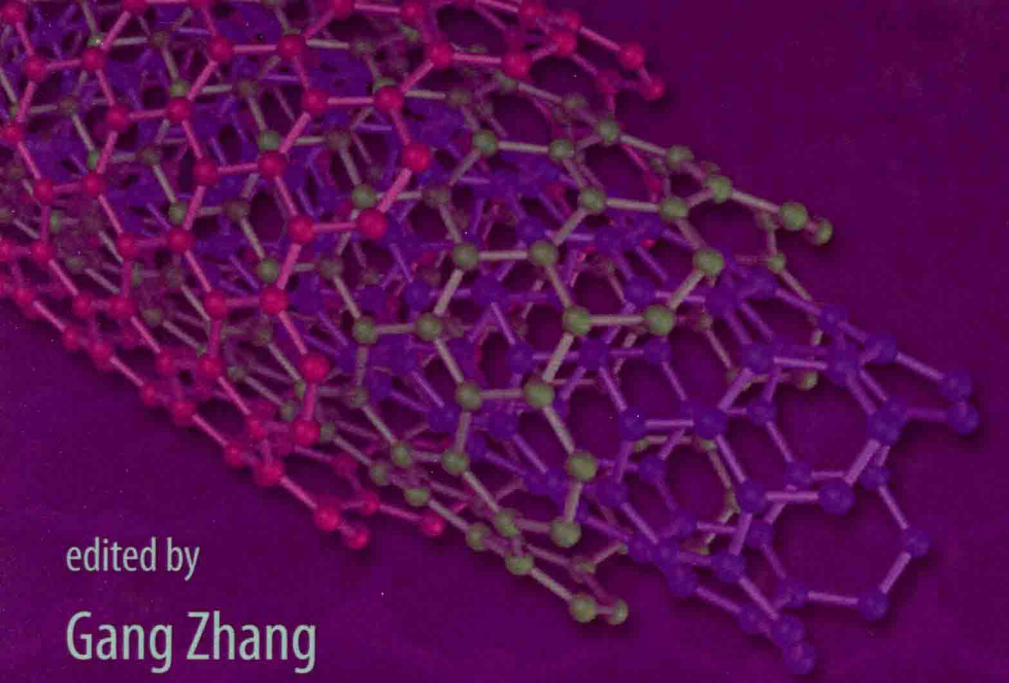

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A COMPUTATIONAL STUDY

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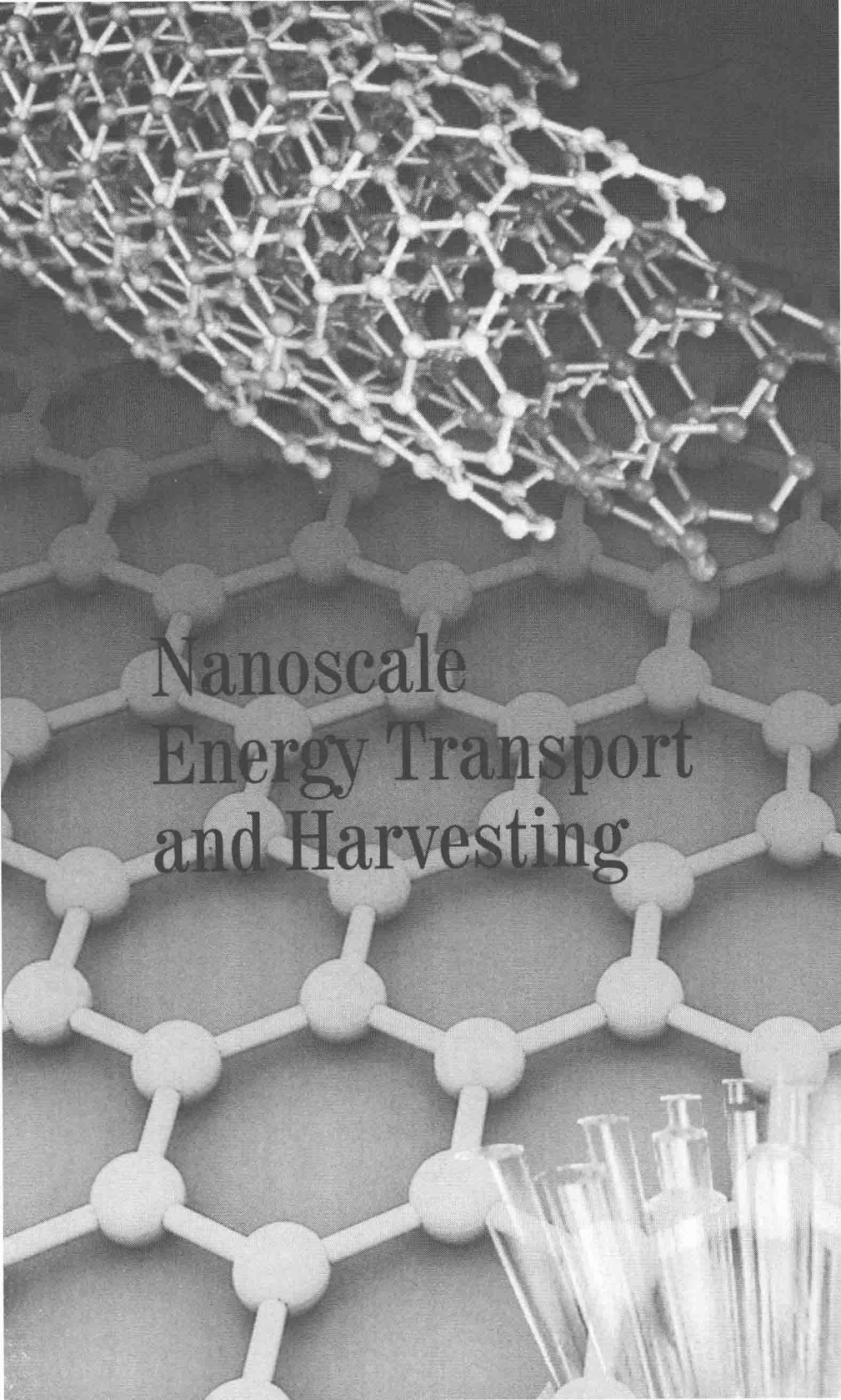
Nanoscale
Energy Transport
and Harvesting

Preface

Energy shortage is a great bottleneck in the supply of energy resources to an economy. The world's power demands are expected to rise 60% by 2030. Actually, people can solve the global energy crisis by enhancing the utilization efficiency of energy. Today, approximately 80% of the world's power is generated by heat engines that use fossil fuel combustion as a heat source, which is believed to be responsible for a large fraction of carbon dioxide emissions worldwide. The heat engines used in most thermal power station typically operate at 30–40% efficiency. This means that roughly 10 TW of heat energy is lost to the environment. Thermoelectric modules can potentially convert part of the wasted heat directly into electricity, reduce the usage of fossil fuels, and lower carbon emission. Moreover, microelectronic processors generate huge amount of heat in very small areas. Traditionally, this heat is considered as waste and may lead to the partial or total loss of the functionality of the processors. Power dissipation issues have recently become one of the greatest challenges for integrated electronic devices, and it is becoming a bottleneck for further development of smaller and faster devices. Currently, for every kilowatt-hour of energy consumed by a computer in a data centre, another kWh is needed for cooling. With the application of advanced thermal management and energy conversion technologies, world's household PCs can be converted to billions of mini power plants and up to 50% electric energy can be saved.

In addition, thermal management is also significantly important for solar energy harvesting. The solar cell technology can harvest and convert part of the solar energy into electricity by using the photovoltaic effect. The efficiency of conventional solar cells is usually quite low and limited because about 50% of the solar energy

is lost to heat through radiation to the environment. Based on the thermoelectric effect, it is in principle possible to further convert the heat energy to electricity, which provides a new channel for solar energy harvest and may significantly improve the efficiency of solar cells.

Thermoelectric energy conversion efficiency depends on the figure of merit ZT, which is proportional to the Seebeck coefficient, electrical conductivity, and absolute temperature, but inversely proportional to thermal conductivity. Recently the basic possibility of significantly increasing ZT through creation of new classes of thermoelectric materials with low-dimensional nanoscale structures has been demonstrated. The term nanoscale systems denote structures composed of a limited, small number of atoms. The interest of the scientific community in nanoscale systems has been boosted by the recent advent of micromanipulation techniques and nanotechnologies. Nanoscale materials have generated broad excitement both for fundamental science and for their potential applications in technology because of their scientific richness and promise in technological applications involving various devices. Efficient conversion between different forms of energy: thermal, electric, and optical, is a key enabler in many areas of science and engineering. Development of nanofabrication, characterization, measurement, and atomistic simulation tools can contribute to inspire new and better technologies for potential applications in energy saving and conversion.

The application of nano energy devices has highlighted the need for greater quantitative understanding of materials at the nanoscale. Understanding the physics of such systems by computational study is particularly important because their small size makes it is challenging to apply standard experimental measurement methods. Over the past decades, advances in computer science have spurred advances in fundamental theoretical techniques, mathematical modelling, and numerical simulation, giving rise to a revolution with extraordinary impact on nanoscience and nanoengineering.

The aim of this book is to provide an introduction for both theorists and experimentalists to the current computational

technology and then looking at the applications of nanostructures in renewable energy and the associated research topics. The book should also be useful for graduate-level students who want to explore this new field of research. The book addresses the current and commonly used computational technologies and their applications in study of nanoscale energy transport and conversion. With content relevant to both academic and commercial viewpoints, the book will interest researchers and postgraduates as well as consultants in the renewable energy industry.

The chapters have been written by internationally recognized experts in computational physics and provide in-depth introductions to the directions of their research. This approach of a multiauthor reference book appeared to be particularly useful in view of the vast amount of literature available on different forms of computational study. While there exists excellent reviews highlighting single facets of computational methods for renewable energy, we feel that the field lacks a reference that brings together the most important contributions to this topic in a comprehensive manner. This book is an attempt to fill the gap. Along these lines, our intention was to embed research on new energy materials into a wider context of computational researches. We thus hope that this book may serve as a catalyst both to fuse existing computational approaches and to inspire new computational tools in the rapidly growing area of new energy material research.

Accordingly, the book is organized into five chapters: The first chapter features a pedagogical introduction to molecular dynamics simulations. For large systems, molecular dynamics is a useful tool for investigating atomic motion. The trajectories of molecules and atoms can be determined empirically using a force field. The applications of molecular dynamics simulation have covered a wide range of research topics, such as liquids, defects, fatigue, surface, clusters, and biomolecules. Therefore, molecular dynamics simulation has become indispensable in today's research of physical and material science. The second chapter outlines the ballistic phonon transport theory in a quasi-one-dimensional (quasi-1D) system whose length is much shorter than the coherence length, which is bound by phonon scattering events. Landauer approach

for describing the coherent phonon transport in a quasi-1D system was introduced. Thermal conductance of carbon nanotubes is reviewed.

Chapter three systematically discusses the non-equilibrium Green's function (NEGF) method and tries to offer a complete theory for the investigation of quantum thermal transport. The NEGF method is widely and successfully used for the study of electronic transport. Here the method is generalized for thermal transport. After this theoretical opening, thermal conductance of graphene, a two-dimensional crystal consisting of a single atomic layer of carbon, has been reviewed. The following chapter summarizes groundbreaking work on ballistic phonons thermal transport at low temperature in low-dimensional quantum structures. Within the Landauer transport theory, the authors present a general formula to calculate the ballistic thermal conductance associated with phonon in the linear response limit. Then, a comparative analysis for the ballistic thermal transport is made between two-dimensional and three-dimensional models. The fifth chapter provides a systematic review on the effect of surface passivation on the phonon thermal conductivity and thermoelectric property of nanowires, based on introduction of molecular dynamics simulations. The underlying physical mechanism and analysis method are also presented. These results are helpful to understand the enhancement of thermoelectric performance of nanomaterials and to the design of renewable energy devices.

I finally remark that the various points of view expressed in the single chapters may not always be in full agreement with each other. As editor, I do not necessarily aim to achieve a complete consensus among all authors, as differences in opinions are typical for a very active field of research such as the one presented in this book.

I am most grateful to Stanford Chong, director of Pan Stanford Publishing, for his invitation to edit this book, and for his help in getting the project started. We also thank Sarabjeet Garcha from Pan Stanford Publishing for kind and efficient assistance in editing this book. I gratefully acknowledge financial support from National Natural Science Foundation of China (Grant No. 11274011) and the Ministry of Education of China (Grant No. 20110001120133).

I finally wish to thank all book chapter authors for sharing their expertise in this review volume. Their strong efforts and enthusiasm for this project were indispensable for bringing it to success.

Gang Zhang
Beijing
Winter 2014

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Chapter 1

Molecular Dynamics Simulations for Computing Thermal Conductivity of Nanomaterials

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1.1 Introduction to Molecular Dynamics

The physical properties of matter are found in its structure and motion of its constituent building blocks, and the dynamics are contained in the solution to the many-body problem. The many-body problem originated from the dynamics of the solar system, and its analytic solution turns out to be insoluble for three or more bodies. Although it is quantum mechanics instead of classical mechanics that describes the fundamental physics of condensed matter, the

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attempt to numerically solve the Schrödinger equation for a system of many nuclei and electrons is too formidable and not at all feasible in practice. Thus, one has to resort to approximations.

Molecular dynamics (MD) simulation is an extremely powerful tool to handle many-body problems at atomic level based on classical mechanics, which numerically solves Newton's equation of motion for a many-body system. It has the advantage of simulating realistic material with accurate many-body interatomic interaction obtained from first-principles calculations, which was not available but simplified by the two-body potentials with analytical form in the earlier theoretical model. The applications of MD simulation have covered a wide range of research topics, such as liquids [1], defects [2], fatigue [3], surface [4, 5], clusters [6, 7], and biomolecules [8]. Therefore, MD simulation has become indispensable in today's research of physical and material science.

The typical feature size that current first-principle calculations, such as density-functional theory (DFT), can be used to explore the thermal properties of nanostructures is on the order of several nm [9–11]. With MD simulations, the system size under study can be enlarged a lot. For instance, MD simulations of silicon nanowires with length up to μm [12] and cross-sectional area up to 806 nm^2 [13] have been reported. Moreover, Markussen *et al.* [9] studied thermal properties of thin silicon nanowires with both DFT and classical calculations based on Tersoff potential. They found that the calculation results of thermal conductance obtained from DFT and Tersoff calculations agree within 10% [9].

The validity of the classical approximation can be evaluated based on the de Broglie thermal wavelength [14] defined as

$$\Lambda = \sqrt{\frac{2\pi\hbar^2}{mk_B T}}, \tag{1.1}$$

where $\hbar$ is Planck's constant, m is the atom mass, k_B is Boltzmann's constant, and T is the temperature. The classical approximation is valid if $\Lambda << a$, where a is the nearest neighbor separation. Under this condition, the entire system can be treated as dilute gas model based on which the classical kinetic gas theory is formulated [15]. In this case, each molecule can be considered as a classical particle with a well-defined position and momentum. Moreover,

different molecules are distinguishable from each other [15]. Take the diamond-structured silicon for instance, its lattice constant is $L_0 = 5.43$ Å, and $a = \sqrt{3}L_0/4 = 2.35$ Å. The de Broglie thermal wavelength at room temperature is $\Lambda = 0.19$ Å, which is one order of magnitude smaller than the nearest neighbor separation. Therefore, for the group IV semiconductors with diamond structure, such as silicon and germanium, the classical approximation is appropriate above room temperature from the dilute gas point of view. Furthermore, quantum effects become important for any system when the temperature is sufficiently low. The drop of the heat capacity for crystals below the Debye temperature is a well know example of measurable quantum effects in solids. This is of particular importance in the study of thermal transport [16].

In the context of thermal transport, MD simulation is a statistical mechanics approach, which relates the microscopic behavior in a system with its thermodynamics. According to statistical mechanics, physical quantities can be evaluated by averaging over configurations distributed according to a certain statistical ensemble. For the N-particle system, MD simulation calculates the trajectory in a $6N$-dimensional phase space ($3N$ positions and $3N$ momenta) at each instantaneous time. This trajectory obtained from MD simulation provides such a set of configurations. To get the thermodynamic variables such as temperature, it relies on the ergodicity hypothesis of statistical mechanics, which asserts that the phase space can be fully recovered in the long-time limit and the time average is equivalent to the ensemble average. Therefore, thermodynamic variables of interest can be obtained by the time average along the trajectory in MD simulation.

A typical procedure of MD simulation can be described by the following key steps. To begin with, an appropriate force field that can accurately describe the interatomic interaction in the system of interest is required. The next step is to construct the initial position and velocity of each atom in the system, and generate a list for the nearest neighbor interaction. Usually atoms are initially located at their equilibrium positions and assigned with random velocity according to Gaussian distribution. After that, one calculates the force applied to each atom according to the force field, numerically solves Newton's equation of motion, and updates the position and

velocity of each atom. This is a major step in MD simulation, which involves many technical details such as boundary conditions, numerical integration algorithm, and heat bath (reservoir) that can realize the canonical ensemble. Finally, one calculates the ensemble average of the thermodynamic variables of interest with long enough simulation time.

1.2 Force Field Potential

The interatomic force in MD simulation is derived from the system's potential energy. Although a fully quantum-mechanical treatment of the system's Hamiltonian is highly desirable, it can only be applied to a system with very small size due to the large computational load. Therefore, tremendous efforts have been put in the past to develop reliable empirical force field in many material systems that can accurately describe the interatomic interactions and easily be applied to a large system size. The simplest model for interatomic interaction is the van der Waals (vdW) force with pairwise (two-body) interaction. For the covalent bonding, more complicated form of force fields with many-body interaction are used. To illustrate this in more details, we introduce several widely used force field potentials as examples.

1.2.1 *Pair Potential*

The Lennard–Jones (LJ) potential is a widely used pair potential to model the vdW force. It is defined as

$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], \tag{1.2}$$

where ε and σ are characteristic energy and length unit, respectively, and r is the interatomic distance. It is also known as 12-6 potential and can be expressed as

$$V(r) = \frac{A}{r^{12}} - \frac{B}{r^{6}}, \tag{1.3}$$

with A and B denoting the repulsive and attractive constant in LJ potential. As shown in Fig. 1.1, the equilibrium distance in LJ