their potentially remarkable mechanical properties, nano-structured materials have stimulated a lot of interest in the materials research community in the last few years. The design and fabrication of these materials are performed on the nanometer scale, with the ultimate goal of obtaining highly desirable macroscopic properties. In particular, materials such as nanotubes, nanoparticle-reinforced polymers and metals, and nano-layered materials have shown considerable promise. With the advances in materials synthesis and device processing capabilities, the importance of developing and understanding nanoscale engineering devices has dramatically increased over the past decade. Nanotechnology deals with materials, devices, and their applications at the nanoscale, where many diverse enabling disciplines and associated technologies start to merge, because these are derived from the rather similar properties of the atomic or molecular level building blocks. The subject of nanoscience/technology is defined as the science and technology of the direct or indirect manipulation of atoms and molecules into functional structures, with applications that were never envisioned before [Srivastava and Atluri (2002)]. Nano-mechanics deals with mechanics problems associated with modeling, design, fabrication and application of three-dimensional structures and systems with nanometer-scale dimensions. Nanoscale systems have a number of interesting features which distin-

guish them from micro- and macro-scale systems.

An underlying issue in modeling the macroscopic mechanical behavior of nano-materials, based on molecular structure, is the large difference in temporal and spatial scales. Computational molecular dynamics and continuum mechanics are on the opposite ends of the temporal and spatial scale spectrum, and consist of highly developed and reliable modeling methods. Computational continuum mechanics methods predict the macroscopic mechanical behavior of materials idealized as continuous media, based on known constitutive relationships of the bulk material, while computational molecular dynamic models predict molecular properties based on known quantum interactions. However, a corresponding model does not exist in the intermediate time and length scale range, where the disparate length scales associated with molecular and continuum phenomena, and disparate time-scales of the molecular and continuum phenomena, may be present *simultaneously*. If a hierarchical approach is used to model the macroscopic behavior of nano-materials, then a methodology is needed to link the molecular structure and macroscopic properties.

However, systems with multiple length scales are ubiquitous in science, for example, the sub-micron Micro-Electro-Mechanical Systems (MEMS), or even Nano-Electro-Mechanical Systems (NEMS), where the behavior is determined by the interplay between the micron-scale continuum mechanics and the nanoscale atomistic processes. The continuum mechanics is governed largely by the geometry of the device, while the atomistic processes are important only in its smallest features. Continuum analyses are appropriate only for a large enough system. The nano-scale is the length scale of individual atoms, i.e. 1-10 nm. At such small length scales, continuum models are not flexible enough to accommodate the individual atomic scale processes. Alternative to continuum analysis, the atomistic modeling and simulation calculates, individual atoms explicitly, and follows them during their dynamic evolution. Even though

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this atomistic method can trace all the details of atomic-scale processes explicitly, it still has time and length scale limitations from both small and large directions. When the length-scale cannot be accessed either by continuum methods, since it is too small for averaging, or by the atomistic methods (molecular dynamics or quantum mechanics), since it is too large for simulations on the current computers, these two approaches become inadequate, which has presented significant challenges to the scientific community.

The amount of computer resources needed to investigate a given volume of matter dramatically increases as one goes from the top down to the bottom, i.e. from the continuum, through the mesoscopic, the atomistic and to the quantum methods. Quantum mechanics solves Schrödinger's equation for the electrons in the system. Atomistic methods generally model atoms as spheres which may be linked together to form molecules. By assuming point charges on the nuclei of the atoms, electrostatic interactions are included. Mesoscopic methods are based on local groups of atoms, which generally represent many atoms with a considerable internal flexibility. Such groups can also be linked together to represent molecules. There exist a number of continuum approaches, such as the finite element method, the boundary element method and the meshless method *etc.* The length scales of the typical material system in multi-scale structures are shown in Fig. 1. Multiscale modeling is a unifying paradigm to enable the integration of the basic science and the engineering system. It allows for a rigorous correlation of different science and engineering models, representations, languages and metrics.

Carbon nanotubes have attracted considerable attention since they were discovered by Iijima (1991). The extraordinary properties of carbon nanotubes have motivated researchers worldwide to study the fundamentals of this novel material as well as to explore their applications in different fields [Ajayan and Zhou (2001)]. Application

of carbon nanotubes in nanoelectronics, nanocomposite materials, and NEMS is a typical multi-scale problem, which also impels the study on the multi-scale model that directly links the continuum theories to atomistic simulations.

This paper will review the current status of the progresses and developments in computational nanotechnology and multiscale simulation. The paper is organized as follows. Section 2 summarizes the simulation methods from quantum level to atom level; and the long range interactions are also included. Section 3 focuses on the multi-scale methods. Section 4 discusses the simulation methods for nanotubes. Finally, conclusions are made in Section 5.

2 Computational Techniques for Nanoscale Simulations

Since the spatial and temporal scales of nanoscale systems and phenomena have shrunk to the level where they can be directly addressed with high-fidelity computer simulations and theoretical modeling, computational nanotechnology [Srivastava and Atluri (2002a, b); Srivastava, Menon, and Cho (2001)] has become critically important in nanodevice development [Ajayan and Zhu (2001)]. *ab initio* methods are being used extensively, which can determine the electronic and atomic structures of different materials just from its atomic coordinates. However, the applications of *ab initio* methods are limited to very small-scale systems with only a few hundred atoms. Alternatively, tight-binding molecular dynamics (TBMD) and classical molecular dynamics (MD) offer powerful ways to treat even large-scale systems. Tight-binding molecular dynamics (TBMD) is a semi-empirical technique, which is a blend of certain features from both MD and *ab initio* methods. Molecular dynamics (MD) refers most commonly to the situation where the motion of atoms or molecules is treated in approximated finite difference equations of Newtonian mechanics. In fact, *ab initio* and TBMD are the quantum mechanics (QM) schemes. In this section, we summarize the main simulation approaches in computational nanotechnology.

2.1 *Ab initio* methods

Quantum mechanics is a means to understand and predict the interactions between atoms and molecules, and to model the chemical reactions at that scale. It uses

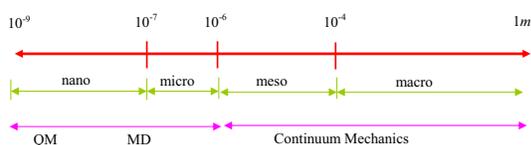


Figure 1 : The length scales of the material system

models based on the electronic structure. The solution of the Schrödinger's equation provides the electronic wave functions. Other properties are then obtained from these functions. The *ab initio* or first-principles method solves the complex quantum many-body Schrödinger equation with numerical algorithms [Payne, Teter, Allan, Arias, and Joannopoulos (1992)]. This method is to regard many-atom systems as many-body systems composed of electrons and nuclei, and to treat everything on the basis of first-principles of quantum mechanics, without introducing any empirical parameters [Ohno, Esfarjani and Kawazoe (1999)]. The *ab initio* method provides more accurate descriptions of quantum mechanical behavior of materials. However, currently the system sizes are limited to only about a few hundred atoms. In the general approach of quantum mechanics, atoms are represented as a collection of quantum mechanical particles, nuclei and electrons; the state of a particle is defined by a wave function ψ , based on the well-known wave-particle duality. The Schrödinger equation is [Born, and Huang (1954)]

$$H\psi(r_i, R_I) = E_{tot}\psi(r_i, R_I) \quad (1)$$

with the full quantum many-body Hamiltonian operator

$$H = \sum_I \frac{P_I^2}{2m_I} + \sum_{I,J} \frac{Z_I Z_J e^2}{R_{IJ}} + \sum_i \frac{p_i^2}{2m_e} + \sum_{i,i} \frac{e^2}{r_{ij}} - \sum_{I,i} \frac{Z_I e^2}{|R_I - r_i|} \quad (2)$$

where ψ is the energy eigenfunction corresponding to the energy eigenvalue E_{tot} , which represents the total energy of the system, R_I and r_i are the nuclei and electron coordinates, respectively, $R_{IJ} = |R_I - R_J|$ and $r_{ij} = |r_i - r_j|$. P_I and p_i are the nuclei and electron momenta, respectively. m_I and m_e are nuclei and electron mass, respectively. e is the electric charge of an electron, and $Z_I e$ is the electric charge of the nuclei of atom I . The Hamiltonian operator in equation (2) is composed of five parts. The first and third terms in equation (2) give the kinetic energy of the nucleus and electron, respectively; the second term gives the nucleus-nucleus Coulomb interaction, the fourth term gives the electron-electron Coulomb interaction, and the last terms gives the nucleus-electron Coulomb interaction.

After solving for the energy E_{tot} , the interatomic potential of the system can be obtained. Then, the interactions F_I , between atoms can be derived from

$$\mathbf{F}_I = -\frac{\partial V}{\partial \mathbf{R}_I} \quad (3)$$

where V is the atomic interaction potential. Since the kinetic energy of the nucleus is independent of its position, V can be replaced by E_{tot} in equation (3). Hence, as long as E_{tot} is determined, the interactions F_I can be obtained according to equation (3). The dynamic motion for the atomic positions is still governed by Newtonian or Hamiltonian mechanics, i.e.

$$m_I \ddot{\mathbf{R}}_I = \mathbf{F}_I = -\frac{\partial V}{\partial \mathbf{R}_I} \quad (4)$$

Equations (4) are approximated as finite-difference equations with discrete time step Δt . Due to the small scale involved, explicit integration algorithms such as the standard Gear's fifth-order predictor-corrector or Verlet's leapfrog methods [Verlet (1967), Berendsen, van Gunsteren (1986)], which will be described in detail in section 2.3, are commonly used to ensure high order accuracy.

In using the *ab initio* method, effective and applicable assumptions are necessary. The most commonly used approximation is the Born-Oppenheimer adiabatic approximation [Ohno, Esfarjani, and Kawazoe (1999)], which assumes that the electrons are always in a steady state, derived from their averaged motion, since their positions change rapidly compared to the nuclear motion. Hence, the motion of the electrons can be considered separately from the motion of the nuclei, as if the nuclei were stationary. Using this approximation, one can reduce the full quantum many-body problem to a quantum many-electron problem:

$$H_{el}(R_I)\psi(r_i) = E_{el}\psi(r_i) \quad (5)$$

where E_{el} is the ground state energy of a many-electron system and can be regarded as the atomic interaction potential, and

$$H = \sum_I \frac{P_I^2}{2m_I} + H_{el}(R_I) \quad (6)$$

It is very difficult to solve the eigen equation (5) exactly, and approximate methods have been developed. The most commonly used approaches are the Hartree-Fock approximation [Fock (1930), Hartree (1928)] and the density functional theory [Hohenberg and Kohn, 1964].

A detailed description and survey of the Hartree-Fock approximation can be found in Clementi (2000) and Ohno, Esfarjani and Kawazoe (1999). Here, we omit

the details. The Hartree-Fock approximation is usually used to describe electron-electron interaction effects. In the Hartree-Fock approximation, the ground state of the Hamiltonian H is obtained by means of the variational principle with a normalized set of wave functions. Actually, the methodology seeks the solution by minimizing the expected value of H with a trial function, similar to the Ritz method. Many *ab initio* simulations used the Hartree-Fock approximation, which translates a many-electronic problem into a single electronic problem. Then, the Hartree-Fock equation can be written as

$$H_{HF}\Psi_i(r) = \varepsilon_i\Psi_i(r) \quad (7)$$

which is derived from the variational principle [Ohno, Esfarjani and Kawazoe (1999)], where H_{HF} is the Hartree-Fock operator, which consists of the one-electron Hamiltonian, the Hartree operator (or Coulomb term), and the Fock operator (or exchange term). Ψ_i is the molecular orbit, and ε_i is the orbital energy of the electron in this orbital. The molecular orbit is assumed to be the linear combination of atomic orbitals (LAO), as

$$\Psi_i = \sum_{\alpha} c_{\alpha}^i \phi_{\alpha} \quad (8)$$

where ϕ_{α} is the α th atomic orbital and c_{α}^i is the coefficient. Adopting the closed shell model, the Hartree-Fock equation can be conveniently written as a matrix form

$$\mathbf{FC} = \mathbf{SCE} \quad (9)$$

The above equation is called Roothaan-Hall equation. The Fock matrix \mathbf{F} can be written as [Leach (1996)]

$$F_{\alpha\beta} = \int dv \phi_{\alpha} \left[-\frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{Z_A}{r_{iA}} \right] \phi_{\beta} + \sum_{\gamma=1}^K \sum_{\kappa=1}^K P_{\gamma\kappa} \left[(\alpha\beta|\gamma\kappa) - \frac{1}{2} (\alpha\gamma|\beta\kappa) \right] + V_{\alpha\beta} \quad (10)$$

where the first term is the core energy, the second term is energy arising from the Coulomb and exchange interaction. It is noted that in this equation, the atomic units are used. \mathbf{P} is the charge density matrix and can be written as

$$P_{\gamma\kappa} = 2 \sum_{i=1}^{N/2} c_{\gamma}^i c_{\kappa}^i \quad (11)$$

$(\alpha\beta|\gamma\kappa)$ and $(\alpha\gamma|\beta\kappa)$ are two-electron integrals that may involve up to four different basis functions ($\phi_{\alpha}, \phi_{\beta}, \phi_{\gamma}, \phi_{\kappa}$), which may in turn be located at four different centers. $V_{\alpha\beta}$ is the influence of external fields, \mathbf{S} is the overlap integrals matrix with

$$S_{\alpha\beta} = \int dv \phi_{\alpha} \phi_{\beta} \quad (12)$$

\mathbf{C} is the coefficient matrix, and \mathbf{E} is the orbital energy diagonal matrix. The Hartree-Fock approximation does not include correlation effects. It is more tractable for a system of a small number of atoms and becomes more complex for crystals. A better approximation, the local-density approximation (LDA), gives ground-state properties almost perfectly and more efficiently. As an alternative to the Hartree-Fock approximation, the LDA replaces the electron-electron interactions by some effective potential acting on the electrons. The LDA is an approximating method, and cannot be applied to excited states and highly correlated systems.

The density functional theory [Hohenberg and Kohn, 1964] has a rigorous mathematical foundation, provided by two important works [Hohenberg and Kohn (1964), Kohn and Sham (1965)]. Hohenberg and Kohn (1964) have developed a theorem: the ground state energy (E_{el}) of a many-electron system is a function of total electron density, $\rho(r)$, rather than the full electron wave function, $\Psi(r_i)$, $E_{el}(\Psi(r_i)) \equiv E_{el}(\rho(r))$. The Hamiltonian operator H and Schrödinger equation are given by

$$H(R_I) = \sum_i \frac{p_i^2}{2m_e} + \sum_{i,j} \frac{e^2}{r_{ij}} - \sum_{I,i} \frac{Z_I e^2}{|R_I - r_i|} + \sum_{I,J} \frac{Z_I Z_J e^2}{R_{IJ}} \quad (13)$$

$$H(R_I)\Psi(r_i) = E_{el}\Psi(r_i) \quad (14)$$

The density functional theory (DFT) is derived from the fact that the ground state total electronic energy is a functional of the total electron density. However, it is very difficult to formulate $E_{el}(\rho(r))$. Kohn and Sham (1965) have shown that the DFT can be formulated as a single-electron problem with self-consistent effective potential including all the exchange-correlation effects of electronic interactions. Then the Kohn-Sham equation can be written as

$$H_1\Psi_i(r) = \varepsilon_i\Psi_i(r), \quad i = 1, \dots, N_{tot} \quad (15)$$

which is the single-electron Schrödinger equation. Here, H_1 is the effective one-electron Hamiltonian, and can be

written as

$$H_1 = \frac{p^2}{2m_e} + V_H(r) + V_{NE}(r) + V_{XC}(\rho(r)) \quad (16)$$

$$\rho(r) = \sum |\psi_i(r)|^2 \quad (17)$$

In equation (16), the first term represents the electron kinetic energy, the second term represents the electrostatic potential, the third term represents the nucleus-electron interaction potential, and the last term denotes the exchange-correlation potential and is a function of the electron density. While the first three terms can be obtained explicitly, the last one must be approximated. The local density approximation (LDA) has been introduced to approximate the unknown effective exchange-correlation potential by Kohn and Sham (1965). The LDA assumes that the exchange-correlation function corresponds to the homogeneous electron gas. This assumption is only valid locally, when the inhomogeneity due to the presence of the nuclei is small. Once ψ_i and ϵ_i are solved from equation (15), the total energy can be obtained. The eigenvalues correspond to the quantum-mechanically possible electronic energy states of the system, and the eigenfunctions contain information about the electronic density distribution in the computed space. The DFT-LDA method has been very successful in predicting the properties of materials without using any experimental inputs other than the identity (i.e. atomic numbers) of constituent atoms [Car and Parrinello (1985)]. The major advantage of using LDA is that the error in the electron energy is second-order between any given electron density and ground state density.

For practical applications, a single electron wavefunction with a plane wave and pseudopotential have been implemented in the DFT-LDA method [Payne, Teter, Allan, Arias, and Joannopoulos (1992)]. These systematic approximations reduce the electronic structure problem to a self-consistent matrix diagonalization problem. The solution procedure requires an iterative diagonalization process, which in general involves $O(N^3)$ order of computation and limits the DFT-LDA method to simple systems, and the system sizes currently are limited to only about a few hundred atoms.

The limitation of the DFT-LDA method mainly comes from two aspects: one is the use of plane waves as a basis to expand the electron wave functions; the other is the inclusion of degrees of freedom from the electron wave functions in the molecular dynamics. The former limits

the number of atoms used in the simulation due to the large number of basis functions required in the calculation, and the latter leads to that the simulation time step has to be chosen much smaller than that in simulations with classical potential (about ten times smaller).

To reduce the order of computation, over the last three decades, a lot of researchers attempted to develop rapid and effective methods for solving the Kohn-Sham equation [Li, Nunes and Vanderbilt (1993), Daw (1993), Mauri and Galli (1994), Kresse and Furthmuller (1996)]. Major improvements have been made using the Car-Parrinello MD (CPMD) method [Car and Parrinello (1985)], cluster variation method [Kawazoe (2001)], and conjugate gradient (CG) minimization methods [Payne, Teter, Allan, Arias, and Joannopoulos (1992)]. CPMD has significantly improved the computational efficiency by reducing the order from $O(N^3)$ to $O(N^2)$. As shown by Payne, Teter, Allan, Arias, and Joannopoulos (1992), the CG method has further improved the efficiency by an additional factor 2-3.

The *ab initio* method makes it possible to model a few hundred atoms without any experimental inputs, and provides a powerful tool to investigate nanomaterials with predictive power. *Ab initio* method possesses high accuracy and transferability, due to there being no experimental inputs. However, the high order of computation limits the applicability of the *ab initio* method. Therefore, other methods, such as the tight-binding method or the classical molecular dynamics, are very important in order to overcome the complexities of some materials. In these methods, the potential parameters are extracted from the experiment or *ab initio* calculations. However, these methods are only valid in the region where they are fitted. Nevertheless, they are useful to study complex materials on the basis of these approximations.

A standard *Ab initio* routine is illustrated in Fig. 2.

2.2 Tight-binding methods

In the intermediate regime of a few hundred- to thousand-atom systems, where classical molecular dynamics method is not accurate enough, nor the *ab initio* computations are feasible, tight-binding [Slater and Koster (1954), Harrison (1980)], or semi-empirical quantum mechanics based methods, provide an important link between the *ab initio* quantum mechanics based approaches described above, and the classical atomistic force field based methods, that will be described below.

The tight binding method can handle a much larger system than the *ab initio* method, and has the information about the electronic structure of the system, while maintaining a better accuracy than the MD simulation. In its nature, the tight-binding method is very similar to Hartree-Fock methods, but the computations of the Hamiltonian and overlap matrix elements are based on semi-empirical formulae. In this method, the atoms are treated as classical particles that interact in part through an effective potential exerted by the electrons that are treated quantum mechanically. Hypothetical basis orbitals with the angular symmetries of single atom eigenstates are centered around each atom. In the tight binding method, the interatomic forces are evaluated in a straightforward way, based on the Hellmann-Feynman theorem and the rest of the procedure is almost identical to the MD simulation, that is the reason why the tight binding method is also referred to as tight binding MD method (TBMD).

The tight-binding method [Harrison (1980)] further simplifies the quantum many electron problem by assuming that the crystal potential is strong, such that when an ion captures an electron during its motion through the lattice, the electron remains at that site for a long time before

leaking, or tunneling, to the next ion site. During the capture interval, the electron orbits primarily around a single ion uninfluenced by other atoms, so that its state function is essentially that of an atomic orbital. Usually, the electron is tightly bound to its own atom. Hence, the total energy (or the interatomic potential) can be expressed as the sum of the eigenvalues of a set of occupied non-self-consistent one electron molecular eigenfunctions, in addition to certain analytical functions [Foulkes and Haydock (1989)]:

$$V_{TB} = \sum_{n=1}^{N_{occ}} \epsilon_n + \sum_{I<J} V^{rep}(\mathbf{R}_{IJ}) \quad (18)$$

The sum is over all occupied states N_{occ} up to the Fermi level. The first term on the right side is the sum of the energies of occupied orbits (i.e., band-structure energy), which can be solved from the Schrödinger equation (5). V^{rep} is the repulsive inter-atomic potential, and the double counting of the Coulomb and exchange-correlation terms inherent in the eigenvalue sum (the first term) are eliminated by the sum of the repulsive interatomic potential V^{rep} (the second term). Many papers [Wang and Ho (1993, 1996), Lewis and Mousseau (1998)] described how to obtain these two terms. Due to that V^{rep} is derived from the experiment, the TBMD method is a semi-empirical method. The eigenvalues ϵ_n corresponding to the one-electron states of a first principles Hartree-Fock or density functional theory are obtained from a nonorthogonal one-electron Hamiltonian

$$\mathbf{H}\psi_n = \epsilon_n \mathbf{S}\psi_n \quad (19)$$

$$\psi_n = \sum_{I\alpha} c_{I\alpha}^n \phi_{I\alpha} \quad (20)$$

where \mathbf{S} is the overlap matrix. It is noted that, in equation (20), a linear combination of atomic orbitals (referred to LACO), which is modulated by a Bloch wave-function phase factor for a periodic lattice, is adopted in the wave function: the one-electron wave function ψ_n is expanded as a linear combination of atomic basis functions $\phi_{I\alpha}$, as discussed in Hartree-Fock approximations. This ensures that an electron in a tight-binding level will be found, with equal probability, in any cell of the crystal, since its wave function changes only by the phase factor, as one electron moves from one cell to another. Here, n denotes

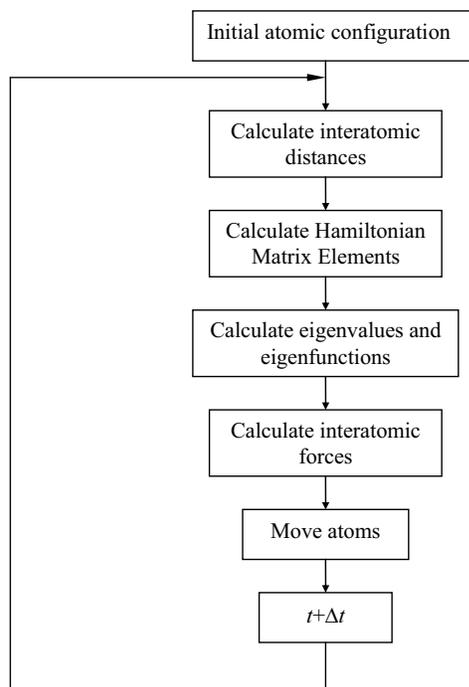


Figure 2 : An illustration of *ab initio* routine

the orbital number, and α denotes the basis functions (in the minimal basis of silicon, these represent s , p_x , p_y , and p_z atomic orbits). The details of the basis functions do not enter into the energy calculation, but only the interactions between basis elements $\phi_{I\alpha}$ that from the overlap and Hamiltonian matrices. The matrix elements within the overlap \mathbf{S} and Hamiltonian \mathbf{H} matrices are obtained by fitting the equivalent integrals within an extensive database of the first-principles calculations to a particular parametric form

$$\begin{aligned} S_{\alpha\beta}(\mathbf{r}_{IJ}) &= \langle \phi_{I\alpha} | \phi_{J\beta} \rangle \\ H_{\alpha\beta}(\mathbf{r}_{IJ}) &= \langle \phi_{I\alpha} | H | \phi_{J\beta} \rangle \end{aligned} \quad (21)$$

The function V^{rep} is also obtained by fitting to a database involving the experimental indirect band gap. The parameters for this fit are given by Bernstein and Kaxiras (1997). Although the exact forms of the basis are not known, the Hamiltonian and overlap matrix can be parameterized, and the total energy and electronic eigenvalues can be easily extracted from the Hamiltonian matrix, which also contains the effects of angular forces in a natural way. There are two approaches to perform parameterization process, one is fitting to results from the *ab initio* methods [Xu, Wang, Chan and Ho (1992), Mehl and Papaconstantopoulos (1996)], the other is computing the matrix exactly based on the localized basis [Liu (1995), Porezag, Frauenheim, Kohler, Seifert, and Kaschner (1995), Taneda, Esfarjani, Li, Kawazoe (1998)].

The process of solving for the coefficient $c_{I\alpha}^n$ is a generalized eigenvalue problem. For a given set of atomic coordinates, the coefficients are found by diagonalization. One-electron states are occupied up to Fermi level. The interatomic forces are evaluated in a straightforward way, based on the Hellmann-Feynman theorem, and the system's dynamic evolution is governed by Hamilton's classical equation of motion from Newton's second law:

$$m_I \ddot{\mathbf{R}}_I = \mathbf{F}_I = - \frac{\partial V_{TB}}{\partial \mathbf{R}_I} \quad (22)$$

After obtaining the force, atomic coordinates can be advanced through time, using the same algorithm as that used for the *ab initio* method or the classical MD, i.e., the standard Gear's fifth-order predictor-corrector or Verlet's leapfrog methods, which will be described in detail in section 2.3.

The TBMD is one of the fastest numerical quantum methods containing electronic structure information, and its application is extensive. Lewis and Mousseau (1998) used it to study defects and disorder in covalently bonded materials. Wang and Ho (1993) employed it to investigate the structure, dynamics and electronic properties of diamond-like amorphous carbon. Colombo (1998) provided a source code for TBMD simulations.

Since the brute force diagonalization is $O(N^3)$, which parallelizes poorly, in general, TBMD is an $O(N^3)$ algorithm. To reduce the order of computation (i.e., improve the scale of computation), Khan and Broughton (1989) implemented a fictitious Lagrangian to reducing the order from $O(N^3)$ to $O(N^2)$. There is much discussion in the literature about $O(N)$ schemes for electronic structure [Li, Nunes, and Vanderbilt (1993), Daw (1993), Canning, Galli, Mauri, De Vita, and Car (1996), Ordejon (1998)]. However, such methods often have problems with situations in which states wander across the Fermi level. Another way to improve the scale of the TBMD is the parallel simulation [Kalia, Campbell, Chatterjee, Nakano, Vashishta, Ogata (2000)]. The parallelization of the TBMD code involves parallelizing the direct diagonalization (of the electronic Hamiltonian matrix) part as well as the MD part. Parallelizing a sparse symmetric matrix with many eigenvalues and eigenvectors is a complex bottleneck in the simulation of large intermediate-range system and requires new algorithms. A survey of the parallel simulation can be found in Heffelfinger (2000).

Although TBMD can consider the quantum structure of electron, its accuracy is less than that of *ab initio*. Hence, some researchers developed the first-principles molecular dynamics by combining the advantages of TBMD and DFT-LDA (*ab initio* method) [Demkov, Ortega, Sankey, and Grumbach (1995), Ortega (1998), Garcia-Vidal, Merino, Peerez, Rincon, Ortega, and Flores (1994), Pearson, Smargiassi, and Madden (1993), Smargiassi, and Madden (1994)]. This method showed a very good accuracy for the problems of defect [Smargiassi (1994)], and lattice dynamics [Pavone, Karch, Schutt, Windl, Strauch, Giannozzi, and Baroni (1993), Adler, Honke, Pavone, and Schroder (1998)].

A major problem with the TBMD method is the way that the parameterization of the Hamiltonian and the overlap matrices, and the function V^{rep} limits its applicability. Harrison (1989) has attempted to provide a mini-

mal tight-binding theory with a set of universal parameters that could describe qualitatively a wide range of materials and properties. However, this approach turns out to be neither transferable nor accurate. Although focusing on tetrahedral solids, he emphasized the necessity of including the nonorthogonality of the local environment in multi-coordinated structures. This important factor has generally been overlooked by those seeking a transferable scheme. After that, Menon and Subbaswami (1997) proposed a nonorthogonal tight-binding scheme with minimal number of adjustable parameters, resulting in a transferable scheme applicable to clusters as well as bulk systems. Although nonorthogonal tight-binding molecular dynamics schemes are more accurate, they are not easily converted to order $O(N)$, and can typically handle only systems with up to a few thousand atoms [Menon and Subbaswami (1997)].

A standard TBMD routine is illustrated in Fig. 3.

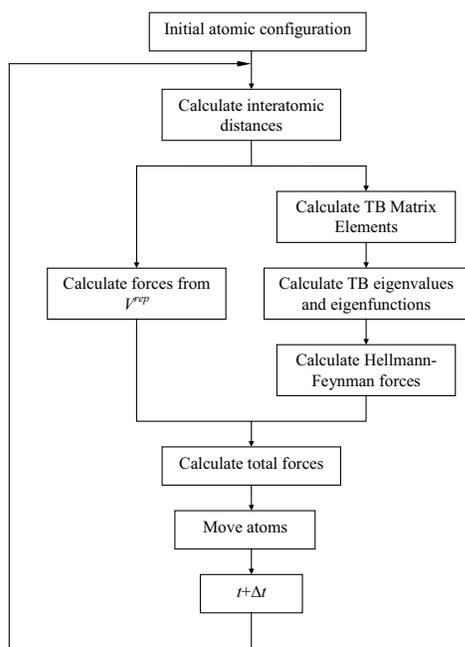


Figure 3 : An illustration of the TBMD routine

2.3 Classical Molecular Dynamics

Up to now, we know that atomistic and electronic-scale simulations can be performed by means of *ab initio* or semi-empirical methods such as tight-binding. However,

these methods are still restricted in their capability with respect to both the number of atoms and the simulation timescale. Classical molecular dynamics is an important substitute to study longer-timescale phenomena of systems composed of larger numbers of particles, which is much simpler but still an atomic scale method. Molecular dynamics is a means to study matter at the atomic level and to predict the static and dynamic properties from the underlying interactions between the molecules. To go from quantum mechanics to molecular dynamics requires averaging over the electrons to obtain spring constants, discrete charges and van der Waals parameters. It is possible to construct realistic classical potentials based on *ab initio* calculations, experimental results or an empirical model. A possible way is to fit the classical potentials to contour maps of the total energy, which may be obtained with an *ab initio* method by changing the position of one atom while fixing the coordinates of all other atoms. With the increase in computing power, the connection between classical MD and *ab initio* calculations are being made in a clear and rigorous fashion. Classical molecular dynamics is an empirical method. Hence, it is easy to implement in larger systems (million to billion atoms). However, for different systems, different empirical parameters may be needed, which limits its transferability.

The method of classical molecular dynamics was first proposed by Alder and Wainwright (1957). Alder and Wainwright applied the method to the simplest system—hard spheres by first assuming an interatomic potential, and found a liquid-solid phase transition in this hard-sphere system. Later, the methods were also applied to various systems with soft potentials [Rahman (1963)] such as the Lennard-Jones potential. Classical MD describes system's atomic-scale dynamics, where atoms and molecules move, while interacting with many of the atoms and molecules in the vicinity. The system's dynamic evolution is governed by Hamilton's classical equation of motion from Newton's second law:

$$m_I \ddot{\mathbf{R}}_I = \mathbf{F}_I = -\frac{\partial V}{\partial \mathbf{R}_I} \quad (\text{no sum on } I) \quad (23)$$

which is derived from the classical Hamiltonian of the system,

$$H = \sum_I \frac{P_I^2}{2m_I} + V(\mathbf{R}_I) \quad (24)$$

where \mathbf{R}_I is the position of atom I , and V is the empirical potential for the system. Each atom moves and acts simply as a particle that is moving in many-body force field \mathbf{F}_I of other similar particles, which can also be obtained from more accurate quantum simulation as described in Sections 2.1 and 2.2. The atomic and molecular interactions describing the dynamics are given by classical many-body force-field functions. The atomic interaction energy function $V(\mathbf{R}_I)$ can be written in terms of pair and many-body interactions, depending on the relative distances among different atoms [Daw and Baskes (1983, 1984)].

An alternate but equivalent approach is to solve the Hamiltonian system of ordinary differential equations

$$\frac{dP_I}{dt} = -\frac{\partial H}{\partial q_I} \quad (25)$$

$$\frac{dq_I}{dt} = \frac{\partial H}{\partial P_I} \quad (26)$$

where (q_I, P_I) are the set of canonically conjugate coordinates and momenta, respectively. Symplectic integrators [Gray, Noid, and Sumpter (1994)] have been developed to solve the above Hamiltonian equations of motion.

In MD simulations, the effects of finite system size and surfaces are always a severe problem. Periodic boundary conditions are usually employed to reduce these effects. All the particles are put inside a unit cell, and if the particle goes outside the cell boundary, it is brought back in from the opposite side of the cell. More descriptions of the general techniques used in molecular dynamics can be found in Allen and Tildesley (1989), Rapaport (1995), and Leach (1996).

Classical molecular dynamics have been applied extensively. Some computer codes can be available on the websites, such as CCP5 on <http://wserv1.dl.ac.uk/CCP/CCP5>, Amber/Sander on <http://www.amber.ucsf.edu/amber/amber.html> (or <http://amber.scipps.edu>), NAMD on <http://www.ks.uiuc.edu/Research/namd>, and LAMMPS on <http://www.cs.sandia.gov/sjplimp/lammps.html>.

2.3.1 Short range interactions

As the simplest interatomic potential in MD simulations, pair potentials are employed to qualitatively model diverse properties of materials, such as Buckingham potential [Wunderlich and Awaji (2001)], Morse potential [Ko-

manduri, Chandrasekaran, and Raff (1998)], and glue potential [Duan, Sun and Gong (2001)]. A very widely used inverse power model, the 12-6 Lennard-Jones (LJ) potential, was introduced by Lennard-Jones (1924a, b) for non-bond atomic interactions, as

$$V_{LJ} = 4\epsilon \left[\left(\frac{\sigma}{R_{IJ}} \right)^{12} - \left(\frac{\sigma}{R_{IJ}} \right)^6 \right] \quad (27)$$

where ϵ denotes the bind energy (the minimum of Lennard-Jones potential), and σ the equilibrium distance between two unbonded atoms or monomers, R_{IJ} denotes the inter-atomic distance between atoms I and J . The Lennard-Jones force (attraction or repulsion) between two atoms can be written as:

$$F_{IJ} = -\frac{\partial V_{LJ}}{\partial R_{IJ}} = -\frac{4\epsilon}{R_{IJ}} \left[12 \left(\frac{\sigma}{R_{IJ}} \right)^{12} - 6 \left(\frac{\sigma}{R_{IJ}} \right)^6 \right] \quad (28)$$

Girifalco and Lad (1956), and Girifalco (1992) employed the Lennard-Jones potential for the carbon-carbon system. Two sets of parameters have been used, one for a graphite system [Girifalco and Lad (1956)] and the second for an *fcc* crystal composed of C_{60} molecules [Girifalco (1992)]. The Lennard-Jones (LJ) potential is a non-bond order potential, which accounts for the steric and van der Waals non-bonded interaction.

To model more realistic materials, such as metals and semiconductors with complex many-body interactions, the pair potentials must be modified. Up to now, many approaches emerged, to improve the pair potentials. However, all of them fall into three categories, which are introduced below respectively.

The first one is to develop potentials by following the Born-Openheimer expansion (many-body potentials), i.e., besides the pair potential, many-body potentials should be added, such as Pearson [Pearson, Takai, Halicioglu and Tiller (1984)], and Stillinger-Weber (SW) [Stillinger, and Weber (1985)] potentials. The interatomic potential V as an infinite sum over pair, triplet, etc., can be expressed by the Born-Openheimer expansion as:

$$V(R_1, R_2, R_3, \dots) = \frac{1}{2!} \sum_{J \neq I} \sum_I V^{(2)}(R_{IJ}) + \frac{1}{3!} \sum_{K \neq J \neq I} \sum_{K \neq J \neq I} V^{(3)}(R_{IJ}, R_{JK}, R_{KI}) + \dots + \frac{1}{n!} \sum_{Q \neq \dots} \dots \sum_{M \neq \dots} \dots \sum_J \sum_I V^{(n)}(R_{IJ}, \dots, R_{IQ}, \dots, R_{MQ}, \dots) \quad (29)$$

$V^{(2)}$, $V^{(3)}$... and $V^{(n)}$ are the interaction potentials of the two-, three- and n -body interactions, respectively; and R_{IJ} is the distance between atoms I and J . It is noted that the n -body potential decreases rapidly with the increase of n . Therefore, in practice, the Born-Openheimer potential is truncated at $n=3$. For covalently-bonded materials, Pearson takes the two-body component to be the Lennard-Jones potential, while triplet interactions are represented by an Axilrod-Teller-type three-body potential [Pearson, Takai, Halicioglu and Tiller (1984)]. The SW potential, which involves both two-body and three-body interatomic terms, is another example of the type of potential that is used to effectively deal with the directional nature of bonding in covalent materials. The SW potential can be written as

$$V_{SW}(R_1, R_2, R_3, \dots) = \sum_{J \neq I} \sum V^{(2)}(R_{IJ}) + \sum_{K \neq J \neq I} \sum V^{(3)}(R_{IJ}, R_{IK}) \quad (30)$$

The exact form of these interactions $V^{(2)}$ and $V^{(3)}$ are given in Stillinger, and Weber (1985). The potentials are assumed to have a cutoff radius, i.e., any atom interacts directly only with those atoms within a distance R_{cut} from it.

There are many different many-body empirical potentials developed during last decades, such as AMBER [Cornell, et al., (1995)], CFF95 [Peng et al. (1997)], CHARMM [Mackerell, et al. (1995)], Dreiding [Mayo, Olafson, and Goddard (1990)], MMFF [Halgren (1996)], MM2 [Allinger (1977), and Allinger, Yuh, Lii (1989)], MM3 [Cui, Li, and Allinger (1993)], MM4 [Nevins, Lii, and Allinger (1996)], OPLS [Jorgensen, et al. (1996)], SHARP [Bearpark, Robb, Bernardi, and Olivucci (1994)], UFF [Rappe, et al. (1992)], and VALBON [Cleveland, and Landis (1996)]. In these models, the total system potential energy V can be expressed as a sum of several individual energy terms [Burkert and Allinger (1982), Leach (1996), Rappe and Casewit (1997)]:

$$V = U_p + U_\theta + U_\omega + U_\tau + U_{vdW} + U_{es} \quad (31)$$

where U_p , U_θ , U_ω , and U_τ are energies associated with bond stretching (two-body), angle variation (three-body), inversion and torsion (four-body), respectively; U_{vdW} and U_{es} are associated with van der Waals and electrostatic

interactions, respectively. Additional energy terms associated with electromechanical or optomechanical interactions can be included in the same way. Different models may include different terms. One can ignore or focus on some selective terms of the total potential energy according to the physics of a specific problem. MM2-MM4, SHAPE, VALBON and UFF models have been applied in the analysis of a variety of organic and inorganic systems. The Dreiding model has been used to analyze the structure of fullerene and carbon nano-tube [Guo, Karasawa, and Goddard (1991), Tuzun, Noid, Sumpter and Merklet (1996)].

The second one is to attempt to model the local environment using electron density distributions, which results in an addition energy, such as the embedded atom method (EAM) [Daw and Baskes (1983, 1984)], and variable charge molecular dynamics (VCMD) [Streitz and Mintmire (1994)]. VCMD is suitable to solving the boundary problems [Campbell, Kalia, Nakano, Vashishta, Ogata, and Rodgers (1999)]. However, it is more complicated than EAM. Based on the quasi-atom approach [Scott, and Zaremba (1980)], Daw and Baskes (1983) developed the EAM potential for metals. In this approach, the energy of an atom in the crystal is divided into two parts, which can be written as

$$E(R_{IJ}) = \sum_I \left\{ F_I(\rho_I) + \frac{1}{2} \sum_{J \neq I} \phi_{IJ}(R_{IJ}) \right\} \quad (32)$$

where the second term on the right side, $\phi_{IJ}(R_{IJ})$, is a two-body core-core interaction energy (pair potential), and the first term is an additional energy needed to embed the atom into the electron system in the lattice. ρ_I is the local electron density. The embedding energy is usually fit to the form

$$F_I = A_I E_I^0 \bar{\rho}_I \ln \bar{\rho}_I \quad (33)$$

where $\bar{\rho}_I$ is obtained by functional fits to the electronic configuration surrounding atom I , E_I^0 is its sublimation energy, and A_I is a constant for atom I . Baskes (1992) proposed a modified embedded atom method by taking the non-sphere-symmetry of the electronic structure into account. Based on variations of the EAM and SW potentials, a wide variety of many-body potentials has been proposed and used in classical molecular dynamics simulations. These potentials are expected to work well within the range of physical parameters in which they were constructed.

EAM is applicable to interface and surface problems. Tan and Yang (1994) used the modified EAM to perform the atomistic simulation of interface fracture, and explained the origin of the crack-tip singularity. Baskes and his coworkers [Baskes, Angelo and Bison (1994), Gall, Horstemeyer, Van Schilfgaarde and Baskes (2000)] applied the modified EAM to study the tensile debonding and fracture of an aluminum-silicon interface, and analyzed the effect of the micro-defect on the interface. Fallis, Daw and Fong (1995) investigated the structure of small Pt clusters on Pt(111) by using EAM. Zhou, Lomdahl, Voter and Holian (1998) studied the three-dimensional fracture via large-scale molecular dynamics by appealing to EAM. Li, Gao, Qiao, Zhou and Chu (2001) simulated the microcrack healing in copper by means of EAM. Liu and Adams (1992), and Longo, Rey and Gallego (1999) used different EAM to simulate the structure of Ni clusters on Ni surface, respectively, and the results depended on the parameters of embedding energy.

The third one is to introduce the local electronic environment directly into pair potentials, such as the Tersoff potential [Tersoff (1986)]. The Tersoff potential was originally from Abell (1985), and then applied as a practical potential energy formalism for modeling covalent materials by Tersoff (1986, 1989). Tersoff potential is a sum of the energy on each bond. The energy of each bond consists of a repulsive and attractive part. A bond order function is embedded in the formulation. The bond order depends on the local atomic environment such as angular dependency due to the bond angles. Brenner (1990) modified the Tersoff potential by introducing additional terms into the bond order function, which is mainly to correct the overbinding of radicals. Wang, Tomanek and Bertsch (1991) introduced local density approximations (LDA) into a Morse-type potential for carbon systems, which derived a more reasonable binding energy than that from the Lennard-Jones potentials [Qian, Liu, and Ruoff (2001)].

A major distinguishing feature of the Tersoff-Brenner potential is that short-range bonded interactions are reactive, so that a chemical bond can form and break during simulation. The Tersoff-Brenner potentials [Brenner, Shenderova, Areshkin (1998)] are used to model carbon based systems using the type II parameterization, and have been used in a wide variety of scenarios. This potential has been successfully applied in the analysis of for-

mation of fullerenes and their properties [Brenner, Harrison, White, and Colton (1991), Robertson, Brenner, and Mintmire (1992), Robertson, Brenner, and White (1992, 1995)], surface patterning [Sinnott, Colton, White, and Brenner (1994)], indentation and friction at nanoscale [Harrison, White, Colton, and Brenner (1992, 1993a, b, 1995), Harrison, Colton, White, and Brenner (1993)], calculating properties of carbon nanostructures [Brenner, Shenderova, Areshkin, Schall, and Frankland (2002)], and energetics of nanotubes [Robertson, Brenner, and Mintmire (1992)].

Up to now, to authors' knowledge, there is no universal classical MD potential, which works for all the materials and in all the scenarios. EAM type potentials are suited for metals, while Stillinger-Weber (SW) and/or Tersoff-Brenner potentials are suited for semiconductors.

Hereinbefore, we only consider the short range interactions. In general, if the potential drops down to zero faster than R^{-d} , where R is the distance between two atoms and d the dimension of the problem, it is called short ranged. In short range interactions, a cutoff radius is introduced, only neighbored atoms up to the cutoff radius are taken into account for the calculation of interactions, beyond the cutoff radius mutual interactions between atoms are neglected. In order to compensate for the neglect of explicit calculations, long range corrections may be introduced. Energy modifying terms in a periodic molecular cell to account for long range interactions were studied in Madelung (1918), Ewald (1921), Deleeuw, Peram, and Smith (1980) and Heyes (1981) with additional references therein.

2.3.2 Long range interactions

In the case of short range potentials, it is easy to calculate the potential or force if one cuts it off at a certain range and uses a neighbor list, that is called a particle-particle method. The amount of calculation of this method is of $O(N)$ for an N -particle system. However, in the case of long range potentials, like the Coulomb potential, interactions between all particles in the system must be taken into account, if treated without any approximation. This leads to an $O(N^2)$ problem, which increases considerably the execution time of a program for larger systems.

The Ewald sum method [Ewald (1921)] is used to decrease the amount of calculation in Coulomb systems by accelerating the force calculation. The Ewald method is limited to fully or partially periodic systems, but has been

widely applied in studies of condensed matter, where it is important to eliminate surface effects arising in a small, isolated system. However, the computational task in this method is still heavy in large system.

There are many algorithms to deal with this problem by accelerating the force calculation, which can be classified into two categories: particle-mesh methods, and hierarchical or multipole methods [Gibbon, and Sutmann (2002)]. Particle-mesh models are more widely used in the field of cosmology than in MD. There are two principal types of particle-mesh simulation models: the particle-mesh (PM) model, and the particle-particle-particle-mesh (P³M) model [Birdsall, and Langdon (1985); Hockney and Eastwood (1981)]. The particle-particle (PP) model uses the action at a distance formulation of the force law, the PM model regards the force as a field quantity – approximating it on a mesh – and the P³M model is a hybrid of the PP model and PM models. The PP method can be used for small systems with long range forces or for large systems with short range forces. In the previous subsection the PP method is employed to calculate the short range forces. The PM method, on the other hand is computationally fast, but can only handle smoothly varying forces, and the result is generally less accurate. The P³M method combines the advantages of the PP and PM methods and enables large correlate systems with long range force to be simulated.

Recently, a PP-MLPG/BIE method is developed to simulate the long range force by Atluri (2004), which will be more accurate and faster than the P³M method. In PP-MLPG/BIE method, the MLPG/BIE (Meshless Local Petrov-Galerkin BIE) method replaces the particle mesh method in P³M method. The MLPG/BIE method was proposed by Atluri, Han and Shen (2003) by using the concept of the general meshless local Petrov-Galerkin (MLPG) approach developed in Atluri et al (1998, 2002a,b), and has been successfully applied in 3D fracture analysis and the crack growth [Han, Atluri (2003a, b)]. Then one will have the best of the worlds offered by pure MD and MLPG/BIE respectively: high resolution of individual encounters, combined with a rapid meshless evaluation of the long range forces.

In this case, the total potential (Coulomb's potential) of the system is

$$\Pi = \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i}^N \frac{q_i q_j}{4\pi\epsilon |\mathbf{r}_i - \mathbf{r}_j|} \quad (34)$$

where N is the total number of the particles, ϵ is the permittivity of free space, and q_j is the charge of the particle j . The force of particle j on particle i is give by Coulomb's law as

$$\mathbf{f}_{ij}^{coul} = \frac{q_i q_j}{4\pi\epsilon} \frac{\mathbf{r}_i - \mathbf{r}_j}{|\mathbf{r}_i - \mathbf{r}_j|^3} \quad (35)$$

The inter-particle force is initially split into two contributions:

$$\mathbf{f}_i = \sum_{\substack{j \neq i \\ j \in \Omega_i^{sr}}} \mathbf{f}_{ij}^{sr} + \mathbf{f}_i^{lr} \quad (36)$$

The first sum represents the direct forces of the particle j on particle i within the short range domain Ω_i^{sr} , as shown in Fig. 4, the shaded box represents the short range domain Ω_i^{sr} , the first sum is over all the black particles. The first term is obtained by the PP method. The second term represents the long range forces which are obtained from the MLPG/BIE method in the global domain.

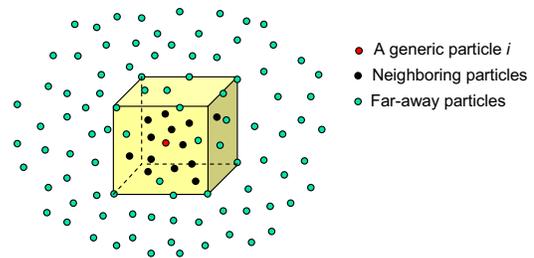


Figure 4 : Force splitting scheme

The long range interaction is assumed to be temporally and spatially smooth enough, so that the long range contribution to the interaction energy is found by solving the Poisson's equation for long range potential [Hockney, Eastwood (1981)] by employing the MLPG/BIE method [Atluri (2004)]. The derived boundary integral equations for the long range potential and the gradient of the potential are weakly singular. The PP-MLPG/BIE method will be faster and cheaper than the P³M method, although both of them are of $O(N)$ computational complexity.

After obtaining the force on the particle i , we should solve the equation of motion. The multiple time scales method [Tuckerman et al. (1991)] in conjugation with

Verlet's leapfrog method is a natural choice to integrate the equation of motion $m_i \ddot{\mathbf{r}}_i = \mathbf{f}_i$, because the force is already subdivided into short and long range components,

$$\mathbf{f}_i = \mathbf{f}_i^{sr} + \mathbf{f}_i^{lr} \quad (37)$$

where \mathbf{f}_i^{sr} varies fast and \mathbf{f}_i^{lr} varies slow. In this multiple time step method, the short range forces are calculated every time step δt by means of PP method, while the long range forces are renewed every n time steps by using MLPG/BIE method. However, it should be pointed out that this multiple time scales method only focus on the calculation of the interaction of the particles, the equation of motion $m_i \ddot{\mathbf{r}}_i = \mathbf{f}_i$ is still integrated every time step δt .

Multipole methods [Pfalzner, and Gibbon (1996)] are based on the observation that distant charges (or masses) may be grouped together and substituted by a single multipole expansion, that lead to a considerable saving in the number of interactions necessary to sum the potential or force. Two approaches proposed in mid-1980 belong to this category: hierarchical tree code method [Appel (1985); Barnes and Hut (1986)], and fast multipole method (FMM) [Greengard and Rokhlin (1987)]. The hierarchical tree code method is $O(N \log N)$ -schemes based on hierarchical grouping of distant particles. The fast multipole method (FMM) is $O(N)$ -schemes with rounding-error accuracy. They serve a good basis for the accelerating calculation of many-body systems governed by long-range potentials. A detailed discussion about Multipole methods can be found in [Gibbon, and Sutmann (2002)].

Instead of accelerating the force calculation, the symplectic method [Channell and Scovel (1990); Candy and Rozmus (1991); and Wisdom and Holman (1991)] can also be employed to improve the accuracy and reduce the required computational time, which integrates the Hamiltonian rigorously and allow one to make the basic time step larger.

2.3.3 Time integrators

In order to obtain a trajectory through phase space for these atoms, an integrator is required for Newton's laws of motion. Numerical integration of the equations of motion is performed either by explicit or implicit methods, such as the Verlet [Verlet (1967)], leapfrog [Hockney (1970)], and velocity Verlet [Swope, et al. (1982)] methods. Because of the lack of numerical stability, the

simple Euler scheme is not appropriate for MD simulations. In Verlet method, the error will accumulate with the time steps and may lead to a serious error in the final results. The leapfrog method was proposed to avoid this accumulation of errors. The leapfrog method is more tractable than the Verlet method when one introduces velocity scaling in a system with periodic boundary conditions. However, the leapfrog method cannot handle the velocity properly, the velocity Verlet method is usually adopted. The explicit velocity Verlet method is very popular in MD simulations due to the fact that it is stable, memory-efficient, and easily augmented to handle multiple timescale MD. The following algorithm is iterated:

$$\dot{\mathbf{R}}_I \left(t + \frac{\Delta t}{2} \right) = \dot{\mathbf{R}}_I(t) + \frac{\Delta t}{2m_I} \mathbf{F}_I(t) \quad (38)$$

$$\mathbf{R}_I(t + \Delta t) = \mathbf{R}_I(t) + \Delta t \dot{\mathbf{R}}_I \left(t + \frac{\Delta t}{2} \right) \quad (39)$$

$$\mathbf{F}_I(t + \Delta t) = \frac{\partial V}{\partial \mathbf{R}_I(t + \Delta t)} \quad (40)$$

$$\dot{\mathbf{R}}_I(t + \Delta t) = \dot{\mathbf{R}}_I \left(t + \frac{\Delta t}{2} \right) + \frac{\Delta t}{2m_I} \mathbf{F}_I(t + \Delta t) \quad (41)$$

At each iteration, each of the four steps is performed sequentially for every atom I in the system. After exiting the last step, the simulation time is incremented by Δt . Another popular implicit integration method for MD is the predictor-corrector scheme, specially the Gear algorithm [Gear (1971)], which can integrate the temporal evolution equation for longer times with more accuracy. For detailed description for the technique of the molecular dynamics simulation, the readers are referred to Rapaport (1995). Tucker and his colleagues [Tucker, et al. (1991), and Tucker, and Berne (1992)] developed the multi-time-step method to improve the accuracy and reduce the required computational time.

The above descriptions are used for a microcanonical simulation (NVE ensemble), where the total energy is a conserved quantity. If the temperature or the pressure should keep constant (the NVT or NPT ensembles), it is not enough to only integrate Newton's equations of motion, the effect of a thermostat interacting with the system should be considered. In canonical simulations (NVT ensemble), to maintain the fixed temperature, one

should use the equipartition theorem and equate the kinetic energy to $\frac{3}{2}Nk_B T$, where N is the total number of the atoms in this system, k_B is the Boltzman constant, and T is the temperature. A number of more sophisticated thermostats have also been developed, such as the Langevin's algorithm or Nosé-Hoover thermostat [Nosé (1984)].

The standard molecular dynamics routine is illustrated in Fig. 5.

The previous treatments, *ab initio* molecular dynamics, tight binding, and classical molecular dynamics are all deterministic. The state of the system is determined completely by the initial condition. These approaches are useful in understanding stable structures, vibrations, and growth at the atomistic level. Another method for treating complex systems is the Monte Carlo method, which investigates problems by sampling from random distributions, and uses concepts of probability theory. It assumes very idealized or simplified interaction parameters and can treat larger number of atoms. Physical and chemical properties of large systems are obtained by statistically averaging over randomly moved particles. Hence, it is a stochastic method. These techniques are now routinely applied in almost every field, from biology to nuclear physics to social studies. The detailed discussion about this method is omitted here, interested readers are refer

to Ohno, Esfarjani and Kawazoe (1999). Some of its applications can be found in Battaile et al. (1997), Bortz et al. (1975), Huang et al. (1998), Gilmer et al. (2000) and Singh et al. (1997).

3 Multi-scale Simulation

Recently, an intense effort has been devoted to the modeling and simulations of physical phenomena occurring on a vast range of length scales. This endeavor has prompted the development of multiscale modeling and simulation strategies. Although constant increases in available computational power and improvement in numerical algorithms, even classical molecular dynamics methods with very simple potentials are still limited to simulating on the order of 10^6 - 10^8 atoms for a few nanoseconds. However, real materials are composed of $\sim 10^{23}$ atoms and molecules, and sometimes it becomes necessary to perform far-larger-scale simulations. For phenomena on a much larger space scale and longer time scale, one possible strategy is the multi-scale methods. The simulation of large systems must be left to continuum methods. Continuum mechanics is used to predict the phenomena described by uniform collective behavior of atoms, while nano-mechanics is used to predict the phenomena described by dramatic changes in the state of few atoms. Multiscale modeling and simulations are being used in diverse fields, such as materials science, nano/micro-electronics, environmental remediation, and biotechnology. The overall goal of multiscale modeling is to predict the response of complex systems across all relevant spatial and temporal scales. It is of interest to build models that can seamlessly simulate multi-scale systems. Several methods have been developed for the multiscale simulations. A recent review paper on the multiscale modeling in nano- and micro-mechanics of materials is written by Ghoniem and Cho (2002).

The traditional approaches to couple spatial and temporal scales are the hierarchical approaches in which a hierarchy of approaches and mathematical/computational models with different physical levels of description is pieced together, and the output of the smaller-scale models is used as input for the larger-scale models. Sinclair (1971) modeled a bcc dislocation core by equilibrating forces between atoms and continua with the continuum region modeled with analytical techniques. Clementi (1988) combined quantum mechanics, molecular dynamics, and fluid dynamics to predict the tidal circulations. In

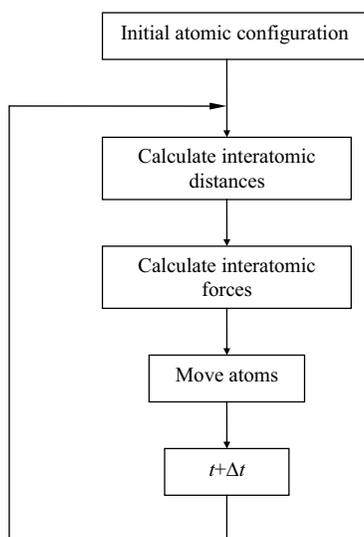


Figure 5 : An illustration of classical MD routine

a series of calculations, each calculation was used as input to next up the length and time hierarchy. Kohlhoff, Gumbsch and Fishmeister (1991) proposed a method incorporating a non-local elasticity theory for a transition region connecting the lattice and continuum regions. Tan and Yang (1994) used the molecular dynamics (EAM) and finite element method to simulate interface fracture. Gumbsch (1996) used the molecular dynamics and finite element method to simulate brittle crack propagation. Noguchi and Furuya (1997) matched displacements between atomistic molecular dynamics and a micromechanics model to simulate elastic-plastic crack propagation. Sham and Tichy (1997) simulated thin film lubrication by means of molecular dynamics and finite element method. However, many gaps still exist in these models. Some of these methods were reviewed by Cleri, et al. (1998). So far, no rational way exists to relate the phenomena at the very small length scales with the macroscopic behavior.

An equivalent-continuum modeling approach was proposed to model structure-property relationships of nanostructured materials by [Odegard, Gates, Nicholson, and Wise (2002)]. This method replaced discrete molecular structures with equivalent-continuum representative volume models by equating the molecular potential energy of nano-structured materials with the mechanical strain energy of the representative volume element (equivalent-energy). This method has been applied to determine the effective geometry and effective bending rigidity of a graphene sheet [Odegard, Gates, Nicholson, and Wise (2002)]. The development of an equivalent-truss model may be used as intermediate step in establishing the equivalent-continuum model. Each atom in the molecular model is represented by a pin-joint, and each truss element represents an atomic bonded or non-bonded interaction. The moduli of the truss elements are based on the molecular mechanics force constants. If one stops at this equivalent-truss model instead establishing the equivalent-continuum model, the so-called molecular structural mechanics is developed [Wang, et al. (2002); Li, and Chou (2003)]. This method focuses mainly on simulating atom mechanics using linear continuum abstractions (trusses and bars). It preserves, and in some cases increases, the number of degrees of freedom compared to the full atomistic system. The expense is paid in order to make the problem quasi-static and linear before the application of a numerical solution procedure. So,

in the end, the atomic positions are easier to obtain than from full molecular dynamics. Wang, et al. (2002) derived the continuum mechanical properties of polymer networks using this molecular structural mechanics. The equivalent-continuum modeling is based on the equivalent-energy, it can not determine the geometry and material properties uniquely at the same time since all the quantities are mixed in the energy, only one of them can be determined given another one is predetermined from the literatures or assumed. Every independent material constant is determined by a different corresponding boundary condition. This method is not self-consistent, nor appropriate to large deformation.

With the advent of parallel computers, another approach to the coupling of length scales, the handshaking approach, appears. In this approach, the problem is divided into its natural components, each of which may be addressed by one or more processors. Then, the “handshaking” between the different regions plays a important role in this method. The “handshaking” is not just an algorithmic issue but also one that requires physical insight [Broughton, Abraham, Bernstein, and Kaxiras (1999)]. The FE/MD/TB model has recently been propounded by Abraham and coworkers [Broughton, Abraham, Bernstein, and Kaxiras (1999), Abraham (2000)]. An example of this handshaking approach for dynamic fracture analysis is shown in Fig. 6. In this model, the problem is divided into three regions: continuum mechanics, the implementation of which is via finite elements (FE); atomistic statistical mechanics, implemented by molecular mechanics; and mean-field quantum mechanics represented by semiempirical tight bind (TB) (or *ab initio* method). Each simulation is performed on a different region of the domain, with a coupling imposed in “handshake” regions where the different simulations overlap. The method is designed for implementation on supercomputers via parallel algorithms, allowing the solution of large problems. A Hamiltonian, H_{tot} , is defined for the entire system, which can be conceptually written as [Broughton, Abraham, Bernstein, and Kaxiras (1999)]

$$\begin{aligned}
 H_{tot} = & H_{FE}(\{\mathbf{u}, \dot{\mathbf{u}}\} \in FE) \\
 & + H_{FE/MD}(\{\mathbf{u}, \dot{\mathbf{u}}, \mathbf{R}, \dot{\mathbf{R}}\} \in FE/MD) \\
 & + H_{MD}(\{\mathbf{R}, \dot{\mathbf{R}}\} \in MD) \\
 & + H_{MD/TB}(\{\mathbf{R}, \dot{\mathbf{R}}\} \in MD/TB) \\
 & + H_{TB}(\{\mathbf{R}, \dot{\mathbf{R}}\} \in TB)
 \end{aligned} \tag{42}$$

The degrees of freedom are atomic positions, \mathbf{R} , and their velocity, $\dot{\mathbf{R}}$, for the TB and MD regions; and displacements, \mathbf{u} , and their time rates of change, $\dot{\mathbf{u}}$, for the FE regions. This equation states that there are three separate Hamiltonians for each subsystem as well as Hamiltonians that dictate the dynamics of variables in the handshake regions. The subscripts “FE/MD” and “MD/TB” denote such handshake regions.

Abraham, Broughton, Bernstein, and Kaxiras (1999) and Abraham, Bernstein, Broughton, and Hess (2000) used this method to simulate the propagation of a crack in a brittle material, where the TB method is used to simulate bond breaking at the crack tip, MD is used near the crack surface, and the surrounding medium is treated with FE. Rafii-Tabar, Hua, and Cross (1998) proposed a related method by a stochastic coupling of a molecular-dynamics region to a finite element region. The system is propagated in time using a stochastic differential equation so as to produce something resembling Langevin dynamics. Simirnova, Zhigilei, and Garrison (1999) studied the propagation of a laser-induced pressure wave in a solid by combining the molecular dynamics and finite element method. This method has been extensively applied in the field of laser of ablation by Zhigilei and his colleagues.

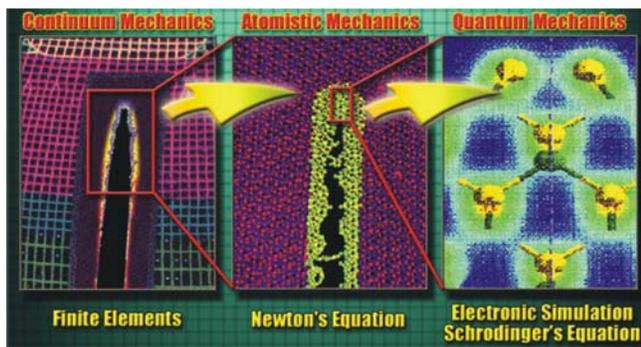


Figure 6 : The multiscale modeling approaches that attempt to link several computational approaches in a combined model for dynamic fracture analysis. In this model, electronic structure model (quantum mechanics) is combined with a molecular dynamics model, which in turn is embedded into a continuum model (discretized) by finite elements [Noor (2002)].

Fig. 6 The multiscale modeling approaches that attempt to link several computational approaches in a combined model for dynamic fracture analysis. In this model, electronic structure model (quantum mechanics) is combined

with a molecular dynamics model, which in turn is embedded into a continuum model (discretized) by finite elements [Noor (2002)].

In the handshaking approach, the standard technique is to a priori identify the atomistic and continuum regions and tie them together with some interface boundary conditions. The challenge for mesh generation is that the mesh should smoothly transition between the true atomic lattice in the MD region and the closely-packed FE meshes. Too abrupt a crossover leads to unphysical behavior, such as elastic wave reflections at the interface [Rudd and Broughton (1998, 2000)]. In addition to the disadvantage of introducing artificial numerical interfaces into the problem, a further drawback of these models is their inability to adapt to changes in loading an evolving state of deformation. To connect seamlessly to molecular dynamics in the atomic limit, Coarse Grained Molecular Dynamics (CGMD) has been developed as a substitute for finite elements Rudd and Broughton (1998, 2000)], which derived the equation of motion directly from finite temperature MD through a statistical coarse graining procedure. Although CGMD reduced unphysical scattering of waves traveling from the atomistic region into the CG region as compare to FE, the short-wavelength wave still reflected from the CG region. Moreover, the computational cost of the CG procedure is far beyond that of FE.

The quasicontinuum method was originally introduced by Tadmor, Ortiz, and Phillips (1996). The theory of the quasicontinuum furnishes a computational scheme for linking the atomistic and continuum realms, and regards that all the system is in the atomistic realm. The basic idea is that every point in a continuum corresponds to a region on the atomic scale, which is homogeneously distorted according to the deformation gradient at the point. The finite strain theory is employed in the continuum realms. The details about the finite strain analysis can be found in Atluri (1979, 1980). A hypothesis to connect the continuum displacement field and the motions of atoms must be employed. The Cauchy-Born hypothesis is the basis for developing the quasicontinuum elastic potentials, from the atomistic description of the system. The Cauchy-Born hypotheses for crystals are equivalent for homogeneous deformations [Born and Huang (1954), Ericksen (1984)].

For simple Bravais lattice that has the centrosymmetric atomic structure, the Cauchy-Born rule [Born and Huang

(1954), Ericksen (1984)] gives

$$\mathbf{r}_{IJ} = \mathbf{F}\mathbf{R}_{IJ} \quad (43)$$

where \mathbf{F} is the deformation gradient, and \mathbf{R}_{IJ} and \mathbf{r}_{IJ} represent the distances between two atoms I and J in the reference configuration and current configuration, respectively. However, it does not for complex Bravais lattice which can be given by means of a number of interpenetrating simple Bravais lattices (sub-lattices) and does not possess centrosymmetry, such as the hexagonal lattice. In this case, the Cauchy-Born rule gives [Zanzotto (1996), Martin (1975), Cousins (1978), Born and Huang (1954)]

$$\mathbf{r}_{IJ} = \mathbf{F}\mathbf{R}_{IJ} + \zeta_k \quad (44)$$

where the internal variable ζ_k are shift vectors, with k ranging from 0 to some integer N (There are $N+1$ sub-lattices in the complex Bravais lattice. If atoms I, J are in the same sub-lattices, $\zeta_k=0$). ζ_k and \mathbf{F} are independent variables. At the static equilibrium state, the vectors ζ_k are to be determined by the minimization of the energy function, so as to reach an equilibrium configuration in the deformed crystal. This means that the equilibrium values of ζ_k can be written as functions of \mathbf{F} . If focusing on dynamical problems, one will avoid making any specific hypothesis on the behavior of ζ_k , what one need is $\partial\mathbf{r}_{IJ}/\partial\mathbf{F} = \mathbf{R}_{IJ}$ from either (43) or (44).

Once the geometry of the deformed lattice vectors is linked to the continuum deformation, a constitutive model based on atomistic description can be constructed by equating the continuum strain energy density to the potential energy of the atomic system for a representative cell, divided by its volume. A continuum finite element formulation is used to characterize the mechanical response of a given system. The difference from standard finite element methodologies is that the constitutive response of the system is obtained from an atomistic calculation rather than an empirical phenomenological rule. This type of approach is due to Kroner (1967). In this method, a set of atoms making up a Bravais lattice has selected from a subset. A triangulation of this subset allows the introduction of finite element-like shape functions at lattice points, allowing the interpolation of quantities at intermediate points in the lattice. The finite mesh permeates the entire system, right down to atomic dimensions. In the inhomogeneous deformation region (such as near defects), the atoms are expressed explicitly, while in

the homogeneous deformation region, the atoms are expressed implicitly by the representative atoms. An underlying atomistic Hamiltonian is used to determine the energy density of the system; a separate atomistic calculation is required for each cell in their finite element mesh. The energy of the atoms in inhomogeneous deformation region is calculated by building the appropriate complement of neighbors as in the classical MD method. In the homogeneous deformation regions, the energy is calculated using a single representative atom in the center of a uniformly deformed crystal in which the deformation gradient is \mathbf{F} . This crystal is always made sufficiently large that there are no boundary effects there. The problem of the minimization of energy to find equilibrium configurations can be written in terms of a reduced set of variables.

The method is made practical by approximating summations over all atoms, as using summation rules analogous to numerical quadrature. The rules rely on the smoothness of the quantities over the size of the triangulation to ensure accuracy. The adaptivity rules allow the reselection of representative lattice points in order to tailor the computational mesh to the structure of the deformation field. The criteria for adaptivity are designed to allow full atomic resolution in regions of large local strain, such as near a defect.

Different variants of the quasicontinuum theory have been developed in a series of publications where numerous examples of application have also been presented, such as the simulation of dislocations, grain boundary interactions, nanoindentation, fracture, and the response of ferroelectric materials to electrical and mechanical loading. Recently, Shenoy (2003) extended the method to dynamics at zero temperature, and a multiple-time-step method was also developed for the time integrating.

There are several limitations in the quasicontinuum method. In particular, cracks and defects are not allowed to form, and since the simulation is carried out at zero temperature, thermally-activated processes are not included [Smith, Tadmor, Bernstein, and Kaxiras (2001)]. Moreover, interface energies between different phases are not taken into account. Due to that the procedure focused on approximating the energy but not the forces, some non-physical forces are induced [Shenoy, Miller, Tadmor, Rodney, Phillips, and Ortiz (1999)]. Actually, another reason for these non-physical forces is the fact that the finite element interpolation is a local interpola-

tion, which disobeys the non-local physics property of the atoms. In addition, in these approaches, the nodes must coincide with atoms at the interface, therefore, the resolution of the discretized continuum nodal space down to the atom scale, that restrict the size of the continuum and leads to smaller overall dimension problem. Chung and Namburu (2003) circumvented the interface entirely through homogenization theory. A lattice statics based tangent-stiffness finite element method is developed for the interface/transition region by Chung, Namburu, and Henz (2004). Wagner and Liu (2003) presented a multiscale method for coupling molecular dynamics and continuum mechanics at finite temperature by using “bridging scale” decomposition and quasicontinuum method, where the entire system is treated as a coarse scale one, first; and then the entire system is treated as a fine scale one, later sequentially. Multiple time steps are employed for wave propagation in the coarse scale and fine scale. A recent review of the quasicontinuum method discussing its theory and applications can be found in Miller and Tadmor (2002).

Recent, by virtue of the dynamic principle of virtual work, an equivalent continuum is defined for dynamically deforming atomistic system by Zhou and his colleague [Zhou and McDowell (2002); Zhou (2003)]. Work-conjugate continuum stress and deformation fields, mass distribution, and all other work- and momentum-preserving kinetic quantities are specified for the equivalent continuum. The resulted equivalent continuum fields represent a continuum reinterpretation of the result of a discrete MD calculation, and have exactly the same number of independent degrees of freedom as the discrete atomistic system. Hence, this equivalent continuum fields is computationally intensive to obtain. This equivalent continuum may offer a theoretical basis for linking MD to continuum in multiscale simulation, just likes the role of the Cauchy-Born hypotheses in the quasicontinuum method.

Other studies describing methods for multi-scale simulations of the atomistic and the quantum regimes or continuum and the atomistic regimes can be found in Hoover, De Groot, and Hoover (1992), Capaz, Cho and Joannopoulos (1995), and Vanduijnen and Devries (1996). Friesecke and James (2000) proposed a scheme of bridging between continuum and atomic structure, focusing on nano-structures in which the size of one dimension is much larger than the other. Zhang, Klein, Huang,

Gao, and Wu (2002) developed virtual-internal-bond (VIB) model to apply continuum mechanics to multi-scale material problems, which incorporated a cohesive-type law into constitutive equations. VIB model provides an effective method to investigate crack nucleation and propagation in engineering materials. Garikipati (2002) embedded micromechanical models in the macromechanical formulation by means of a variational multiscale method. The resulting macromechanical formulation is formed solely in terms of the coarse scale displacements, but is influenced by the fine scale, which is governed by micromechanical models; thereby it has a multiscale character. Insepov et al. (1997, 2000) used a multiscale method to study the effects of impact by atomic clusters on crystal surfaces. In this method, an ensemble averaging technique is employed to pass thermal and deformation from the atomistic region to the FE region.

As we know, in the multiscale simulation, the atomistic method is employed where the displacement field varies on an atomic scale, and the continuum approach is employed elsewhere. For the seamless multiscale simulation, it is important to ensure that the elastic waves generated in the atomistic region can propagate into the continuum region. The continuum region cannot support modes of short wavelength, which is less than the spacing of the nodes. One source of finite size effects is the short waves which are reflected back unphysically from an artificial interface or boundary, which may also produce uneven heating across the interface. In order to minimize such reflections, some interfacial conditions are proposed [Cai et al. (2000), E and Huang (2001), Wagner and Liu (2003)]. Cai et al. (2000), Wagner and Liu (2003) derived the interface conditions as a generalized Langevin equations. However, the time history integral is difficult to compute, especially for moving MD region. E and Huang (2001) minimized boundary reflection in an MD simulation with a reduced weighted sum of history terms. We developed a method for the seamlessly coupling of continuum and MD simulation at finite temperature [Shen, and Atluri (2004)], where alternate interfacial conditions between atomistic and continuum regions were proposed by considering the fluctuation of atoms in the continuum region. Their effectiveness in ensuring the accurate passage of information between atomistic and continuum regions was discussed.

Consider a multiscale system, including an atomistic region, which may contain inhomogeneities, and an equiv-

alent continuum mechanics (ECM) domain, which is defect-free. In the (ECM) region, the deformation is homogeneous, and thus can be approximated by an equivalent continuum mechanics model as in quasicontinuum method, where the individual atomic displacements are not being solved using molecular dynamics. The material in ECM is discretized into a set of nodes, which are not necessarily coincident with the atoms. The positions of the atoms in this region can be interpolated from those of the nodes. Effectively, the ECM model involves an averaging over the atomic degrees of the freedom that are missing from the node. The meshless local Petrov-Galerkin (MLPG) method is employed to solve for the displacements of the nodes in the ECM region. This is illustrated of in Fig. 7. In the ECM region, the nodes can be taken to be arbitrary, and not necessarily be coincident with the atoms. In MD region, the nodes are taken to be the atoms themselves. In the ECM region, the solid points represent the atoms, while the open points represent the nodes of the MLPG method. MLPG5 is implemented in “ECM” region and MLPG2 is implemented in MD region.

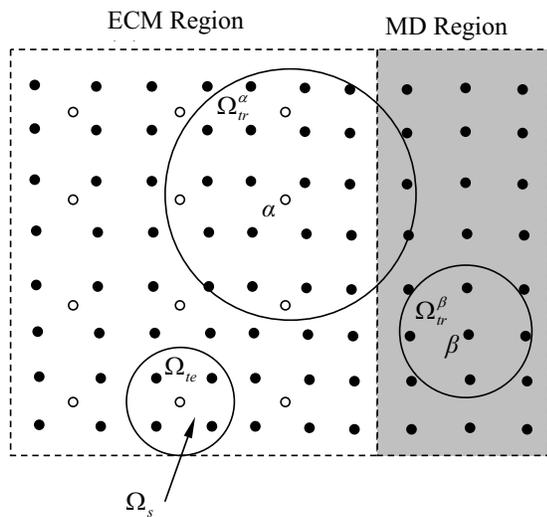


Figure 7 : Illustration of ECM/MD multiscale simulation.

The MLPG method, a truly meshless method developed by Atluri and his colleagues, is a simple and less-costly alternative to the FEM and BEM [Atluri and Zhu (1998), Atluri and Shen (2002a, b)]. Remarkable suc-

cesses of the MLPG method have been reported in solving the convection-diffusion problems [Lin and Atluri (2000)]; beam problems [Raju, Phillips (2003)]; fracture mechanics [Kim & Atluri (2000), Ching & Batra (2001)]; strain gradient materials [Tang, Shen and Atluri, (2003)]; three dimensional elasticity problems [Li, Shen, Han and Atluri (2003)]; elastodynamic problems [Batra, Ching (2002); Sellountos, and Polyzos (2003)]; elastodynamic problems in continuously nonhomogeneous solids [Sladek, Sladek, Zhang (2003)]; thermoelasticity [Sladek, Sladek, Atluri (2001)]; Navier-Stokes flows [Lin and Atluri (2001)]; and plate bending problems [Gu & Liu (2001), Long and Atluri (2002), Qian, Batra, and Chen (2003a, b)]. A comparison study of the efficiency and accuracy of a variety of meshless trial and test functions is presented in Atluri and Shen (2002a, b), based on the general concept of the meshless local Petrov-Galerkin (MLPG) method. The recent review of the MLPG method, regarding its theory and applications can be found in Atluri (2004), and Atluri and Shen (2003).

As mentioned before, the displacement \mathbf{u}_i of an atom in ECM region implies an average value of the atomic displacement, it can not catch the thermal fluctuations. To describe it more accurately, we assume that the “real” displacement \mathbf{q}_i of the atom in the ECM region can be expressed as:

$$\mathbf{q}_i = \mathbf{u}_i + \delta\mathbf{u}_i \quad (45)$$

where $\delta\mathbf{u}_i$ denote the atomic thermal fluctuations, and it is assumed that $\delta\mathbf{u}_i \ll \mathbf{u}_i$ in ECM region. This decomposition has the multiscale feature offered by pure MD and the continuum respectively: short-wavelength fluctuation of individual atom and long-wavelength wave of the continuum. By means of this decomposition, the effects of the thermal fluctuations on the MD region lead to the interface conditions. An optimal method was proposed [Shen and Atluri (2004)] in both reducing the reflection of phonons and in lowering computational cost, especially when the atomistic region moves with time. A multiple time step method was employed for the time integration in both MD and ECM region: the MD simulation is advanced by k steps of size Δt_A , when the ECM simulation is advanced for a step of size $\Delta t_B = k\Delta t_A$. The stability of multiple time step method was studied in Belytschko et al. (1979). Numerical experiments stated that this method was very accurate and efficient. More details about this multiscale method are given in Shen and Atluri

(2004), and Atluri (2004).

For more examples about the multi-scale simulations and their application, see the proceedings of the Training Workshop on Multiscale Modeling, Simulation and Visualization and Their Potential for Future Aerospace Systems [Noor (2002)]. In addition, two special issues of *CMES: Computer Modeling in Engineering & Sciences* (2002a, b) have been devoted to this topic. Srivastava, Menon and Cho (2001) briefly reviewed computational techniques and provided a few examples derived from computer simulations of carbon nanotube-based molecular nanotechnology. Chang and Guo (2002) also reviewed the recent advances in molecular dynamics and Monte Carlo simulations.

Although substantial progress has been made in recent years, multi-scale modeling method is still in its infancy, and it still requires intensive efforts. As pointed by many researchers, the main issues in the development of seamless multi-scale modeling methodology are still the limitations on the length and time scale, and the numerical accuracy and efficiency. Hence, a more accurate and efficient multi-scale modeling methodology is still desirable, and attracts many researchers.

4 Numerical Simulations in Carbon Nanotube

Since the debut of carbon nanotube (CNT) in 1991 [Iijima (1991)], it has stimulated activities in the investigation of the physical and mechanical properties and their potential technological application. CNT can be produced by an array of techniques, such as laser ablation, arc discharge and chemical vapor deposition. They possess exceptional properties, such as high stiffness and strength, the ability to sustain large elastic strain, and high thermal and electric conductivity.

A single-walled carbon nanotube (SWNT) can be viewed as a result of rolling a graphene sheet, by specifying the direction of rolling and the circumference of the cross-section. A multi-walled carbon nanotube (MWNT) is composed of concentric graphitic cylinders with closed caps at both ends and the graphitic layer spacing is about 0.34 nm. In the graphene sheet, carbon atoms are arranged in a hexagonal array, and each has three nearest neighbors. The atomic structure of nanotube is described in terms of the tube chirality, or helicity, which is defined by the chiral vector \mathbf{C}_h and the chiral angle θ , as shown in Fig. 8. After cutting the graphite sheet along the dotted

lines and rolling to form a nanotube, the two end nodes of the chiral vector coincide. The chiral vector, i.e. the roll-up vector can be expressed as a linear combination of base vectors \mathbf{a}_1 and \mathbf{a}_2 of the hexagonal:

$$\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2 \quad (46)$$

where the integers (n, m) , which uniquely define the type of the nanotube, are the number of steps along the zigzag carbon bonds of the hexagonal lattice. Three major categories of nanotube are defined based on the chiral angle θ . The chiral angles are 0° and 30° for the two limiting cases which are referred to as zigzag and armchair, respectively. The chiral angle is between 0° and 30° for chiral. The zigzag nanotube is denoted by $(n, 0)$ and the armchair nanotube (n, n) . The roll-up vector of the nanotube also defines the diameter of the nanotube. The physical properties of CNTs are sensitive to their diameter, length and chirality [Dresselhaus, et al. (1997); Popov, et al. (2000); Hernandez, et al. (1998)]. A survey about the mechanics of carbon nanotubes can be found in Qian, Wagner, Liu, Yu and Ruoff (2002). Here, we only review the latest achievements in this field.

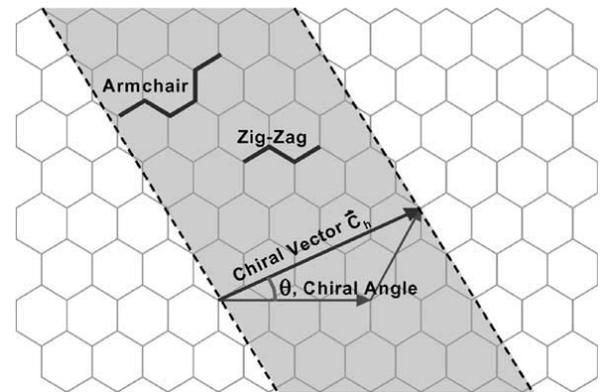


Figure 8 : Schematic diagram of a hexagonal graphene sheet [Thostenson, et al. (2001)].

Ab initio, TBMD and classical MD methods were employed to perform the analysis of CNT. They are the “bottom up” methods. By means of MD, Iijima, et al. (1996) studied the structural flexibility of CNTs, and Yakobson, et al. (1997) simulated the high strain fracture in CNTs. Hernandez, et al. (1998) investigated the elastic properties of nanotubes using TBMD. Sanchez-Portal

(1999) studied the elastic and vibrational properties of CNTs resorting to density functional theory (*ab initio*). Belytschko et al. (2002) simulated the nanotube fracture using MD methods, and showed moderate dependence of fracture strength on chirality. Dumitrica et al. (2003) proposed a brittle bond-breaking CNT failure mechanism by using the density functional theory (DFT). Troya, et al. (2003) presented quantum mechanical studies of CNT fracture using two different semiempirical methods. The different fracture mechanisms from quantum mechanics and empirical potentials were explored. Guo and Guo (2003) investigated the coupled mechanical and electrostatic properties of single walled open CNTs under applied electric field and tensile loading by means of quantum mechanics and quantum-MD techniques. Quite different failure mechanisms in electric or mechanical loading were predicted. Guo and Guo (2003) simulated an exceptional large axial electrostrictive deformation in CNTs using Hartree-Fock and density functional theory. The volumetric and gravimetric work capacities are predicted to be three and six orders higher than those of the best known ferroelectric, electrostrictive, magnetostrictive materials and elastomers, respectively.

Multiwalled carbon nanotubes (MWNTs) have been proposed as candidates for nanoscale molecular bearings, spring, and oscillators. Zhao, et al. (2003) used MD to study the energy dissipation mechanism for isolated systems of two coaxial carbon nanotubes, which may serve as a nearly frictionless nano-oscillator. Guo, et al. (2003) also performed MD simulations of a double walled CNT oscillator to show that the rate of energy dissipation depends on the commensuration and relative morphology of the bitube. Zhang, et al. (2003) studied double-walled CNTs-based bearings using MD simulations. Their results showed that dynamic effects dominate the friction in these DWCNT bearings and the interlayer friction is very small. In their simulations, the intralayer interaction is described by a Brenner potential, and the interlayer interaction is represented by the registry-dependent graphitic potential developed by Kolmogorov and Crespi (2000). Qian et al. (2003) studied the nature of load transfer in a single walled carbon nanotube bundle using a Lennard-Jones potential for the inter-tube interactions. Their results revealed that the radial deformation strongly depended on the twist angle, which consequently changes the nature of the contact and contributes a new interlayer tribology. Zhang, et al. (2003) inves-

tigated the mechanical properties of SWNTs filled with small fullerenes (C₂₀, C₃₆ and C₆₀) using MD simulation. The interaction between carbon atoms was described by a combination of Brenner potential with a two-body pair potential. Their mechanical properties depended on the filling-density and the radius of the tube. Such peapod types of structures may use in functional nanoscale devices such as nano-pistons, nano-bearings, nano-writing implements, or as a nano-capsule storage system. Wei and Srivastava (2003) studied the transport of long polymer molecules through CNT channels using the MD simulations. A polymer molecule is adsorbed into a NT due to van der Waals interactions, which is modeled as Lennard-Jones potentials. Tersoff-Brenner potentials were used for carbon-carbon and hydrogen-carbon interactions.

As discussed in previous sections, these atomistic modeling techniques are limited to systems containing a small number of molecules or atoms and are usually confined to studies of relatively short-lived phenomena, from picoseconds to nanoseconds. Nanotubes dominated by atomistic effects exhibit continuum-like behavior. Continuum-like methods that have been developed for nanoscale devices rely on parameterizations of more detailed calculations, e.g. from molecular dynamics and/or *ab initio*, to be fed into existing continuum models such as shell [Yakobson, Brabec, and Bernholc (1996)] and beam [Wong, Sheehan, and Lieber (1997)] theories. Yakobson, Brabec, and Bernholc (1996) studied the nanotube instability problem by means of the shell theory. Pantano and his colleagues (2003) used a continuum/finite element approach to model the structure and the deformation of SWCNTs and MWCNTs. In their works, individual tubes are modeled using shell elements, the effects of van der Waals forces are simulated with special interaction elements. Vodenitcharova and Zhang (2003) investigated the effective wall thickness of a single-wall carbon nanotube using the continuum ring theory. Savinskii and Petrovskii (2002) calculated the vibration spectrum of a nanotube in the long-wavelength limit as a function of the radius and thickness of the nanotube, which was represented as an elastic cylindrical shell of a finite thickness. Harik (2002) analyzed the applicability of continuum-beam models and continuum shell theories to the global mechanical behavior of SWNTs, and concluded that the direct use of the beam theory should be limited to SWNTs with very small

diameters. Sudak (2003) presented a multiple column model for the linearized column buckling of multi-walled carbon nanotubes using the theory of nonlocal continuum mechanics. Gao and Li (2003) developed another continuum-based model for computing strain energies and Young's modulus of SWCNT, which is viewed as a continuum hollow cylinder by rolling up a flat graphite sheet that is treated as an isotropic continuum plate. In their model, kinematics of finite deformations was employed with the Hencky strain and the Cauchy stress. All these kinds of continuum models can be used to analyze the static or dynamic mechanical properties of nanotubes. However, these models neglect the detailed characteristics of nanotube chirality, and are unable to account for forces acting on the individual atoms. Moreover, developments such as these are difficult to extend to general computational methods due to the strict assumptions associated with shell and beam theories.

The equivalent-continuum modeling approach [Odegard, Gates, Nicholson, and Wise (2002)] and molecular structural mechanics method [Li, and Chou (2003)], as introduced in section 3, were also used to treat nanotubes. Odegard, et al. (2003) developed constitutive models for nanotube-reinforced polymer composite system, where the nanotube, the local polymer near the nanotube, and the nanotube/polymer interface were modeled as an effective continuum fiber using the equivalent-continuum modeling approach. Li and Chou (2003) used the molecular structural mechanics method to model the deformation of single-walled CNTs, the elastic properties was obtained. Then, they extended this method to simulate the elastic behavior of multi-walled CNTs under tension and torsion. The van der Waals interactions are accounted by introducing a nonlinear truss rod model. They also analyzed the interfacial load transfer in the carbon nanotube reinforced polymer composite by combining this method and continuum FEM, where the CNT is modeled by the molecular structural mechanics method, and the matrix is modeled by FEM. CNTs are regarded as ideal reinforcing materials for high-performance nanocomposites [Maryyama, and Alam (2002)], a review of nanotube-based composites can be found in Thostenson, et al. (2001).

Crystal elasticity theories based on the Cauchy-Born rule, as discussed in quasicontinuum method in section 3, have also been applied to CNTs. A continuum theory for modeling carbon nanotubes was proposed by directly in-

corporating interatomic potentials into a continuum-level constitutive relation on the basis of the Cauchy-Born rule in Zhang, Huang, Gao, et al. (2002), same as the quasicontinuum method. The SWCNT is assumed to be a cylindrical with vanishing thickness. The theory was first used to study the elastic modulus of a SWNT [Zhang, Huang, Geubelle, et al. (2002)], and then applied to the study of fracture nucleation in SWNTs [Zhang, Huang, Gao, et al. (2002)]. It was also employed to investigate the effect of nanotube radius on the constitutive model of SWCNTs [Jaing, et al. (2003)], and the influence of mechanical deformation on the electrical properties of SWCNTs via the k-space tight-binding method [Liu, et al. (2004)]. This method is limited to uniformly deformation, and the cross-section of the SWCNT must remain circular during the deformation (since this method required that the sequence of deforming a CNT and "unroll" the deformed CNT to a plane can be exchanged). Therefore, this method can be applied to tension and torsion, but not bend. Qian, Liu and Ruoff (2001) proposed a combined continuum/MD models for the analysis of interaction between C60 and nanotube, where the nanotube is modeled as a cylindrical shell with finite thickness using the Cauchy-Born rule as in quasicontinuum method, and the C60 is modeled directly by MD. The direct application of the Cauchy-Born rule to CNT will result in inconsistency, since a CNT is not space-filling, but composed of a curved single-atom-thickness atomic layer. Arroyo and Belytschko (2002) corrected this inconsistency by introducing the exponential map from differential geometry. Using the modified Cauchy-Born rule, a quasicontinuum method was developed for single layer crystalline films, and the CNT is modeled as a continuum membrane with no thickness. Good results for the bending of nanotubes were presented [Arroyo and Belytschko (2002)]. However, it is not an easy task to evaluate the exponential map for a complicated configuration.

5 Conclusion

The recent developments and applications of the multi-scale modeling in nanomechanics and nanotubes are reviewed in this paper. Although many promising methods are proposed, a number of challenges still remain, such as the limitations on the length and time scale, the numerical accuracy and efficiency, the self-consistency (or non-reflection/seamless) of multiscale models. The numerical accuracy depends on the accuracy of interatomic poten-

tials, and the self-consistency depends on the interfacial condition between MD/continuum or QM/MD.

The Cauchy-Born rule and energy-equivalent assumption play important roles in reasonably bridging the continuum level to atomistic level. But the homogeneous-deformation assumption limits the application of the Cauchy-Born rule. The Cauchy-Born rule is only appropriate for bond interaction. For non-bond interaction, an accuracy, efficiency and reasonable continuum model is still lacking. The energy-equivalent assumption involves too many assumptions and mixed many quantities; these are the main reasons why there is a wide varieties in the values of Young's modulus/wall-thickness pair for SWCNTs in the literatures. Rather than Cauchy-Born rule and energy-equivalent assumption, possibly, a new generalized multiscale method should be directly based on the force (conservation of *local* linear momentum) and averaging techniques (constitutive equations represent some averaged behavior of collective atoms). For deriving the electric properties of the nanomaterials, the simulation must be taken down to quantum mechanics. An effective electromechanical multiscale model may be helpful.

Nanomechanics is a developing field which is rich of numerical, computational, physical and mathematical challenges. A novel and seamless multi-scale modeling methodology will play a key role in the simulation and design methodology for nanotechnology.

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