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CHAPTER

FOUR

MOLECULAR DYNAMICS IN MICROSCALE THERMOPHYSICAL ENGINEERING

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ABSTRACT

Because of rapid developments in computer speed and memory over the last 2 decades, the field of molecular dynamics (MD) has experienced explosive growth. The molecular basis and computationally intensive nature of the MD technique render it particularly effective for modeling systems of limited size and for studying short time scale phenomena. This paper presents a critical review of recent MD developments in microscale thermophysical engineering. Existing works on thermal conductivity, radiation-related manufacturing, thermal convection, and other short length and time scale studies are evaluated in detail. Limitations of MD and prospects for future development are also assessed. It is found that MD is well suited to study microscale topics such as thermophysical properties of complex microstructures, thermal convection with size effects, and ultrashort pulse laser melting.

NOMENCLATURE

k_B	Boltzmann's constant
N	number of atoms
r_i	position of particle i
r_{ij}	distance between particles i and j
Γ	aspect ratio

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ε Lennard-Jones well depth parameter
Φ inter-particle potential
v_N N-body potential
ρ dimensionless number density
σ Lennard-Jones equilibrium separation parameter

1 INTRODUCTION

Devices and materials with ultra-small dimensions are becoming increasingly important in modern technology. Films with characteristic dimensions on the order of microns and below are critical components in integrated-circuit transistors, quantum-well lasers, and microelectromechanical systems (MEMS). Also, thin films of materials with favorable optical properties may play an important role in the optical computing devices of the future [1]. Operating temperatures have a significant impact on device and material performance in the above applications. For example, heating adversely affects the operation of vertical-cavity surface-emitting lasers [2] and edge-emitting lasers [3], and temperature strongly influences the short time scale optical properties of porous silicon films [4]. In the aforementioned length and time scales, the properties of materials and the dynamic behavior of devices cannot be predicted with the conventional continuum theory. To best understand phenomena at these scales, microscale engineering techniques that account for molecular motion must be developed. Additionally, there is an urgent need to bridge microscale engineering and conventional macroscopic continuum engineering and to determine regimes of applicability for each approach. Several approaches exist for molecular-scale simulations, such as lattice dynamics [5], Monte Carlo simulations, and MD simulations. In this chapter, the review focuses on molecular dynamics simulations in microscale thermophysical engineering. Concerning the development of MD in fluid mechanics, there is a good review paper by Koplik and Banavar [6].

1.1 Short History of MD

Molecular dynamics is a computational technique that simulates the behavior of materials by solving Newton's classical equations of motion for a set of molecules. This was first accomplished, for a system of hard spheres, by Alder and Wainwright [7]. Following Verlet's success in solving the equations of motion for a set of Lennard-Jones (LJ) particles [8], the properties of the LJ system were well explored (e.g., [9]). After this initial work, the scope of MD simulations was broadened beyond the LJ model. Several early researchers developed interatomic potentials to model different materials, such as diatomic molecular liquids [10], water [11], flexible hydrocarbons [12], proteins [13], and silicon [14]. Others advanced the field of nonequilibrium MD, a method useful for direct calculation of transport coefficients such as thermal conductivity [15]. Some workers studied

phase transitions and behavior at interfaces [16]. Still others have studied the vibrational and thermophysical properties of nanoscale systems [17,18]. More early works related to the above development can be found in the book by Allen and Tildesley [19].

1.2 Advantages of MD

Molecular dynamics simulation provides a route from microscopic details of a system such as atomic interactions and molecular geometries to macroscopic properties of engineering interest such as transport coefficients and structural order parameters. Knowledge of these properties in microscale systems are especially important in phonon engineering, which is the design of materials with desired thermophysical properties. Additionally, computer simulation provides a way to access extremes of temperature and pressure that are difficult or impossible to explore with experiments. Quite subtle details of molecular motion and structure are difficult to probe experimentally, but can be extracted readily from a MD simulation.

1.3 Lattice Dynamics, Monte Carlo Method, Boltzmann Transport Equation, and MD

Popular particle-based approaches for calculating material properties are lattice dynamics (LD), the Monte Carlo method (MC), the Boltzmann transport equation (BTE), and MD. The LD method [5] calculates vibrational frequencies of the dynamical system of interacting atoms comprising a solid lattice. An important disadvantage of this method is its limitation to the study of solid materials. Another disadvantage is that systems with defects and other irregularities are not easily treated, because inverting the dynamical matrix and solving for the particle positions becomes especially cumbersome in such systems. Monte Carlo determines particle trajectories using statistical molecular collision probabilities. This method is advantageous in treating a large-scale system if reasonable particle collision probabilities are provided, because it does not involve intensive force calculations such as those required by MD. Monte Carlo is also easier to implement for systems in which it is difficult to extract the intermolecular force law from the potential function, such as those composed of molecules that interact through discontinuous forces or in those where the potential function is a complicated multidimensional surface.

Because it is based on physical particle-particle interactions, MD has a stronger physical basis than statistical approaches such as MC and BTE. The use of a good interaction potential, however, is required to make reasonable predictions from MD. This method can provide information about collision dynamics, which is the most unknown quantity in MC and BTE. For determination of simple equilibrium properties such as the pressure in atomic fluids, MC and MD are equally effective. Molecular dynamics, however, is more efficient in evaluating properties such as heat capacities and interfacial properties, and it provides access to dynamic quantities such as transport coefficients.

2 FRAMEWORK OF MD

Much of the molecular dynamics research in the literature employs the classic Lennard-Jones (LJ) argon-type potential model to describe interactions between pairs of atoms. The LJ potential, described in more detail in Section 3.1, has a simple two-body form that results in much shorter simulation times than more complex potentials.

In MD simulations of materials, the first thing that must be done is to determine the size of the system that is to be studied. Even the largest MD simulations [20] can only model domains on the order of tens to hundreds of nanometers. To address this problem for bulk material simulations, periodic boundary conditions are used. In this scenario, the actual simulation cell of a small number of atoms is essentially repeated infinitely in all directions. Increasing the number of atoms in the computational domain will produce "bulk" results that are more realistic [21], but there is a point of diminishing returns at which the additional computational cost brings only incremental improvement in the calculated values.

To choose the optimal simulation cell size, one must consider two important factors. The first consideration is the speed and storage capacity of the computer to be used. A conventional workstation can simulate systems on the order of thousands of atoms and smaller in a reasonable time. Here, "reasonable time" is defined as shorter than a few days. The actual duration of the simulation depends not only on the number of atoms in the computational domain, but also on program optimization, competition for CPU time from other users, the number of time steps needed to observe the phenomenon of interest, and the frequency and quantity of writing data to files.

The other important consideration is the state and temperature of the system. In fluid systems a cubic simulation cell of side 6σ, where σ is the Lennard-Jones equilibrium separation parameter, is usually big enough to capture the most of the essential physics [19]. For solid systems, however, Lukes et al. [22] found that this condition did not necessarily guarantee physically meaningful results. Long-wavelength phonons in solids are artificially excluded in MD simulations of "bulk" systems because spatial fluctuations with wavelengths larger than the simulation cell size cannot be captured [23]. At lower temperatures, the exclusion of long-wavelength phonons is more pronounced. Lukes et al. [22] developed a criterion based on the Wien's law for phonons that indicates the minimum MD simulation cell dimensions needed at a given temperature to yield physically meaningful results for solids.

An MD simulation starts by setting initial atomic positions and velocities and calculating the initial interatomic forces by taking the derivative of the potential and summing over all pairs of atoms. After initialization, the main program loop begins. This loop should perform four primary functions. The first function is to advance the difference equations of motion at every time step. The second is to calculate the quantities of interest, which can include but are not limited to thermodynamic properties such as free energy, pressure, and temperature. The third function is to record information in data files at regular intervals for later analysis and for record

keeping. Finally, the program should monitor the stability of the system. The first and fourth functions are particularly important and are discussed in more depth below.

Many types of algorithms have been used to advance the difference equations of motion in MD simulations, but two of the most popular are Gear methods [24] and the so-called "velocity Verlet" algorithm [25]. For more detailed discussion of the merits and shortcomings of these methods as applied to MD, see Allen and Tildesley [19]. The widely used velocity Verlet method is simple, convenient, and has low storage requirements. To keep computation time reasonable, the common convention of a cutoff radius is employed in calculating forces. This means that only the neighbors of an atom within a certain radius are included in the force calculations, as faraway atoms have a negligible contribution to the total force on a given particle. Such a convention should only be applied to systems in which atoms are subject to short-range forces [19].

At the beginning of the simulation, it is common practice to allow the system to evolve for a short time to allow it to reach an equilibrium state from its initial configuration. After this equilibration, time averaging of the desired quantities then begins, continuing for the duration of the simulation. Longer simulations are desirable because they provide better statistics and reduce variability of the data, but they have the disadvantage of increased computational cost. Throughout the simulation, parameters such as kinetic energy and potential energy should be tracked to provide a check on the stability of the system. These quantities should remain constant for systems at steady state. They will not be strictly constant due to the discontinuity in potential energy experienced by atoms crossing the cutoff radius but will show some fluctuation about a mean constant value. Fluctuations larger than one ten thousandth of the total energy and/or a steady drift in the mean value of total energy over time indicate that there is some source of instability in the program. This often means that the time step is too large. Stability is increased by using a smaller time step, but then simulation time also increases due to the finer time mesh. A balance between stability and computational cost must be made when choosing the time step. For dense fluids and solids, a good guideline for the time step is that it should be on the order of one-tenth the typical atomic vibrational period, and for dilute gases, the time step should be a few times smaller than the collision time [15]. For argon-model systems, time steps from 1 to 10 femtoseconds are commonly used.

The discussion above is geared toward equilibrium MD simulations (EMD). Although transport is an inherently nonequilibrium process, transport parameters such as mass diffusion coefficient, viscosity, and thermal conductivity can be extracted from EMD. This is done by calculating the equilibrium time correlation function of the relevant flux operator and using this function in the Green-Kubo formula [26] to obtain the transport parameter of interest. The problem with this method is that time correlation functions represent the average response to the small, naturally occurring fluctuations in the system properties. The response of systems to large perturbations thus cannot be treated by EMD. Even for systems with small perturbations from equilibrium, EMD is not ideal because the Green-Kubo formulation requires long simulation times to obtain reasonable results.

Nonequilibrium MD simulations (NEMD) address these problems. Such simulations follow the same general framework as EMD, with the significant difference that a modification to the program must be made to enforce the nonequilibrium condition. Historically, NEMD has not been treated as thoroughly in the literature as EMD, but it is the subject of increasing emphasis in more recent MD works. An advantage of NEMD is that systems far from equilibrium can be studied because a much larger fluctuation may be induced when compared with EMD. This causes dramatic improvement of the signal-to-noise level of the measured response [19]. Additionally, NEMD is generally less computationally expensive than EMD [27]. This improves the efficiency with which transport coefficients are calculated.

In NEMD studies, as discussed above, some method must be used to implement a nonequilibrium condition. One way of doing this, known as homogeneous NEMD, is to add additional terms to the normal equations of motion for all atoms to simulate the effect of a gradient. No true physical gradient exists in homogeneous NEMD simulations, but the atoms behave, to first order, as if one does exist. The other method, known as nonhomogeneous NEMD, is to maintain spatially separated boundary regions in the computational domain, which impose a gradient of some property such as concentration, velocity, or temperature. This method has the advantage of being directly analogous to a real system subjected to a gradient. An important disadvantage is that large gradients must often be imposed on the system to obtain a high enough signal/noise ratio from the simulation.

For more background on NEMD, the excellent review by Hoover and Ashurst [15] covers the early NEMD work through the mid-1970s, and the review by Hoover [28] covers more recent developments. The discussion by Allen and Tildesley [19] is also a valuable reference.

3 INTERMOLECULAR POTENTIALS

A comprehensive description of the constituent particles is the basis of microscopic-level simulations of matter. This description depends on interatomic or intermolecular potentials. Molecular dynamics generally adopts a classical point of view, typically representing atoms or molecules as point masses interacting through forces that depend on the separation of these particles. Precise description of the intermolecular potential requires the knowledge of the relative orientation between molecules [19]. In principle, the potentials are based on quantum mechanics because of the overlapping of electron clouds. Quantum-mechanical calculation supplies a way to solve the total energy of a system as a function of atomic coordinates. The rigorous quantum mechanics solution is still extremely difficult to obtain, although there are some such efforts in very small systems, using *ab initio* or first principle MD methods [29–31]. A large computational effort is required to accurately solve the Schrödinger equation, so these methods are currently limited to the studies of static properties for systems only involving a few tens of atoms. Hence, the empirical interatomic potentials, although generally not

as accurate as the first principle methods, are more widely applied because they can deal with much larger systems and can model static as well as dynamic properties of systems [32]. They are a compromise between accuracy and speed and provide a means of investigating problems that are currently beyond the purely *ab initio* approach. The following sections discuss empirical and semiempirical potentials and *ab initio* calculations in more detail.

3.1 Empirical and Semiempirical Potentials

A general form of a potential Φ describing interactions among N identical particles can be divided into one-body, two-body, three-body, and higher-order contributions as follows:

$$\Phi(1,2,\ldots,N) = \sum_i \nu_1(\mathbf{r}_i) + \sum_i \sum_{j>i} \nu_2(\mathbf{r}_i,\mathbf{r}_j) + \sum_i \sum_{j>i} \sum_{k>j>i} \nu_3(\mathbf{r}_i,\mathbf{r}_j,\mathbf{r}_k) + \ldots + \nu_N(\mathbf{r}_i,\mathbf{r}_j,\mathbf{r}_k,\ldots,\mathbf{r}_N) \tag{1}$$

where $\mathbf{r}_i$ is the position of the ith particle and the function ν_N is called the N-body potential. To be useful, the component function ν_N should converge quickly to zero with increasing N. The first (one-body) term represents external potentials such as wall and external forces to which the system is subject. In many cases, this term is absent. In principle, the second term, which describes the interactions between two particles, is the beginning of the expansion. It is the simplest possible model. The best-known two-body potential is the Lennard-Jones (LJ) potential,

$$\Phi(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] \tag{2}$$

where r_{ij} is the distance between particles, ε is the energy parameter, and σ is the length parameter. This potential has a weakly long-range attractive tail of the form $-1/r^6$, a negative well of depth ε, and a steeply rising repulsive wall at distances less than $r \sim \sigma$. In application, the long tail is truncated at relatively short distances. The well depth is often quoted in units of temperature as ε/k_B, where k_B is Boltzmann's constant. The LJ potential is a short-range interaction between particles and is usually used to describe properties of liquids and gases for which polarization and van der Waals forces are dominant in atomic bonding. This potential has been used successfully to model liquid argon. One can find energy and length parameters for other materials in Allen and Tildesley [19]. Many papers apply this potential, as shown later in Tables 1 to 3, to gases, liquids, and even solids [33] due to its simplicity.

Although pair potentials are very simple and can be directly applied to a completely arbitrary configuration of atoms, they do not accurately describe any but the

Table 1 Comparison of Existing Works on Thermal Conduction by Molecular Dynamics Simulation.

References	Dimensions	Solid/ liquid/gas	Potentials/ materials	EMD or NEMD [cause → effect]	Notes and comments
Payton et al. (1967) [67]	1-D and 2-D	Solid	Modified Lennard-Jones	NEMD [$\Delta T \rightarrow Q$]	*Temperature jumps at boundaries (apparent surface resistance).
Jackson et al. (1968) [68]	1-D	Solid	Specified Hamiltonian function	NEMD [$\Delta T \rightarrow Q$] and EMD	*Calculated temperature distribution did not match the applied temperature gradient.
Alder et al. (1970) [69]	3-D	Liquid	Hard sphere	EMD	*108 and 500 particles.
Gass et al. (1971) [70]	3-D	Solid	Hard sphere	EMD	*107, 108, and 500 particles.
Levesque et al. (1973) [71]	3-D	Liquid	Lennard-Jones (LJ)	EMD	*864 particles.
Hoover and Ashurst (1975) [15]	3-D	Dense fluid	Soft sphere and LJ	NEMD [$\Delta T \rightarrow Q$]	*"Thermal reservoir method" used to impose temperature gradient. *108 particles.
Ciccotti et al. (1978) [72]	3-D	Liquid	LJ	EMD	*256 particles. *According to Evans [27], Eq. (13) in this chapter is incomplete.
Ciccotti and Tenenbaum (1980) [73]	3-D	Liquid	LJ	NEMD [$\Delta T \rightarrow Q$]	*256 and 864 particles. *"Thermal wall technique" used to impose temperature gradient. *Temperature jumps at boundaries (apparent surface resistance).
Hoover et al. (1981) [74]	2-D	Dense fluid	Inverse 12th-power potential	NEMD [$\Delta T \rightarrow Q$]	*A violation of Fourier's heat conduction law in the angular direction for a rotating disk was found due to Coriolis's force.

Tenenbaum et al. (1982) [75]	3-D	Dense fluid	LJ	NEMD [$\Delta T \rightarrow Q$]	*256 particles. *"Stochastic walls" were used, but the solid wall introduces large inhomogeneities into the fluid.
Evans (1982) [27]	3-D	Dense fluid	LJ	NEMD	*"Zero wavevector method" (homogeneous NEMD).
Gillan and Dixon (1983) [76]	3-D	Liquid	Smoothly truncated LJ	NEMD and EMD	*256 particles. *"Zero wavevector method."
Massobrio and Ciccotti (1984) [77]	3-D	Dense fluid	LJ	NEMD	*256 particles. *"Subtraction technique" was used. It applied external fields several orders of magnitude smaller than those of Evans (1982) [27] did.
Evans and Murad (1989) [78]	3-D	Liquid HCl	Site-site LJ with point dipoles and quadrupoles	NEMD	*256 HCl molecules. *A NEMD algorithm was developed for fluids composed of rigid bodies possessing rotational degrees of freedom.
Lee et al. (1991) [79]	3-D	Solid	SW potential and WWW amorphous Si model/amorphous silicon	EMD	*216 atoms. *Stillinger-Weber Si potential (1985) [14]. *Wooten-Winer-Weaire amorphous Si model (1985) [80]. *Quantum statistics of the phonon was included, so that low temperature properties were apparent.
Michalski (1992) [81]	2-D	Crystal and glass	Modified Penrose tiling	NEMD	*400 atoms. *Penrose, R., *Bull. Inst. Math. Appl.*, 10, 266 (1974). *Crystalline, amorphous, and quasi-crystalline classic models of solid and glass.
Murad et al. (1993) [82]	3-D	Liquid	LJ shifted-force potential	NEMD	*108 particles. *The thermal conductivity of fluids in an infinite system of plane slit micropores with permeable walls can exhibit strong anisotropy.
Kotake and Wakuri (1994) [33]	2-D	Solid	LJ	NEMD [$Q \rightarrow \Delta T$]	*Layer thickness effect and lattice defect effect on the developed temperature gradient.

Table 1 (continued)

References	Dimensions	Solid/ liquid/gas	Potentials/ materials	EMD or NEMD [cause → effect]	Notes and comments
Hansen and Evans (1994) [83]	2-D	Dense fluid	Soft disk	NEMD	*56, 224, 896, 3584 particles.
Poetzsch and Böttger (1994) [84]	2-D	Solid	Specific potential	NEMD [$\Delta T \rightarrow Q$] and EMD	*Disordered systems. *Effect of 3rd and 4th-order anharmonicity on the heat conductivity. *Triangular lattice.
Ikeshoji and Hafskjold (1994) [85]	3-D	Liquid/gas	Smooth truncated LJ	NEMD [$Q \rightarrow \Delta T$]	*Thermal conductivity for the 128 particle system was 10% smaller than experimental data. *1024 particles system showed better agreement (within 1 to 2%).
Daivis and Evans (1994) [86]	3-D	Liquid butane	Ryckaert-Bellemans model	NEMD	*108 particles. *Ryckaert-Bellemans model (*Discuss. Faraday Soc.*, 66, 95 (1978)). *A version of Evans NEMD algorithm for thermal conductivity that can be applied to molecules with arbitrary internal degrees of freedom including rigid-body rotation.
Daivis and Evans (1995) [87]	3-D	Liquid butane	Ryckaert-Bellemans model and AUA model	NEMD	*108 particles. *Anisotropic United Atom model (S. Toxvaerd, *J. Chem. Phys.*, 93, 4290 (1990)). *AUA model gave better results than the Ryckaert-Bellemans model.
Maeda and Munakata (1995) [88]	1-D	Solid	FPU β-model	NEMD	*Fermi-Pasta-Ulam (FPU) model (*Lect. Appl. Math.*, 15, 143 (1974)). *Temperature-dependent thermal conductivity.

Baranyai (1996) [89]	3-D	Liquid	WCA spherically symmetric potential	NEMD [$\Delta T \rightarrow Q$]	*2048 particles; periodic boundary conditions. *Weeks-Chandler-Anderson potential (*J. Chem. Phys.*, 54, 5237 (1971)) is the Lennard-Jones potential cut at its minimum and shifted upward. *Thermal conductivity was found to be independent of the size of temperature gradients.
Risso and Cordero (1996) [90]	2-D	Gas	Hard disk	NEMD [$\Delta T \rightarrow Q$]	*100–8000 hard disks. *For numbers of hard disks greater than 1500, temperature profiles agree with the continuous theory, but conductivity differs.
Omeltchenko et al. (1996) [91]	3-D	Amorphous silicon nitride	A specific potential with two- and three-body terms	EMD and NEMD	*36288 particles. *The specific potential was also used in Vashishta, Kalia and Ebbsjo, *Phys. Rev. Lett.*, 75, 858 (1995). *MD on a parallel machine. *Thermal conductivity was calculated from the difference between the NEMD and EMD values of the heat current. *Thermal conductivity was found to scale as density to the 1.5 power.
Inoue et al. (1996) [92]	3-D	Clathrate hydrate	Pairwise-additive	EMD and NEMD	*Evaluated thermal conductivities of clathrate hydrate are lower than those of ice from both EMD and NEMD.
Volz et al. (1996) [93]	3-D	Solid	LJ	EMD and NEMD [$\Delta T \rightarrow Q$]	*1408 particles. *Heat flux and phonon relaxation time computations were done using EMD. *NEMD simulations at short time scales reveal acoustic and thermal wave behavior with both coherent and incoherent characteristics.
Volz et al. (1996) [94]	3-D	Solid	LJ	EMD and NEMD [$\Delta T \rightarrow Q$]	*1408 particles. *Heat flux relaxation time calculated from MD was found to agree with the phonon mean relaxation time. *At short times, NEMD simulations do not agree with the hyperbolic heat conduction model.

Table 1 (continued)

References	Dimensions	Solid/ liquid/gas	Potentials/ materials	EMD or NEMD [cause → effect]	Notes and comments
Müller-Plathe (1997) [95]	3-D	Fluid	LJ	NEMD [Q → ΔT]	*2592 atoms. *Uses a "velocity exchange" technique to impose heat flux. *Advantages of this technique include compatibility with periodic boundary conditions, conservation of energy and linear momentum, and quicker convergence of the calculations by imposing heat flux rather than temperature gradient.
Paolini et al. (1997) [96]	3-D	Solid, KCl and KCl doped with RbCl	Shell-model and rigid-ion potentials	EMD	*64-ion KCl system. *It was found that polarization strongly alters the calculated conductivity at a given temperature.
Lukes et al. (1998) [22]	3-D	Solid	LJ	NEMD [Q → ΔT]	*Showed the effect of film thickness on the thermal conductivity and found an unusual wave effect. * Developed a regime map delineating which periodic-direction simulation cell sizes and which temperature conditions are necessary for MD to produce physically meaningful results.
Volz and Chen (1998) [97]	3-D	Solid, silicon	SW potential	EMD	*1536 atoms. *Calculated thermal conductivity in silicon nanowires using both EMD and Boltzmann Transport Equation (BTE). *Deduced specularity parameter p = 0.585 from comparison of EMD and BTE, indicating that inelastic scattering may be responsible for diffuse phonon scattering. *EMD calculations reveal that nanowires have a thermal conductivity 40 times smaller than bulk silicon at 500 K.

Note: EMD, Equilibrium Molecular Dynamics; NEMD, Nonequilibrium Molecular Dynamics.

simplest closed-shell systems. In particular, pair potentials are completely inapplicable to strongly covalent systems such as semiconductors [34]. For materials such as silicon, which have complex interatomic interactions, potentials require three-body or higher-order terms. The choice of potential determines the simulation accuracy and the computational cost. The existence of more than 30 empirical silicon potentials in the literature [35] shows the difficulty of building appropriate potentials and the lack of specific theoretical guidance.

Most silicon potentials fall into either Stillinger-Weber (SW) [14] or Tersoff [34, 36–37] forms. The SW potential is a linear combination of two- and three-body terms. The range of the SW potential is just short of the second-neighbor distance in the equilibrium diamond lattice. The pair potential has a deep well at the first neighbor distance to represent the restoring force against stretching sp^3 hybrid covalent bonds [35]. The three-body term captures the nature of covalent sp^3 bonds and favors the diamond lattice over close-packed structures. The fitting parameters used in this potential were determined from experimental properties of solid cubic diamond and liquid silicon. Applications of the SW potential can be found in Tables 1 and 2.

The Tersoff-type potential functions, which contain multi-body effects and are environmentally dependent, are fundamentally different from the SW type. The strength of the individual bonds is affected by the presence of surrounding atoms. This feature makes the Tersoff potentials more time consuming than the SW potential in calculations because the coordination number of each atom must be determined in order to obtain forces between atoms at each time step. There are three versions of Tersoff potentials [34,36-37]. Each version uses different fitting parameters to better reproduce particular properties of silicon. Comparisons of the various silicon potentials have been made by Balamane et al. [32], Cook and Clancy [38], and Halicioglu et al. [39].

Building a potential usually starts from physical intuition and theoretical guidance combined with fitting parameters. One can improve the existing potential with more flexible forms, more elaborate schemes, and more adjustable parameters. However, too many adjustable parameters make it difficult to gain physical insight from the simulation results. An alternative to fitting guessed functional forms is to derive potentials by systematic approximation of quantum mechanical models [31]. Although this approach has failed to produce superior models, important connections between electronic structure and effective interatomic potentials have been revealed.

3.1.1 *Ab initio* Calculation

As mentioned previously, the algebraic functional form of intermolecular potentials is determined by the measured properties of bulk materials. Although such empirical potentials work well in many cases, sometimes they should be modified [40]. Moreover, when there is not enough experimental data to develop a good algebraic empirical potential, there is no way to carry out MD simulations other than by using theoretically obtained intermolecular potentials [41]. For materials such as amorphous indium phosphide [42] and especially for new structures or combinations of

Table 2 Comparison of Existing Works on Radiation-Related Material Processing and Phase Change Phenomena by Molecular Dynamics Simulation.

References	Dimensions	Processing/ materials	Potentials	Notes and comments
Rahman and Schuller (1985) [100]	3-D	Homogeneous melting/ Lennard-Jones crystal	LJ	*4000 particles, periodic boundary conditions. *Homogeneous melting: the temperature of the system was raised suddenly to a temperature slightly above the melting temperature. *For melting to occur, energy has to be exchanged between the electron and phonon system through inelastic electron-phonon collisions. *The inelastic electron collision time has been measured to be about 10 nsec.
Abraham and Broughton (1986) [101]	3-D	Pulsed melting/silicon	SW potential	*Approximately 1800 atoms; periodic in the lateral directions. *First use of nonpairwise potentials to study interfaces between condensed phases. *The equilibrium crystal-melt interface was found to be sharp for the (111) orientation and broad for the (100) orientation.
Landman et al. (1986) [102]	3-D	Melting and faceting/silicon	SW potential	*1008 and 3456 particles. *Following equilibration of the total system, a portion of the system was heated via scaling of particle velocities. *Equilibrium structure of the crystalline Si (100)-melt interface are described and a (111)-faceting transformation at the interface is evidenced.
Chokappa and Clancy (1987) [103]	3-D	Melting/Lennard-Jones system	LJ	*108–4000 particles. *The solid was shown to superheat quite considerably, and it is believed by the authors that the lack of a surface and periodic boundary conditions are of major importance in producing the superheating of the solid.

Chokappa and Clancy (1987) [104]	3-D	Cooling/Lennard-Jones system	LJ	*128–2048 particles. *Glassy amorphous solids were produced by the rapid quench of the system (8×10^{14} K/s), and the glass transition temperature was in good agreement with earlier studies.
Kluge et al. (1987) [105]	3-D	Rapid quenching/amorphous silicon	SW potential	*216 atoms; periodic boundary conditions, homogeneous cooling. *By quenching the melt at a rate of 3×10^{14} K/s, amorphous silicon was formed. *Excellent agreement with the experimental neutron scattering factor is obtained.
Kluge et al. (1987) [106]	3-D	Pulsed laser melting/crystal silicon	SW potential	*216 atoms; periodic boundary conditions, homogeneous heating. *23 ps laser pulse of 0.2 J/cm^2 is assumed to deliver 9×10^{13} W/g. *At 14 ps, the crystal reaches the limit of superheating and melts over the next 4 ps.
Chokappa and Clancy (1988) [107]	3-D	Laser annealing/ Lennard-Jones system	LJ	*1000–4000 particles; periodic boundary conditions. *15 ps of 0.025 J/cm^2 laser heating is simulated by fictitious energetic particles ("energy transfer agents").
Chokappa and Clancy (1988) [108]	3-D	Melting/Lennard-Jones system	LJ	*A "sandwiching" system with 439 to 464 atoms in liquid portions and 500 particles in solid. *The presence of a solid/liquid interface was shown to prevent the superheating and supercooling found in the previous surfaceless system.
Chokappa et al. (1989) [109]	3-D	Laser annealing/Lennard-Jones system	LJ	*1000, 2744 and 4096 particles; periodic boundary conditions are applied only in the two lateral directions with a reflective wall at the top of the vapor section. *Fictitious "energy carriers" supply a given energy fluence over a given pulse duration with a Gaussian intensity-time shape. *The interface response function shows an asymmetry of melting and freezing kinetics (the former being significantly faster). *Predictions of the extent of superheating and supercooling were made. *Good qualitative agreement with experimental results for silicon was obtained.

Table 2 (continued)

References	Dimensions	Processing/ materials	Potentials	Notes and comments
Clancy (1991) [110]	3-D	Crystal growth and dissolution/ metals and semiconductors	Embedded atom method [111]	*2048, 4096, and 8072 atoms. *The thermal conductivity was underestimated and the temperature gradient was overestimated. *No segregation of one component into the liquid phase was observed in the alloy because the regrowth velocity was too large.
Richardson and Clancy (1992) [112]	3-D	Crystal regrowth/metals and metal alloys	Embedded atom method (EAM)	*2048, 4096, and 8072 atoms; the prediction of regrowth velocity was shown to be fairly insensitive to the system size. *Due to the neglect of the free-electron contribution to the transport properties, the thermal conductivity is approximately 68 times too low for EAM-modeled Cu compared to experiment; for EAM-modeled Au, it is 178 times too low; in EAM-modeled Cu and Au, the heat gradients were roughly 90 times larger than experimental ones.
Kotake and Kuroki (1993) [113]	2-D	Laser irradiation	LJ	*About 200 atoms. *By absorbing laser light energy, atoms in the solid are excited into different, higher energy potential wells. This changes their interaction forces. *The laser energy of irradiation has a considerable effect on the phase change of vaporization and melting.
Shibahara and Kotake (1993) [114]	2-D	Radiative heating and cooling	LJ	*About 200 atoms. *The radiative absorption and emission were assumed to be a function of the vibration frequency. *The temperature change of the solids by radiative heating and cooling were proportional to the difference between the product of the vibrational probability, the absorption intensity, and the emission intensity.

Baez and Clancy (1995) [115]	3-D	Crystal growth and dissolution/ Lennard-Jones system	LJ	*13500 atoms, periodic boundary conditions. *Implanted fcc nanocrytallites in a subcooled liquid *The rate of growth showed minimum, suggesting the existence of "magic numbers" in crystal growth from the melt.
Marques et al. (1996) [116]	3-D	Ion beam induced recrystallization/amorphous silicon	SW potential	*4096 and 32768 atoms. *The growth of small crystalline grains embedded in an amorphous matrix was used to simulate the ion bombardment. *Thermal effects were simulated by heating the sample above the amorphous melting point.
Yu et al. (1996) [117]	3-D	Solidification/SiGe alloys	SW potential	*$5 \times 5 \times 10$ and $7 \times 7 \times 14$ unit cells. *Interface response functions and solute redistribution at the regrowing solid/liquid interface were investigated. *The maximum crystallization velocity of SiGe alloys was found to decrease below the pure component values.
Silvestrelli et al. (1996) [45]	3-D	Laser melting/crystal silicon	*Ab initio*	*64 atoms, periodic boundary conditions. *Relaxation time for the electrons is ~ 10^{-14} sec, while the electron-ion relaxation time is ~ 10^{-12} sec.
Dubey and Gumbs (1997) [118]	3-D	Heating and cooling/silicon cluster	Kaxiras and Pandey potential	*Kaxiras and Pandey potential (*Phys. Rev. B*, 38, 12736 (1988)) was derived from a microscopic calculation with the density functional method. *MD simulation began with 45-atom clusters, and the end result was a 39-atom cluster after several heating and cooling cycles. *Annealing process started at 4000 K and cooled down to 20 K with five rates: 2, 5, 10, 20, and 30 K fs^{-1}. The rates of cooling have a nontrivial effect on the structure of the cluster.
Shibahara and Kotake (1997) [46]	2-D	Light irradiation/two metallic atom system	Quantum molecular dynamics method (QMD)	*QMD can be loosely defined as any MD method that incorporates some quantum mechanical features by considering electronic motion. This method calculates new intermolecular potentials at every time step like the Car-Parrinello (CP) method, but does not necessarily solve the full quantum mechanical problem to do so. In this sense, *ab initio* MO methods, the CP method, or any other variation of MD which includes quantum effects in the calculations can be considered QMD.

Table 2 (continued)

References	Dimensions	Processing/ materials	Potentials	Notes and comments
Shibahara and Kotake (1997) [46] (continued)				*For a simple atomic system: two ions and two valence electrons. *The wave function of free electrons can be obtained by solving the Schrödinger equation, and the potential between ions is expressed by the Lennard-Jones type potential. *Two photon parameters were considered: the light angular frequency calculated from photon energy and the light electric field calculated from photon energy density or laser beam output.
Shibahara and Kotake (1998) [119]	2-D	Light irradiation/seven and 13 atom system	QMD	*Under infrared light irradiation, the atomic fragments have translational velocities parallel to the direction of light fluctuation. *Under light irradiation at electron energy levels, the fragments tend to be isolated and atoms have random translational velocities. *Under infrared light irradiation, the light interaction comes through fluctuations of effective dipole moment, whereas light irradiation at electron energy levels comes from changes in the potential energy between atoms associated with the electron excitation.

the elements, such a theoretical approach is required. Also when quantum effects take an important role, for example, in chemical reactions [43] and photon absorption [44–46], the transient molecular structure should be considered dynamically coupled with molecular motion.

The growth of nanotechnology requires reliable calculations for small clusters of molecules in place of the band calculations used for bulk materials because large surface area and/or complicated atomic structures such as those found in superlattices, quantum dots, and superfine particles cause fundamental changes in the properties and behavior of materials. The electronic states and total energy of such structures can be obtained by solving the Schrödinger equation. Such analysis yields fundamental characteristics of the material such as the intermolecular forces, the stable structure [47], and the optical properties [48–49]. This procedure gives a nonempirical intermolecular potential and is called *ab initio* or first principle calculation because it needs no empirical data except the atomic number of the target material.

Several numerical methods for calculating the electronic structure have been developed to solve for the fundamental properties of materials. Using the molecular orbitals (MO) obtained from these methods, approximate algebraic intermolecular potential functions can be constructed for any combination of molecules. Because *ab initio* calculation of MO is very time-consuming, especially for large molecules, it is impractical to do this at each time step of an MD simulation. For this reason, many studies calculate the MO and intermolecular potential a single time at the beginning of a simulation. The precalculated algebraic potential is then used for the entire MD simulation. Of all the quantum calculation approaches used to determine MO, local density functional techniques (LDF) have been the most successful. Such calculations require a significant amount of computational time because the calculations should be performed iteratively until self-consistency of the electron density is reached. Detailed explanations of this and other MO techniques are given in many recent books, for example, Parr and Yang [50]. Commercial software packages are also available for MO calculations on stable structures of base states and transition states, vibration/thermodynamic property calculations, and ion structure calculations, but calculations for large systems of more than 100 atoms are still not feasible [47,51]. The use of precalculated pair potentials obtained from MO methods is expected to give more accurate results than empirical methods and also offers a significant savings in computational time over methods that calculate transient intermolecular potentials at every time step [52–57].

Car and Parrinello [58] derived an *ab initio* MD method that considers electronic states by using the equations of motion of the wave functions. This explicit algorithm makes it possible to calculate the full Schrödinger equation for the entire system and to determine a new intermolecular potential at every time step. The Car-Parrinello (CP) method takes less time than *ab initio* MO calculations but is still very computationally intensive. The CP method is considered the most promising approach for obtaining realistic results for small dynamic systems without any empirical data. This method has been applied to many kinds of phenomena [59–62]. Also, slightly modified techniques have been examined [63]. Other methods are being

Table 3 Comparison of Existing Works on Thermal Convection by Molecular Dynamics Simulation.

References	Dimensions/ flow type	Potentials	Particles/ computation time or number of collisions	Dimensionless number density, ρ/ aspect ratio, Γ	Notes and comments
Mareschal and Kestemont (1987) [120]	2-D/Rayleigh-Bénard Flow (RB)	Hard disk	5040 disks/35 × 10^6 collisions	$\rho = 0.2$ $\Gamma = 2(2)^{0.5}$	*Thermal wall with partial slip, smooth lateral walls. *Roll nucleation occurred at the lateral wall and three-roll pattern developed for Rayleigh number estimated to be 1780. There are no stable ordered structures for Rayleigh number 990.
Rapaport (1988) [121]	2-D/RB	Hard disk	14160 disks/ 86 × 10^6 collisions	$\rho = 0.4$ $\Gamma = 4$	*Slip thermal wall and periodic lateral boundaries. *Stable four-roll pattern for several values of ΔT. Metastable six-roll pattern appeared in one case.
Mareschal et al. (1988) [122]	2-D/RB	Hard disk	1500 and 5000 disks/50 × 10^6 collisions	$\rho = 0.2$ $\Gamma = 2$	*Thermal walls conserved the tangential velocity and thermalized the normal component. *Stable two-roll pattern.
Puhl et al. (1989) [123]	2-D/RB	Hard disk	5000 disks/50 × 10^6 collisions	$\rho = 0.2$ $\Gamma = 1, 2$	*Thermal walls conserved the tangential velocity and thermalized the normal component. The vertical sides are specularly reflecting. *Stable two-roll pattern in the case of $\Gamma = 2$, but a stable single-roll pattern was observed in the case of $\Gamma = 1$.
Given and Clementi (1989) [124]	2-D/RB and Poiseuille flow	Hard disk	5040 and 10200 disks/about 50 × 10^6 collisions	$\rho = 0.4$ $\Gamma = 2(2)^{0.5}$	*"Cell boundary method." *This study pointed out that stochastic boundary algorithms seem constrained to give vortex cells with unit aspect ratio. *This work found that moderate-sized MD simulations are capable of showing stable convection cells, at least for systems with slip boundary conditions.

Bhattacharya and Lie (1989) [125]	2-D/channel flow	LJ	2500 gas particles	$\rho = 0.13 - 2.72 * 10^{-4}$ $\Gamma = 1$	*Knudsen number (Kn) = 0.01 – 0.3. *Navier-Stokes equations seem to be valid up to Kn = 0.27 in this study. *For Kn < 0.05, the calculated slip coefficient 1.16 is in good agreement with existing theoretical results.
Rapaport (1991) [126]	2-D/RB	Hard disk	57600 disks/ 2×10^9 collisions	$\rho = 0.4$ $\Gamma = 1$	*Nonslip thermal and lateral walls. *An oscillatory roll pattern emerged when the system was increased from about 20000 to 57600 disks.
Rapaport (1992) [127]	2-D/RB	Hard and soft disks	57600 and 115600 disks/10^{10} collisions for hard disks and 5×10^6 time steps for soft disks	$\rho = 0.4$ $\Gamma = 1$	*Nonslip thermal and lateral walls. *This study showed that different simulation runs under identical conditions but with initial states that differed in ways that are seemingly irrelevant at the macroscopic level exhibited very different forms of pattern evolution.
Rapaport (1994) [128]	2-D/RB	Hard and soft disks	57600 and 115600 disks	$\rho = 0.4$ $\Gamma = 1$	*Nonslip boundary conditions. *This study focused on the different kinds of time-dependent roll structure observed in studies of soft- and hard-disk fluids. In both cases periodic oscillations were observed, but despite similar imposed conditions the periods and amplitudes differed significantly.
Vannitsem and Mareschal (1995) [129]	2-D/RB	WCA potential	5000 and 9800 particles/750000 time steps	$\rho = 0.4, 0.7$ $\Gamma = 2$	*Periodic lateral boundaries and thermal walls with partial slip. *The enhancement of diffusion with respect to molecular self-diffusion is shown to scale as $Pe^{0.5}$, where Pe is the Peclet number. This behavior is in agreement with previous theoretical and experimental results.
Ibsen et al. (1995) [130]	2-D/RB	Hard disk	1444 and 8100 disks	$\rho = 0.25, 0.05, 0.01$ $\Gamma = 1$	*Lateral boundaries are periodic or nonslip. *For a nonuniform thermalizing wall there exists a phenomenon known as "thermal slip." Two complementary arguments show that the velocity field by a nonuniform thermalizing wall is proportional to the ratio between the heat flux and the pressure.

Table 3 (Continued)

References	Dimensions/ flow type	Potentials	Particles/ computation time or number of collisions	Dimensionless number density, ρ/ aspect ratio, Γ	Notes and comments
Watanabe and Kaburaki (1996) [131]	2-D/RB	LJ	7200 particles/ 40000 time steps	$\Gamma = 2$	*The macroscopic flow transition between heat conduction and convection in the 2-D Rayleigh-Bénard system is simulated using MD. *The temperature of the top wall is 120 K, and that for bottom wall ranged from 120 to 600 K.
Khare et al. (1997) [132]	2-D/Couette flow	Purely repulsive potential	1552 fluid atoms and 256 wall atoms/ 4×10^5 time steps	$\rho = 0.844$	*It was shown that results for transport coefficients are significantly affected by thermostatting; in fact, the transport properties of the fluid determined with and without a thermostat exhibit a qualitatively different shear rate dependence. It is also shown that the temperature profiles observed in the simulation can be described by continuum mechanics, provided the temperature dependence of the viscosity and thermal conductivity is taken into account.

developed to incorporate the quantum effect appropriately and efficiently for each target situation. Most microscale engineering phenomena can be divided into quantum and molecular contributions, which can be treated separately [43,64–65]. Focusing on the most dominant factor will bring a clearer understanding even for complicated phenomena. For example, consideration of only the valence electron is still enough to represent the essential physics in the case of photon absorption by alkali metals [46,66]. The decision whether *ab initio* calculation is necessary or not would be most important for engineering applications.

4 EXISTING WORKS ON THERMAL TRANSPORT

Existing works on thermal conduction, radiation-related manufacturing processes, and thermal convection are shown in Tables 1 to 3. Table 1 is a survey of MD works on thermal conduction. For each reference, this table indicates the type of MD simulation, the intermolecular potential used, and brief comments about key aspects of the work. In nonhomogeneous NEMD, there are two different approaches, in terms of cause and effect, to calculate the thermal conductivity: impose a temperature gradient to calculate the heat flux ($\Delta T \rightarrow Q$), or impose a heat flux to calculate the resulting temperature gradient ($Q \rightarrow \Delta T$). Note that in Table 1, studies using nonhomogeneous NEMD are indicated as NEMD [cause $\rightarrow$ effect], while homogeneous NEMD studies are simply listed as NEMD. Early nonhomogeneous NEMD works focused on the $\Delta T \rightarrow Q$ approach. The primary issue in these studies was how to model the hot and cold walls. Methods such as thermal reservoirs [15] and stochastic thermal walls [73,75] were developed to impose temperature gradients. The approach $Q \rightarrow \Delta T$ was used by Kotake and Wakuri [33] and Ikeshoji and Hafskjold [85]. The advantages of this approach are reported by Müller-Plathe [95].

Early studies used simple intermolecular potentials such as hard spheres, soft spheres, and the LJ potential for thermal conductivity calculations. Lee et al. [79] used the SW potential [14] and the Wooten-Winer-Weaire a-Si model (WWW) [80] to simulate heat conduction in bulk crystalline silicon and amorphous silicon, respectively. After that, many other potentials were proposed for different materials. One should note that the majority of the existing works are for gases and liquids, and only a few deal with thermal conduction in solids. Allen et al. [17] and Dickey and Paskin [18] performed simulations of nanoscale solid materials using the LJ potential. The vibrational and specific heat behavior calculated from these simulations corresponds well qualitatively with experimental data. More recently, Kotake and Wakuri [33] have shown for a two-dimensional solid system subjected to a constant flux that the resultant temperature gradients sharply increase as the system width is decreased, and Volz and Chen [97] found that solid silicon nanowires exhibit a strong reduction in thermal conductivity when compared with the bulk. Also, Lukes et al. [22] have observed unusual wave-like size effects on the thermal conductivity of a thin solid argon-type film.

Table 2 is a survey of the existing MD research on radiation-related material processing and phase change phenomena. Works on melting before 1986 can be found in the review by Allen and Tildesley [19]. Concerning the solid-liquid and liquid-vapor phase-change thermophysics and transport, there are two recent review papers by Carey [98–99]. One can see in Table 2 that the Lennard-Jones and Stillinger-Weber potentials were overwhelmingly used before 1989. Clancy [110] and Richardson and Clancy [112] adopted the embedded atom method (EAM) [111] for metals, semiconductors, and metal alloys. They found that the thermal conductivity was underestimated and the temperature gradient was overestimated due to the neglect of the free-electron contribution to the transport properties. After 1993, short time scale radiation heating was initially considered for argon-type solids and silicon by using Lennard-Jones and Stillinger-Weber potentials. Recently, *ab initio* MD [45] and quantum MD [46,119] were employed to study the laser melting of crystal silicon with 64 atoms and light irradiation of a few atoms, respectively.

Table 3 is a survey of existing literature on convection. All of these studies consider two-dimensional flow systems. Rayleigh-Bénard (RB) flow, which is a buoyancy-induced flow caused by heating the fluid at the bottom wall and cooling at the top wall, is the primary topic of these works. Poiscuille flow [124] and Couette flow [132] have also been studied. Hard disk, soft disk, and LJ potentials are the most frequently used potentials in these studies. The ratio of channel width to channel height, or the aspect ratio Γ, affects the pattern of vortex rolls for RB flow. Because of limited computational power, the values of aspect ratio in the above studies were less than 4. As in thermal conduction studies, a major issue in the MD simulation of thermal convection is the modeling of thermal walls. Several different models for thermal walls have been proposed. In conventional wall models, particles are reflected from an imaginary wall with velocities determined by the wall temperature after reaching a defined spatial position. Instead of using this type of model, Khare et al. [132] used a true physical wall with 256 atoms.

5 OTHER THERMOPHYSICAL ENGINEERING APPLICATIONS

In this paragraph, applications of MD other than those shown in Tables 1 to 3 will be described briefly. It is not intended to give a complete survey of each field. Rather, a few studies are chosen to demonstrate the breadth of MD applications in microscale thermophysical engineering.

5.1 Thermal Properties and Temperature Variation of Mechanical Properties

The phonon density of states of high-temperature ceramic silicon nitride was investigated by inelastic neutron scattering and MD by Loong et al. [133], and the specific heat calculated from the total density of states of α–Si_3N_4 was in good agreement with the measurements over a wide range of temperatures. Tang and Yip [134]

studied the phonon dispersion curves, thermal expansion coefficient, and temperature variation of the elastic constant of β–SiC by MD.

5.2 Kapitza Resistance

An MD simulation was performed by Lumpkin et al. [135] to determine the thermal boundary resistance between two dissimilar classic one-dimensional harmonic chains of atoms directly. The phonon mismatch theory gives only an order of magnitude agreement with the MD simulation results.

5.3 Thermal Disorder

The accurate analysis of both X-ray diffraction and extended X-ray absorption fine structure spectroscopy data demands a proper understanding of disorder. Thermal disorder arises from the temperature-dependent vibration of atoms within the sample. MD was used by Edwards et al. [136] to explore thermal disorder in face-centered cubic copper.

5.4 Vibration Cooling and Heating, Superheating, Temperature Control of Clusters

MD simulations of clusters containing hundreds of naphthalene molecules were used to investigate vibration cooling and vibration heating by Kim et al. [137] and Kim and Won [138]. Broughton [139] showed by MD simulation that coated clusters could be superheated above their internal pressure-corrected thermodynamic melting points. An MD study of the high-temperature properties of Al(111) surfaces by Bilalbegovic [140] revealed that after going through the superheating regime, melting occurs over the whole crystal in a narrow temperature range. Westergren et al. [141] used MD simulations to investigate temperature control of unsupported clusters using a noble gas atmosphere.

5.5 Viscosity

Viscosity is a fluid transport property that can be calculated by MD. Several early works can be found in the survey of Ashurst and Hoover [142] and in Hoover et al. [143] and the references therein. Recently, the temperature dependence of viscosity was studied by Khare et al. [132] in simulations of nonisothermal planar Couette flows.

5.6 Interface Phenomena

The computer simulation of interface phenomena has been surveyed thoroughly by Nicholson and Parsonage [144]. Henderson and van Swol [145] have simulated the wetting of an LJ fluid against hard, smooth, rigid, and structureless CO_2 walls. Talbot et al. [146] have simulated N_2 fluid adsorbed on a graphite surface.

5.7 Phonon Transport in Crystals with Defects

Ozawa and Hiki [147] carried out MD simulations to investigate phonon scattering in defective crystals at finite temperatures. Transport of pulsed phonons in a mass-defect crystal was simulated to evaluate the thermal diffusivity of the crystal.

5.8 Mass Diffusion

Surface diffusion of Ge on Si(111) at high temperatures has been investigated with MD by Allen et al. [148]. The simulations yielded evidence for high-temperature island phenomena at picosecond time scales.

5.9 Nanoscale Phenomena

Understanding the variation of a material's properties with size, form of aggregation, and dimensionality is becoming important in the face of increasing miniaturization of electronic and mechanical devices. Barnett and Landman [149], through *ab initio* MD simulations, found that the electronic spectral and conductance characteristics of the atomic-scale contacts in nanowires exhibit dynamical thermal fluctuations on a subpicosecond time scale.

5.10 Deposition

Molecular dynamics is widely used in simulations of the deposition process. Kelchner and DePristo [150] presented MD results for low-energy deposition of 5- and 10-atom clusters on Pd(001) and Cu(001) substrates near 0 K. The growth of diamond-like thin films on substrates was investigated by Kaukonen and Nieminen [151] by MD. It was found that decreasing the substrate temperature and increasing the substrate thermal conductivity at high deposition energies were found to favor diamond-like properties.

5.11 Micro/Nanotribology and Friction

In developing low friction, durable surfaces for micro/nanotribology, MD simulations have been conducted by Hayashi et al. [152] and Landman et al. [153] for a better understanding of the atomistic mechanism of sliding friction. A spatial distribution of local quasitemperature, defined by averaging over time, was found to be a potentially convenient measure of heat generation and transport accompanying friction [152].

5.12 Reflow Process

It is important that aluminum films fill the grooves on silicon substrates for high-density electronic devices. Saito et al. [154] used MD to calculate changes in the free-

surface profiles of deposited aluminum films in a high-temperature reflow process on flat and grooved substrates.

6 LIMITATIONS OF MD AND FUTURE DEVELOPMENT

The primary disadvantage of MD is that it is limited to short length and time scales. Short time scales are typically not a concern unless very slow phenomena are being investigated, but the short length scales treatable with MD pose a problem when trying to model bulk materials. The use of periodic boundary conditions in bulk materials, however, inhibits the occurrence of long-wavelength fluctuations. For a cubic simulation domain of side L, the periodicity will suppress any density wave with a wavelength greater than L. Thus, it would not be possible to simulate a liquid close to the gas-liquid critical point, where the range of critical fluctuation is macroscopic. The same limitations apply to the simulation of long-wavelength phonons in modeling solids, where, in addition, the cell periodicity picks out a discrete set of available wave-vectors in the first Brillouin zone [155]. Periodic boundary conditions have also affected the rate at which a simulated liquid nucleates and forms a solid or glass when it is rapidly cooled [156]. For short length scale materials, the need to impose an artificial periodic boundary condition is removed in the size-limited dimension(s). Hence, size-limited materials are natural candidates for study with MD. Only for nanoparticles will the simulation be truly free of any periodic boundary condition artifacts, because there are no bulk longitudinal or in-plane dimensions as there are in nanowires and thin films. Despite the above remarks, the common experience in simulation is that periodic boundary conditions have little effect on the equilibrium thermodynamic properties or structures of fluids away from phase transitions in cases where the interactions are short-ranged [19].

A number of MD simulations have been employed to explore the thermophysical characteristics of small length scale materials. Thermophysical engineering applications, however, demand more practical studies on the simulation of metallic and covalent materials. To be most realistic, simulations of these materials should include the effects of electrons. There is much to be done with the new ideas for electronic motion simulation begun by Car and Parrinello [58]. This approach is very computationally intensive, however, and is subject to even stronger limitations on temporal and spatial domain sizes than classic MD. For this reason, there is a clear need to broaden the scope of MD. Hoover [28] outlines several approaches that could be used to accomplish this. Unfortunately, these methods are fully as time-consuming as in the solution of the partial differential equations of continuum mechanics.

The first direction for future development of MD methods is to build up better potential models for semiconductors and insulators [157–158]. Another is to further explore *ab initio* MD so that electron contributions, such as those in metals, can be treated explicitly. Terakura [159] outlines three important goals of *ab initio* MD: (1) to elucidate the electronic structures of complex systems efficiently, (2) to determine

the stable structures of complex systems theoretically, and (3) to perform MD simulations with forces acting on atoms that are obtained by first-principles electronic structure calculations.

In tandem with the development of better potentials and progress on *ab initio* approaches, work can also be done to apply MD to situations for which it is especially suited. For example, nanoscale and nanostructured materials are prime candidates for study with MD due to their small dimensions. Molecular dynamics can handle the nonuniformly distributed impurities, voids, cracks, and dislocations found in real thin films and the complex geometries present in novel materials much more easily than other approaches like MC and BTE. Irregularities can create localized, fractal, or other types of vibrational modes in a material, calling into question the assumption of pure phonon transport implicit in thermal studies utilizing MC and BTE. The MD method can predict the qualitative features of heat conduction without any introduction of the phonon concept [160].

Numerous articles on topics such as density of states in microcrystalline and glassy materials, phonon transport in crystals with defects, thermal disorder, and the effect of intricate nanostructure on thermal conductivity show that MD is a good technique for analyzing nanoscale phenomena in solid-phase materials. Further work should be done to study such phenomena using MD. Short time-scale phenomena are also a topic for further exploration. Molecular dynamics provides a way to ascertain the behavior of materials at time scales that are often hard to access with experiments. Only time scales on the order of nanoseconds and shorter can be treated in a reasonable time by MD simulations, because the finite-difference schemes used in such simulations require small time steps for energy conservation. The transient heat conduction work of Volz et al. [93–94] and the study of silicon cluster annealing with different cooling rates by Dubey and Gumbs [118] are good examples of short-time-scale MD studies in the literature. Further studies in this area will help elucidate the transient heating/cooling behavior of materials.

The MD literature on thermal convection is still limited. The results of existing works agree with bulk behavior, such as RB flow, Poiseuille flow, and Couette flow. More MD research should be devoted to study how coulombic forces, van der Waals forces, electrostatic forces, and steric forces [161] influence the thermal convection characteristics in size-limited flow configurations such as micro- and nanochannels.

7 CONCLUSION

Molecular dynamics is a valuable analysis tool for microscale thermophysical engineering. The primary advantages of this technique are its adaptability to complex materials, its ability to capture short time scale behavior, and its strong physical basis. Its disadvantages include the suppression of long-wavelength density fluctuations, the size limitation of the computational domain, and the long simulation times required to model systems with sizes greater than a few nanometers. The existing works primarily contribute to the studies of thermophysical properties and transport

coefficients for bulk materials. The limitations of MD in simulating bulk materials, however, can be turned to advantage for novel nanometer-scale materials. Future work should be done to apply this versatile, conceptually simple technique to micro- and nanoscale problems where other experimental and analytical approaches are difficult. Molecular dynamics is especially suited for the study of short time scale phenomena and for the calculation of thermophysical properties of materials with elaborate structures and compositions.

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