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**Theoretical Study of the Structure, Energetics, and Dynamics of
Silicon and Carbon Systems Using Tight-binding Approaches**

by

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Theoretical study of the structure, energetics, and dynamics
of silicon and carbon systems using tight-binding approaches

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Under the supervision of Kai-Ming Ho
From the Department of Physics and Astronomy
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Semiempirical interatomic potentials are developed for silicon and carbon by modeling the total energy of the system using tight-binding approaches. The parameters of the models were obtained by fitting to results from accurate first-principles Local Density Functional calculations. Applications to the computation of phonons as a function of volume for diamond-structured silicon and carbon and the thermal expansions for silicon and diamond yields results which agree well with experiment. The physical origin of the negative thermal expansion observed in silicon is explained. A tight-binding total energy model is generated capable of describing carbon systems with a variety of atomic coordinations and topologies. The model reproduces the total energy versus volume curves of various carbon polytypes as well as phonons and elastic constants of diamond and graphite. The model has also been used in the molecular-dynamics simulation of the properties of carbon clusters. The calculated ground-state geometries of small clusters ($C_2 - C_{10}$) correlates well with results from accurate quantum chemical calculations, and the structural trend of clusters from C_2 to C_{60} are investigated.

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Chunhui Xu

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TABLE OF CONTENTS

ACKNOWLEDGEMENTS	iv
CHAPTER 1. INTRODUCTION	1
CHAPTER 2. TOTAL ENERGY EXPRESSIONS	9
General E_{tot} Expression	9
LDA Approach	10
E_{tot} in TB Models and the Associated Applications	12
CHAPTER 3. THERMAL EXPANSION OF SI AND DIAMOND	15
Introduction	15
Calculation	17
Explanation of Negative Thermal Expansion	20
Conclusion	26
CHAPTER 4. A TB POTENTIAL FOR CARBON	28
Introduction	28
Generating TB Interatomic Potential	33
Small Carbon Clusters and the Liquid Phase	40
Charge Transfer Effects	42
CHAPTER 5. CARBON CLUSTERS ($C_2 - C_{60}$)	46

Introduction	46
The TB-MD Scheme	47
A Simulation Method	48
Formation and Structural Trend of C-Clusters	50
Discussion	61
CHAPTER 6. CONCLUSIONS	65
BIBLIOGRAPHY	67
APPENDIX A: TIGHT-BINDING METHOD	72
APPENDIX B: A FITTING SCHEME	76

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CHAPTER 1. INTRODUCTION

In physics, chemistry, and materials science, there are many problems which require for their solution a knowledge of the total energy of a system of atoms as a function of the atomic positions. Such a function $E_{tot}\{\vec{r}_i\}$, where $\{\vec{r}_i\}$ represents a set of atomic coordinates, can be used to model the behavior of the system in a variety of situations. An apparent example is the determination of the equilibrium configurations of a collection of atoms. As the atomic positions $\{\vec{r}_i\}$ change, $E_{tot}\{\vec{r}_i\}$ changes accordingly. The equilibrium atomic pattern is obtained when E_{tot} reaches its minimum value. More examples of the topics that can be studied are: phonon dispersions, surface reconstructions, structures of liquid and amorphous states, and mechanical and thermal properties of materials.

The accurate determination of E_{tot} as a function of atomic configuration is essentially a quantum mechanical problem which involves solving the Schrodinger equation for a system of many electrons moving in a field of ionic potentials. Exact solutions are most of the time unavailable either because of analytical difficulties or because of numerical complexities unless appropriate approximations are made.

One of the approaches developed in the last fifteen years is the Density Functional Theory (DFT) with the Local Density Approximation (LDA) [1]. DFT states that the total ground state energy of an electron system in the presence of an applied

potential is a unique functional of the electron density only, and reduces the many electron problem to a set of effective one electron problems which have to be solved self-consistently. LDA has a key assumption that the non-local exchange-correlation energy density due to the electron-electron interaction can be approximated by a local function of the local electron density with the form of the local function determined from results for a uniform electron gas. The calculations performed in the Density Functional Formalism are first-principles (or ab-initio) calculations: the only information needed as input data are the atomic numbers of the elements involved. DFT with LDA has been applied to calculate the E_{tot} for perfect crystals, and has proved to yield very accurate and reliable results compared with various experimental data. With the advent of supercomputers, self-consistent DFT has been introduced into more complicated studies such as simulations of the liquid and amorphous states of silicon and carbon (considering small number of atoms) [2, 3, 4, 5] with the Car-Parrinello approach [6], a method which combines molecular dynamics with LDA. For most of the complex problems involving large systems (e.g., clusters of large size) or requiring statistical averages (e.g., molecular-dynamics simulations of phase change), DFT calculations are at present not feasible because they are computationally very costly. However, they can provide valuable results to benchmark the accuracies of other more empirical approaches.

There have been attempts to avoid the cumbersome, expensive and sometimes insufficiently accurate direct solutions of the Schrodinger equation. Numerous phenomenological treatments of $E_{tot}\{\vec{r}_i\}$ as a function of $\{\vec{r}_i\}$ have been proposed. These theoretical treatments of the properties of materials start from the description of inter-particle potentials of a many particle system, of which the functional

forms are designed so that E_{tot} gives a correct picture of the interactions among the particles, and the selected parameters are usually fit to reliable experimental or theoretical results. It is expected that the model potential is sufficiently easy to calculate, and gives a sufficiently accurate description of the real physical system of interest, so that one can perform realistic calculations of the properties for quite large systems. Although approaches like this will inevitably involve a significant loss of accuracy, compared with first-principles LDA calculations, development in this direction has continued to be very active over the last decade because of the growing demand in materials studies. Potential models with different approximations have been proposed for different applications in modeling material behaviors.

In this thesis, focus is placed on silicon and carbon systems. In addition to interests in technology, these systems are interesting scientifically because of the presence of strongly directional covalent bonding which stabilizes the occurrence of the diamond structure for both elements. In addition, carbon systems can exhibit a wide variety of coordination numbers from 2 (linear chains or carbyne phase), to 3 in graphite and 4 in diamond. The presence of directional bonds also invalidates the use of traditional simple classical two-body potentials. It is worthwhile then to go through briefly some relevant previous work in this respect before going on to our present models.

Empirical potential models developed previously can be divided into mainly two classes. One class describes the properties of small distortions around the equilibrium lattice positions for use in studies of lattice dynamics and elastic deformation. Such potentials can be quite inaccurate when extrapolated to situations far away from the equilibrium lattice positions. The other class focuses attention on a correct global

description of the relative energetics and equilibrium lattice volumes of the solid in various crystalline structures.

The empirical models devoted to the accurate description of lattice dynamics of solids, especially diamond structured materials, started with a classic paper by Born [7]. He proposed a model with nearest-neighbor central and noncentral force constants which were determined from the experimental elastic constants. In his model, the stability of the diamond lattice against shear distortions is provided by the noncentral force constants. However, severe discrepancies were found between the predictions of Born's model and the results of the inelastic-neutron-scattering experiments [8] later performed. A serious deficiency lies in the fact that, due to the short-ranged nature of the model, it fails to describe the flattening of the transverse acoustic phonon branches with very low frequencies. In addition, the noncentral two-body forces of this model also violate the rotation invariance condition. The need to improve Born's model has inspired much relevant work in this direction. Approaches such as the shell model [9], the bond-charge model [10] and the Keating model [11] were proposed to overcome the shortcomings associated with Born's model. The related models in this direction are mainly constructed to treat accurately small distortions from the ground state in a system, so they usually cannot describe the energy of states that differ significantly from the ground state. (The functional forms of these approaches are analogous to Taylor expansion of the energy about its minimum.)

The second approach started from the construction of pair potentials, which is usually the second term in the expansion of N-body interactions. A few examples of pair potentials are the Lennard-Jones potential and the exponential Morse potential. Such potentials can be directly applied to a completely arbitrary configuration of

atoms, but they do not accurately describe any but the simplest closed-shell systems, such as rare-gas atoms, simple metals, and highly ionic systems. Pair potentials are completely inapplicable in covalent systems, such as semiconductors, ceramics, polymers, and refractory metals. This approach can be improved by incorporating three-body terms into the total energy of the N-body system [12, 13, 14, 15, 16, 17]. The added terms $V(\vec{r}_{ij}, \vec{r}_{ik}, \vec{r}_{jk})$ describe the interactions among 3 particles i, j , and k , so that energy changes due to bond-bending can be taken into consideration and that open structures such as covalent systems can be stabilized. For example, in a potential model for Si proposed by Stillinger and Weber [12] bond angle terms have been added to E_{tot} in order to stabilize the diamond structure. A newer approach to the three-body potential was introduced by Biswas and Hamann [13], who used the available cohesive energies of the polytypes of silicon from LDA calculations as a database, and fitted the parameters to reproduce the energy versus volume behavior over a wide range of coordination and bonding topology. More recently, a potential was proposed by Tersoff [14, 15], with an idea that, in real systems, the bond order (i.e., the strength of each bond) depends upon the local environment. However, all of these potential models show the inability (more or less) to describe a wide range of bonding geometries. It has been pointed out, for example, that the Stillinger-Weber potential works well for crystalline and liquid silicon but not for amorphous silicon [18], the Biswas-Hamann model cannot describe the energetics of all the diverse bonding geometries which they initially considered [19], and the Tersoff-potential (for carbon) has a problem dealing with small clusters [20]. It has also been reported [17] that none of these three models provides a fully satisfactory description of the lattice vibrations of silicon.

It is then worthwhile to reconsider the advantages and shortcomings of empirical methods in studying the physical and chemical properties of a system, in order to find where future developments of total energy modeling can be made. On one hand, empirical interatomic potentials can model the total energy E_{tot} of a set of particles as a simple and explicit function of particle coordinates. The functional form and the selection of parameters are under the users' control in fitting to some reliable experimental data or theoretical LDA results. The simple functional form of the total energy makes calculation convenient even for a complicated quantum-mechanical system. Also with many simplifications, the results of empirical calculations can often be given a simple physical or chemical interpretation, so that the same ideas can be a qualitative guide in more complicated cases. Moreover, there are always interesting problems which are beyond the reach of ab-initio approaches, but which are solvable in the regime of empirical modeling. On the other hand, empirical potentials have been reported to have some problems in describing physical systems. The reason is that when various approximations are made to a complex many-body system, the picture the models depicted can deviate significantly from that of a quantum mechanical treatment. The ability of such potentials to accurately describe the diverse properties of real materials thus remains controversial.

Recently, there have been efforts in developing empirical approaches, which are practical in computation and which are closer to quantum mechanical descriptions of physical systems. The total energy E_{tot} in these models is usually written as the combination of a quantum term and a classical term. A popular approach is the tight-binding (TB) model, which takes the electronic band structure energy E_{bs} (see Chapter 2 for details) explicitly into account in the total energy expression and

treats the rest of the total energy by parametrized analytical models or by parameters [21, 22]. An example of using TB models in lattice dynamics studies dates back to the 70's, when W. Weber and C. M. Varma [23] used a TB model to study the phonon anomalies in refractory metal alloys and compounds. Their model was very successful in describing the experimentally observed phonon dispersion curves because of the inclusion of long-range interactions in E_{bg} . The model which is most widely applied to semiconductors and their surfaces was introduced by Chadi [22], who utilizes a scaling function r^{-2} [21] with sp^3 parameters and models the repulsive term as a polynomial. However, it has been known that the Chadi model works well only for diamond-structured (or zincblende-structured) materials. This is not only because the Chadi parameters were fitted only to properties of diamond structures, but also because the r^{-2} scaling factor is too simple to describe sp^3 parameters as a function of r . Later developed TB models show lots of similarities to the earlier ones in the ways of scaling sp^3 parameters, except for a recent one for Si designed by Pettifor et al. [24], who further adjusted sp parameters and rescaled the parameters' r-dependence as exponential functions. Pettifor's approach reproduced cohesive energies for Si prototypes compared with those of LDA, and also predicted well the structures and energetics of small Si clusters. TB models have been mostly successful in their applications. Further improvement in this direction may allow more realistic atomistic simulations of complex structures. Motivated by these, we fitted and generated some new TB potentials and used them in the theoretical studies of structural, energetic, and dynamical properties of Si and C.

The contents of the thesis are arranged into the following four chapters: Chapter 2, derives the total energy expression of an electron-ion system in the LDA approach,

and discusses the TB total energy models and their applications, Chapter 3 presents the results of thermal expansion calculations for Si and C using a TB approach [25], Chapter 4 describes the generation of a new TB interatomic potential for carbon, and Chapter 5 shows the application of the new generated TB model to the molecular-dynamics simulations of carbon clusters ($C_2 - C_{60}$).

CHAPTER 2. TOTAL ENERGY EXPRESSIONS

The total energy of a complex electron-ion system is considered from the point of view of quantum-mechanics. Simplifications such as the adiabatic approximation and single-particle approximation are made so that the total energy can be written in forms that are useful for theoretical modeling. The total energy expressions in the LDA approach are presented, providing a theoretical background for using the form $E_{tot} = E_{bs} + U$ in the TB models. A comparison of these approaches to the total energy may give insight to where improvements of empirical TB models can be made.

General E_{tot} Expression

The Hamiltonian for a system of an array of atoms is

$$H = T_e + T_c + V_{cc} + V_{ee} + V_{ec}. \quad (2.1)$$

In Eq. (2.1), T is the kinetic-energy operator, and V is the potential energy; the subscript c refers to the ion cores and e to the valence electrons. In the adiabatic approximation for the electron-ion system, the electrons are assumed to respond instantaneously to the ionic motion. Thus we may write for the total energy of the system (at zero temperature, neglecting zero point motion)

$$E_{tot} = E_{el} + E_{ion}, \quad (2.2)$$

where E_{el} is the total electronic energy which depends on ionic configurations and E_{ion} is the ionic energy corresponding to the Coulomb interaction of static ions.

The E_{el} is defined in quantum mechanics to be

$$E_{el} = \langle \Psi | H_{el} | \Psi \rangle, \quad (2.3)$$

where

$$H_{el} = T_e + V_{ec} + V_{ee} \quad (2.4)$$

is the Hamiltonian of electronic part, and Ψ is the electronic ground-state wavefunction.

LDA Approach

The framework of the DFT with LDA has been an elaborate approach to the description of the total energy of an electron-ion system. The DFT of Hohenberg and Kohn proved that the total electronic energy E_{el} is a unique functional of the charge density $n(r)$, (for simplicity, we write r instead of $\vec{r}$, and dr instead of d^3r), i.e.,

$$E_{el}[n] = T[n] + \int V(r)n(r)dr + \frac{1}{2} \int n(r)n(r')v(r-r')drdr' + E_{xc}[n], \quad (2.5)$$

where $T[n]$ is the kinetic energy of a non-interacting system of electrons having a ground state density of $n(r)$, and $V(r)$ and $v(r)$ represent the electron-ion and

electron- electron interactions respectively. The term $E_{xc}[n]$ is the exchange and correlation energy of the interacting many-electron system with density $n(r)$.

Hohenberg and Kohn showed that E_{el} is a minimum for the correct charge density of the many-particle ground state. Kohn and Sham proved that the ground-state density $n(r)$ can be obtained if the following set of Kohn-Sham equations is solved self-consistently

$$h\psi_i(r) = [-\frac{1}{2}\nabla^2 + V_{eff}(r)]\psi_i = \epsilon_i\psi_i, \quad (2.6)$$

$$V_{eff}(r) = V(r) + \int n(r')v(r-r')dr' + \mu_{xc}(r), \quad (2.7)$$

$$n(r) = \sum_i |\psi_i(r)|^2. \quad (2.8)$$

Here $\psi_i(r)$ are orthonormal eigenfunctions and ϵ_i are the associated eigenvalues of the one-body Hamiltonian h in Eq. (2.6), and the sum in Eq. (2.8) extends over the lowest occupied eigenvalues. The exchange potential is given by

$$\mu_{xc} = \frac{\delta E_{xc}[n]}{\delta n(r)}. \quad (2.9)$$

A common approximation for $E_{xc}[n]$ has the local form

$$E_{xc}[n] = \int n(r)\epsilon_{xc}(n(r))dr, \quad (2.10)$$

where $\epsilon_{xc}(n(r))$ is the exchange and correlation energy per electron of a uniform electron gas of density n , so we have $\mu_{xc} = \mu_{xc}(n(r)) = d(n(r)\epsilon_{xc}(n))/dn$. In this

form, the total energy may be expressed in terms of the sums of the eigenvalues of the occupied states and a correction term for electron-electron interactions:

$$E_{tot} = E_{ion} + E_{bs}[n] - E_{ee}[n], \quad (2.11)$$

where

$$\begin{aligned} E_{bs}[n] &= \sum_i \epsilon_i \\ &= -\frac{1}{2} \sum_i \int d\mathbf{r} \psi_i^*(\mathbf{r}) \nabla^2 \psi_i(\mathbf{r}) + \int d\mathbf{r} V(\mathbf{r}) n(\mathbf{r}) \\ &\quad + \int d\mathbf{r} \int d\mathbf{r}' n(\mathbf{r}) v(\mathbf{r} - \mathbf{r}') n(\mathbf{r}') + \int d\mathbf{r} n(\mathbf{r}) \mu_{xc}(n(\mathbf{r})), \end{aligned} \quad (2.12)$$

and

$$E_{ee}[n] = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' n(\mathbf{r}) v(\mathbf{r} - \mathbf{r}') n(\mathbf{r}') + \int d\mathbf{r} n(\mathbf{r}) [\mu_{xc}(n(\mathbf{r})) - \epsilon_{xc}(n(\mathbf{r}))] \quad (2.13)$$

E_{tot} in TB Models and the Associated Applications

In the construction of the total energy models using tight-binding approaches, the expression $E_{tot} = E_{bs} + U$, where $U = E_{ion} - E_{ee}$, is often used. Instead of solving the elaborate system of self-consistent Schrodinger equations for E_{tot} , E_{bs} in our models is obtained by summing over ϵ_i , the lowest N eigenvalues of an empirical TB Hamiltonian (details of the TB method are described in Appendix A), and U is modeled by short-ranged empirical functional forms so that E_{tot} fits available data from accurate LDA calculations for some reference systems.

This simple TB approach has been widely used in theoretical studies because of its advantage in partially including quantum-mechanical terms. Some examples are :

i) In studying the lattice dynamics of a crystal, we have the force-constant $K_{i\alpha,j\beta} = \frac{\partial^2 E_{tot}}{\partial x_{i\alpha} \partial x_{j\beta}}$, with i and j denoting two atoms in unit cells, x the atomic displacements, and α and β components of atomic displacements in cartesian coordinates. Using 2nd order perturbation theory,

$$K_{i\alpha,j\beta} = \frac{\partial^2 U}{\partial x_{i\alpha} \partial x_{j\beta}} + 2 \sum_n f_n \langle n | \frac{\partial^2 h}{\partial x_{i\alpha} \partial x_{j\beta}} | n \rangle + 2 \sum_{n,n'} \frac{f_n - f_{n'}}{\epsilon_n - \epsilon_{n'}} \langle n | \frac{\partial h}{\partial x_{i\alpha}} | n' \rangle \langle n' | \frac{\partial h}{\partial x_{j\beta}} | n \rangle, \quad (2.14)$$

where h is the tight-binding one-electron Hamiltonian, $|n\rangle$ are electronic eigenstates, and f_n are Fermi occupation factors. The first term is short-ranged because U is short-ranged in nature. The second and the third terms represent the contributions from E_{ts} . The integrals $\langle n | \frac{\partial^2 h}{\partial x_{i\alpha} \partial x_{j\beta}} | n \rangle$ in the second term extend to the same range as the TB parameters. But the third term is long-ranged, even when atoms i and j are far apart, their interactions can be mediated by electronic excitations across the Fermi level ($E_n - E_{n'}$).

Because the TB total energy models involve naturally the underlying electronic structure in the description of the system, effects such as long-range interactions between ions and angular restoring forces in covalently bonded systems can be correctly included without the introduction of ad-hoc terms as in classical potential models. Applications of such models resulted in much successful work on the lattice dynamics of materials with different bonding mechanisms.

ii) The $E_{tot} = E_{bs} + U$ form has also been used to determine the cohesion and

structure of solids. In some frequently used TB models the scaling function $s(r)$ (see Appendix A) is simply chosen as r^{-2} , and U as a polynomial function of r . The resulting $E_{tot}(r)$ is then used to determine properties such as cohesive energies vs. volume, bulk modulus, and equilibrium structures. However, such models have difficulty in reproducing simultaneously the properties of different crystalline phases of the material. For example, if the parameters or coefficients in $E_{bs}(r)$ and $U(r)$ were fitted to accurate data for diamond-structure crystal, the model is good only for the description of this specific structure but not for others such as simple cubic, fcc, etc. of the same material. The adjustment of $s(r)$ and also $U(r)$ is essential to obtain transferability of the TB models. We will discuss an exponential-like form for $s(r)$ and $U(r)$ in Chapter 4 of this thesis.

CHAPTER 3. THERMAL EXPANSION OF SI AND DIAMOND

In this chapter, we will use the phonon dispersion curves and lattice mode Grüneisen parameters obtained from a tight binding approach to calculate the coefficients of thermal expansion for crystalline Si and diamond. The results are found to be in good agreement with experimental data. In particular, crystalline silicon exhibits the well-known negative thermal expansion behavior at low temperatures. The origin of the negative thermal expansion is examined and we find that the different thermal expansion behaviors between Si and C can be explained by the different relative strengths of bond-bending and bond-stretching forces.

Introduction

In studying the dynamics of solids the assumption of small oscillations of ions about their equilibrium sites is usually made. The ionic interaction energy of a solid is then expanded about equilibrium ionic positions, and appropriate approximations are made by retaining certain terms in the expansion and discarding the others, so that different physical phenomena can be separately discussed. An approximation including the first two terms in the expansion is a harmonic model. The cubic and higher-order terms contribute anharmonic effects to ionic motions.

Thermal expansion is a phenomenon which relates to the anharmonic motions

of ions in a solid. The coefficient of thermal expansion is defined as: $\alpha = \frac{1}{3V}(\frac{dV}{dT})_P$, where V , T , and P represent the volume, temperature, and pressure of the solid of interest, respectively.

Thermal expansion in semiconductors is a topic of some technological as well as scientific interest since it plays an important role in determining the residual stresses in solid-state devices. While most materials expand upon heating, many tetrahedral semiconductors (e.g., Si, Ge, and GaAs) exhibit negative thermal expansion at low temperatures [26, 27, 28, 29], i.e., the solids contract when heated. This problem has received a fair amount of theoretical attention, mostly empirical studies relying heavily upon experimental input [30]. An exception is the recent work of Biernacki and Scheffler [31], who calculated the negative thermal expansion of Si with a simple model based on two force constants extracted from local density functional calculations. It is generally believed that the unusual negative thermal expansion behavior can be attributed to the negative Grüneisen parameters (i.e., phonon frequency increases as crystal volume increases) of the transverse acoustic (TA) phonons near the Brillouin zone boundary, which have also been reproduced by first principles theories [32, 33]. Using Si and C as prototypical tetrahedral semiconductor systems, we demonstrate that a simple tight-binding model [25] can describe the thermal expansion behavior accurately in these systems without fitting to experimental information. The origin of the negative thermal expansion behavior is explained with a simple physical model. The difference in thermal expansion behavior between Si and C arises from the difference in the relative strengths of the central forces and angular forces in the crystal in agreement with ideas in previous investigations [34].

Calculation

We start from obtaining the free energy, F , of a crystal as a function of the volume V and the temperature T , in order to determine the thermal expansion and compressibility of the system by the V , T relation involved.

The free energy of the system can be expressed as

$$F(V, T) = E(V) + \frac{1}{2} \sum_i h\nu_i(V) + k_B T \sum_i \ln[1 - \exp(-h\nu_i(V)/k_B T)] \quad (3.1)$$

where $E(V)$ is the energy of the static lattice with volume V , and $\nu_i(V)$ are the normal-mode frequencies of small-amplitude oscillations for the crystal at volume V . The employment of Eq. (3.1) in the present case needs an assumption (besides the adiabatic approximation) that the phonon energy levels of the system are those of independent harmonic oscillators with volume-dependent frequencies $\nu_i(V)$, the quasiharmonic approximation [35]. The term quasiharmonic is often used to refer to that anharmonic effect which gives a volume dependence to the phonon frequencies.

To obtain the phonon frequencies ν_i at a given crystal volume, we employ a simple model in which the total energy of the crystal $E(V)$ is expressed as a sum of two terms: E_{bs} , the electronic band structure energy, is the sum of single-electron energies over all occupied electronic states, and $U = \frac{1}{2} \sum_{i,j} \phi(r_{ij})$, is a sum of nearest-neighbour pair interactions. The band structure is evaluated using an empirical tight-binding model following the previous work of Chadi [36, 37]. The nearest-neighbor sp^3 parameters are determined by fitting the electronic bands of Si and C in diamond structures: $\epsilon_s = -5.25\text{eV}$, $\epsilon_p = 1.20\text{eV}$, $V_{ss\sigma} = -1.938\text{eV}$, $V_{sp\sigma} = 1.745\text{eV}$, $V_{pp\sigma} = 3.05\text{eV}$, and $V_{pp\pi} = -1.075\text{eV}$ for Si; and $\epsilon_s = -2.99\text{eV}$, $\epsilon_p = 3.71\text{eV}$,

$V_{ss\sigma} = -5.55\text{eV}$, $V_{sp\sigma} = 5.91\text{eV}$, $V_{pp\sigma} = 7.78\text{eV}$, and $V_{pp\pi} = -2.50\text{eV}$ for C. These parameters are scaled with interatomic separation r as r^{-2} . Unlike the Chadi model [37], the short-ranged pair potential $\phi(r)$ in our calculation is determined [25] by subtracting the E_{bs} contribution from first principles local-density functional results for the volume-dependent total energy of the crystal in the ideal diamond structure [33, 38]. Thus the parameters of our model can be extracted entirely from first principles calculations without fitting to any experimental data.

The force-constant matrix is obtained by taking second derivatives of the total energy with respect to the atomic displacements and, using second order perturbation theory, can be expressed as

$$K_{i\alpha,j\beta} = \frac{\partial^2 U}{\partial x_{i\alpha} \partial x_{j\beta}} + 2 \sum_{n\vec{k}} f_{n\vec{k}} \langle n\vec{k} | \frac{\partial^2 H}{\partial x_{i\alpha} \partial x_{j\beta}} | n\vec{k} \rangle + 2 \sum_{n\vec{k}, n'\vec{k}'} \frac{f_{n\vec{k}} - f_{n'\vec{k}'}}{\epsilon_{n\vec{k}} - \epsilon_{n'\vec{k}'}} \langle n\vec{k} | \frac{\partial H}{\partial x_{i\alpha}} | n'\vec{k}' \rangle \langle n'\vec{k}' | \frac{\partial H}{\partial x_{j\beta}} | n\vec{k} \rangle, \quad (3.2)$$

where H is the tight-binding Hamiltonian, $|n\vec{k}\rangle$ are electronic states, and $f_{n\vec{k}}$ are Fermi occupation factors. The first term in Eq. (3.2) is the contribution from the short-ranged pair potential. The second and the third terms represent the contributions from the electronic band structure.

Using the above force-constant matrices, we can evaluate the dynamical matrix [39] for any wave vector $\vec{q}$. We obtained the phonon frequencies on a grid of 240 wavevectors in the irreducible part of the Brillouin zone. The calculated dispersion curves for Si and C are compared with experimental data in Figure 1. Good agreement is achieved for the acoustic phonon modes. Our model tends to overestimate

Figure 1: Phonon dispersion curves for a) Si, and b) diamond. Solid lines show the tight-binding calculation results. The experimental data (open circles) are from Ref. 26.

the optical mode frequencies by $\sim 10\%$. Using the calculated phonon frequencies, $F(V, T)$ is evaluated for a set of volumes and temperatures. The equilibrium volumes at various temperatures are determined by minimizing $F(V, T)$ as a function of V . The results for the linear expansion coefficients of Si and diamond are shown in Figure 2 in comparison with experimental results [40, 26]. Our calculations give a very good description of the thermal expansion in both Si and diamond. In particular, the low-temperature negative thermal expansion behavior in Si and the absence of negative thermal expansion in diamond are well reproduced.

Explanation of Negative Thermal Expansion

From Eq. (3.1), the thermal expansion coefficient can be related to the Grüneisen parameters of the various phonon modes [41]

$$\alpha = \frac{1}{3B_0V} \sum_i \gamma_i h\nu_i \frac{d}{dT} \{[\exp(h\nu_i/k_B T) - 1]^{-1}\} \quad (3.3)$$

in which $\gamma_i = -d(\ln\nu_i)/d(\ln V)$ is the Grüneisen parameter for the i^{th} normal-mode. Eq. (3.3) shows that a negative thermal expansion can only occur when some of the phonon modes have negative Grüneisen parameters. Since the interatomic forces in the crystal usually weaken when the lattice expands, the Grüneisen parameters are usually positive for all the phonon modes in most materials. The results for the Grüneisen parameters of Si and diamond are plotted respectively in Figure 3 (a,b), where available experimental data [26] are also displayed. The acoustic phonon modes of Si behave anomalously: strong negative Grüneisen parameters are found for the TA branches, especially near the Brillouin zone boundaries X and L . On the other hand, such behavior is not observed in the corresponding phonon branches of

Figure 2: Linear thermal-expansion coefficient of a) Si, and b) diamond as a function of temperature. Results from our calculations are indicated by solid lines. Experimental data (open circles) are from Ref. 40 and Ref. 26, respectively.

Figure 3: Mode Grüneisen parameters for a) Si, and b) diamond. Solid lines (acoustic modes) and dashed lines (optical modes) are results from our calculations. The experimental data (●, ■ acoustic modes; ○, □ optical modes; ●, ○ longitudinal; ■, □ transverse.) are from Ref. 26.

diamond.

The physical origin of the anomalous behavior of the TA modes in Si can be elucidated by a simple model where we consider only nearest neighbor interactions. We show in Figure 4 the patterns of atomic vibrations associated with the TA(X) and the TA(L) modes. The polarizations of these two modes are determined by the symmetry of the diamond lattice and are associated with pure bond-bending motion: the bonds between atoms are either undisturbed or are distorted by atomic motions perpendicular to the bonds. In such cases, we can describe the restoring force on the atoms as the sum of a central force part ω_{cen} and a non-central angular part $\omega_{non-cen}$ coming from the directional covalent bonds stabilizing the diamond structure. Thus

$$\omega_0^2 = \omega_{cen}^2 + \omega_{non-cen}^2 \quad (3.4)$$

The central force contribution is well described by a spring model. For displacements perpendicular to a spring, the restoring force depends on the tension in the spring (T_s). At the equilibrium volume V_0 the tension in the spring is zero and $\omega_0 = \omega_{non-cen}$. Thus $\omega_{cen}^2 = 0$ for $V = V_0$. When $V > V_0$ the spring is stretched, $T_s > 0$ giving a restoring force $\omega_{cen}^2 > 0$. When $V < V_0$, the spring is compressed, $T_s < 0$ leading to $\omega_{cen}^2 < 0$. We can relate ω_{cen}^2 to the bulk modulus as follows:

First, the central force contribution to the force constant is related to the spring tension and the bond length d ,

$$m\omega_{cen}^2 = 2CT_s/d \quad (3.5)$$

where C takes into account the number of bonds bent by the phonon distortion (C equals 1 for TA(L) and 2 for TA(X)) and m is the mass of the atom.

Figure 4: Vibrational motion corresponding to the a) TA(X) mode, and b) TA(L) mode in the diamond structure. The displacements of the ions are along the $[110]$ direction in (a) and along the $[11\bar{2}]$ direction in (b).

Now T_s is related to the spring constant k and the deviation of the bond length from its equilibrium value d_0 . Then k and $d - d_0$ can be related to the bulk modulus B_0 and $\Delta V/V_0$. Thus,

$$T_s = k(d - d_0), \quad (3.6)$$

and

$$2 \times \frac{1}{2} k(d - d_0)^2 = \frac{1}{2} B_0 \left(\frac{\Delta V}{V_0} \right)^2 V_0 \quad (3.7)$$

Finally,

$$\gamma_{cen} = -\frac{d(\omega_{cen}/\omega_0)}{d(\ln V)} = -\frac{4C}{\sqrt{3}} \frac{B_0 d_0}{m\omega_0^2} \quad (3.8)$$

Thus γ_{cen} is negative. This is the origin of the negative Grüneisen behavior of the TA modes in Si.

To get a complete description, we have to obtain the contribution from the angular forces. Using the bond orbital approximation [42], the change in covalent bond energy when the lattice is distorted with bond-bending motion is $dE \propto \eta \theta^2$ where η is the tight-binding matrix element between bond orbitals on the two atoms at the ends of the bond and θ is the angle of rotation of the bond. Now η varies as $1/d^2$ and $\theta = 2u/d$ where u is the atomic displacement, so $\omega_{non-cen}^2$ varies as $1/d^4$. Thus,

$$\gamma_{non-cen} = -d(\ln \omega_{non-cen})/d(\ln V) = \frac{2}{3}. \quad (3.9)$$

Within our simple model, the Grüneisen parameters of the TA(X) and TA(L) modes can be written as

$$\gamma = \frac{2}{3} - \frac{4C}{\sqrt{3}} \frac{B_0 d_0}{m\omega_0^2} \quad (3.10)$$

By using the bulk moduli and phonon frequencies from our tight-binding calculations, we can estimate from Eq. (3.10) the TA(X) and TA(L) mode Grüneisen parameters of Si, diamond, and Ge. The results are listed in Table 1. Our model predicts that the TA modes have negative Grüneisen behavior in Si and Ge but not in diamond. The reason for the difference is that the directional covalent bonding is much stronger in diamond than in Si. Thus the angular forces are dominant in diamond and our analysis indicates that non-central forces favor positive Grüneisen behavior. For negative thermal expansion, the angular forces should be weak but not absent, because otherwise the diamond structure would not be stable at all.

Conclusion

The above model can also be applied to the discussion of thermal expansion of zincblende semiconductors, although the analysis will be much more complicated because of the unequal masses of the atoms in the zincblende structure. However, in such cases, we expect tight-binding calculations will still give accurate answers.

We have shown that detailed calculations based on a simple tight-binding model can provide accurate thermal expansion results (for Si and diamond). We have given a microscopic analysis of the origin of the anomalous mode (TA(X) and TA(L)) Grüneisen parameters in Si. Our analysis provides a simple explanation of the negative thermal expansion behavior in Si and the difference in thermal expansion behavior of diamond and Si. We hope our work will provide a basis for considering thermal expansion behavior in more complicated materials such as amorphous semiconductors, graphitic fibers, and polymer chains.

Table 1: The Grüneisen parameters $\gamma_{TA(X)}$ and $\gamma_{TA(L)}$ for Si, diamond and Ge are calculated from Eq. 3.10. The estimated $\gamma_{TA(X)}$ and $\gamma_{TA(L)}$ are compared with experimental data (Ref. 26) and Tight-Binding calculation results.

	Si	diamond	Ge
$\gamma_{TA(X)}(\text{TB-calc.})$	-1.08	0.042	
$\gamma_{TA(X)}(\text{expt.})$	-1.4		-1.53
$\gamma_{TA(X)}(\text{Eq. 3.10})$	-1.67	0.017	-1.08
$\gamma_{TA(L)}(\text{TB-calc.})$	-1.15	-0.047	
$\gamma_{TA(L)}(\text{expt.})$	-1.3		-0.4
$\gamma_{TA(L)}(\text{Eq. 3.10})$	-1.54	-0.060	-0.77

CHAPTER 4. A TB POTENTIAL FOR CARBON

Although the TB model described in Chapter 3 has been successful in quite a number of applications (see for example, Ref. [25, 43, 44]), we found that it does not always yield satisfactory results when applied to the calculations of a broader range of atomic configurations, (for example, the structures of the liquid and amorphous states of Si and C and the geometries of Si and C clusters), in other words, the model is not transferable. The development of transferable models for Si and C then becomes an immediate task if we are to study many interesting problems in complex systems of these materials through practical computation.

In this chapter we will describe the construction of a new interatomic potential for carbon using the tight-binding approach. The model reproduces faithfully the energy versus volume diagram of carbon polytypes as well as the elastic constants and phonon frequencies of carbon in the diamond and graphite structures. To further test the transferability of the model to different atomic environments, we have also performed molecular-dynamics simulations to study clusters and the liquid phase.

Introduction

Carbon, with atomic number 6 and ground-state electronic configuration $1s^2 2s^2 2p^2$, holds a special place among the elements. It is well known that carbon atoms form

with each other some of the strongest chemical bonds. As a consequence the symmetrical tetrahedral bonding in diamond causes it to be the hardest and strongest known material, and the asymmetrical resonance and π -bonding in graphite causes it to be the strongest known material in two-dimensions (the a-b planes) but weak in the c-direction. Carbon's uniquely strong bonds and high melting point make it at once fascinating and technologically important.

Since the carbon phase diagram originally proposed by Bundy [45](a), and experiments of the 1960s and 1970s [45](b), the properties of condensed phases of carbon have been investigated widely both experimentally and theoretically, of which those at extreme conditions have received special interest.

One example is the high-pressure properties of carbon. The use of the diamond anvil cell is of enormous importance in high-pressure physics [46], for example the determination of the structural stability and general high-pressure behavior of solids in solid state physics. With the techniques using diamond anvil cells, the stability of diamond effectively imposes an upper bound on the pressures which can be statically generated in the laboratory.

Another example is carbon clusters (sometimes referred to as poly-carbons) [47]. In the last decade, there have been advances of methods for the production of cold cluster beams, containing species up to C_{200} . The properties and spectroscopy of these C_n species show fascinating and unexpected complexities in the laboratory. And it has become apparent that these species are possible contributors to the formation of the carbon dust, diffuse interstellar bands, etc. which are of astrophysical significance [48].

The study of carbon has received more attention because of the recent discovery

of a new form of carbon: molecular C_{60} or solid C_{60} [49]. It is found that the unusually large abundance and low reactivity of the C_{60} cluster were due to its assuming the structure of a soccerball with the C atoms situated at each vertex [50] (see Figure 5). The preparation of C_{60} molecular solids, the measurement and calculation of its properties, including the mysterious high-temperature superconductivity [51], opened a new, very active research area.

Other challenging topics include the properties of disordered phases such as the liquid and amorphous states [52, 4, 5]. Liquid carbon was previously conjectured not to exist at atmospheric pressure, but recent reports suggested it may exist at least in a small range of temperature at low pressures. Amorphous state materials can be obtained through methods such as condensing the vapor or quenching the liquid. There is considerable interest in the conditions under which liquid and amorphous carbon can form and exist, in the formation mechanisms of these systems, and in their structural and energetic properties. Studies on these disordered systems are at an early state where theory requires direct and reliable experimental results to develop models, and experiment needs accurate and fundamental theoretical models to obtain physical insight.

The theoretical study of carbon condensed phases has attracted a lot of attention. Accurate and reliable results have been calculated for various systems using DFT with LDA, of which, the most notable are the general high-pressure properties of crystalline phases [53]. Accurate quantum chemical calculation results (with configuration-interactions included) are available for small carbon clusters [54]. Molecular dynamics studies of small liquid and amorphous carbon systems have been carried out within LDA using the Car-Parrinello method [4, 5]. However, as we

Figure 5: Buckminsterfullerene Cluster (C_{60}).

have shown in the general introduction, for complex carbon systems, first-principles studies are limited because of its intense demand in computation. On the other hand, empirical interatomic potentials applicable to carbon systems have only recently been developed. A very recent work is that of Tersoff [15], who constructed a bond-order-related three-body potential for carbon. The test of the potential was made by calculating the cohesive energies of several carbon polytypes, as well as a few selected properties in diamond and graphite. Although the accuracy of these calculations, based on comparison with experiment or with the LDA, is impressive, there have been some doubts about the reliability of the Tersoff model when applied to carbon clusters C_n of $n \leq 50$. In particular, there is evidence that the model is not valid in describing clusters of size $n \leq 10$ [20].

It is therefore our intention to generate new interatomic potential models for carbon, which can accurately predict a wider range of properties. Since there have been lots of new models proposed for Si [12, 13, 14], we have attempted to utilize some of them as a guide, considering the similarities of the two elements in forming chemical bonds. A recent TB potential model by Pettifor, et al. [24] has been successful in reproducing accurately the energies of polytypes of Si, as well as the structure of small Si clusters. The model is believed to be better than the three-body potentials (such as the Stillinger-Weber model, the Biswas-Hamann model, and the Tersoff model) in its quantum-mechanical description of chemical bonding, and also in its ability to predict properties of Si systems.

In this chapter, we generated a tight-binding interatomic potential for carbon, which absorbs the scaling forms of the TB hopping parameters and the pair-wise potential vs. interatomic separation from Pettifor et al. [24] for Si. The transferability

of the model has been widely tested, and its usefulness was proved.

Generating TB Interatomic Potential

We write the total energy in our model as

$$E_{tot} = E_{bs} + E_{rep}, \quad (4.1)$$

where E_{bs} is the sum of single-electron energies over all occupied electronic states, and E_{rep} is a term related to the sum of nearest-neighbor pair interactions. The single-electronic energies are obtained by solving an empirical tight-binding Hamiltonian, of which the off-diagonal elements are described by a set of orthogonal sp^3 two-center hopping parameters, $V_{ss\sigma}$, $V_{sp\sigma}$, $V_{pp\sigma}$ and $V_{pp\pi}$, scaled with interatomic separation r as a function $s(r)$; and the on-site elements are the orbital energies of a neutral atom. The remainder of the E_{tot} is a repulsive term E_{rep} , which corrects for the double counting of the electron-electron interactions in E_{bs} , models the ion-ion repulsion, and takes account of the effect due to the non-orthogonality of the atomic orbitals. We model this term as

$$E_{rep} = \sum_i f(\sum_j \phi(r_{ij})), \quad (4.2)$$

where $\phi(r_{ij})$ is a pair-wise potential between atoms i and j , and f is assumed to be an n th order polynomial with $n = 5$. We adopt the functional form suggested by Goodwin, Skinner, and Pettifor [24] (GSP) for the scaling function $s(r)$ and the pair-wise potential $\phi(r)$:

$$s(r) = \left(\frac{r_0}{r}\right)^n \exp[n\{-(\frac{r}{r_c})^{n_c} + (\frac{r_0}{r_c})^{n_c}\}] \quad (4.3)$$

and

$$\phi(r) = \phi_0 \left(\frac{d_0}{r}\right)^m \exp[m\{-(\frac{r}{d_c})^{m_c} + (\frac{d_0}{d_c})^{m_c}\}] \quad (4.4)$$

where r_0 denotes the nearest-neighbor atomic separations in the equilibrium diamond carbon, and $n, n_c, r_c, \phi_0, m, d_c$ and m_c are parameters that need to be determined.

Unlike the GSP model, the scaling parameters r_c and n_c for $s(r)$ are not necessarily the same as the corresponding d_c and m_c for $\phi(r)$ in our model. Moreover, we require that the r dependence of the interactions, $s(r)$ and $\phi(r)$, to be such that they go smoothly to zero at some designated cutoff distances. This is done in our model by replacing the tail of $s(r)$ with a third order polynomial $t_s(r)$ whose coefficients are determined by requiring that the connection of $s(r)$ and $t_s(r)$ at r_1 , (match point, $r_1 \leq r_m$), be smooth up to the first derivative, and $t_s(r)$ and its first derivative be zero at r_m . The same procedure is used to determine $t_\phi(r)$, which replaces the tail of $\phi(r)$. We chose the cutoff distance, for r_m and d_m as well, to be 2.6 Å, which is between the nearest neighbor and next-nearest neighbor distance of carbon atoms in the equilibrium diamond structure. (The match points r_1 and d_1 are treated as adjustable parameters in the fitting procedures.) We find that the TB potential with such a treatment can yield consistent results when applied to a variety of structures possessing different atomic coordinations.

The above parameters for the potential are chosen primarily by fitting the local density functional results of energy vs. nearest-neighbor interatomic separation for different carbon polytypes [53], with weighting factors favoring lower-energy struc-

tures, i.e., diamond, graphite and linear chain. Details of the fitting procedure are discussed in Appendix B. Moreover, the additional constraints of having better electronic bands, elastic moduli and phonons in diamond are considered, though these constraints do not enter explicitly into the fitting program. The resulting sp^3 tight-binding parameters are: $E_s = -2.99\text{eV}$, $E_p = 3.71\text{eV}$, $V_{ss\sigma} = -5.0\text{eV}$, $V_{sp\sigma} = 4.7\text{eV}$, $V_{pp\sigma} = 5.5\text{eV}$ and $V_{pp\pi} = -1.55\text{eV}$. The parameters for $s(r)$ and $\phi(r)$, the coefficients for the tail functions $t_s(r)$ and $t_\phi(r)$, and the coefficients for the polynomial function $f(x) = \sum_{n=1}^5 a(n)x_{(n-1)}$, with $x = \sum_j \phi(r_{ij})$ are given in Table 2.

As one sees from Figure 6, these parameters reproduce excellently the energy curves of the two most stable structures, graphite and diamond. The energy curve of the linear chain is also sufficiently good. Although the model does not predict well the shapes of the energy curves for higher-coordinated structures, it does yield reasonably good cohesive energies and equilibrium volumes for these structures in comparison with the results of LDA calculations [53]. Such a comparison is shown in Figure 7.

To test the model's ability to predict phonons and elastic properties of carbon systems, we have calculated the frequencies of the optical phonon at the gamma point ($\nu_{LTO}(\Gamma)$), as well as the TA, TO, and LA modes at X ($\nu_{TA}(X)$, $\nu_{TO}(X)$ and $\nu_{LA}(X)$), and the elastic constants $C_{11} - C_{12}$, C_{44}^0 and C_{44} in diamond. The results, together with the experimental data [26] and those from Ref. [15], are listed in Table 3. Very good agreement is achieved between our calculated phonon frequencies and the experimental data [26] (errors all within 10%). The elastic moduli are adequately described, though the estimated $C_{11} - C_{12}$ is 40% smaller and that of C_{44} is 20% smaller than those from experiment. We have also tested the phonons in

Table 2: Parameters for the functions $s(r)$ and $\phi(r)$, and coefficients of tail functions $t_s(r - r_1)$, $t_\phi(r - d_1)$ and the polynomial function $f(x)$ of our TB interatomic potential of C. See Eqs. (4.3), (4.4) and the text for details.

n	n_c	$r_c(\text{\AA})$	$r_0(\text{\AA})$	$r_1(\text{\AA})$	$r_m(\text{\AA})$
2.0	6.5	2.18	1.536	2.45	2.60
m	m_c	$d_c(\text{\AA})$	$d_0(\text{\AA})$	$d_1(\text{\AA})$	$d_m(\text{\AA})$
3.303	8.666	2.105	1.64	2.57	2.60
c_0	c_1	c_2	c_3	c_4	
-3.9750	0.57212	-1.7896×10^{-3}	2.3539×10^{-5}	-1.2425×10^{-7}	
$t_s(r - r_1)$	a_0	a_1	a_2	a_3	
	6.7393×10^{-3}	-8.1885×10^{-2}	0.19324	0.35349	
$t_\phi(r - d_1)$	b_0	b_1	b_2	b_3	
	2.7493×10^{-9}	-1.7603×10^{-7}	2.5708×10^{-6}	8.0660×10^{-6}

Figure 6: Cohesive energy vs. nearest-neighbor atomic distance curves for carbon structures of diamond, graphite, and linear chain. Solid and dashed lines show the results from tight-binding calculation and those from LDA calculation, respectively. The LDA data for diamond are from Ref. 49.

Figure 7: Cohesive energy vs. nearest-neighbor atomic distance curves for carbon structures of diamond, graphite, linear chain, sc, β -Sn, bcc, hcp and fcc. The LDA data are from Ref. 53 except those of graphite and linear chain.

graphite. The graphite structure has been considered as perfectly two dimensional in our study, since the interlayer spacing of graphite is much larger than the cutoff distance of our TB potential. Two phonon modes, E_{2g_2} and A_{2u} , (Figure 8) were calculated. The phonon frequencies are predicted well with the potential, $\omega_{TO}(E_{2g_2}) = 1664.0 \text{ cm}^{-1}$ and $\omega_{TO}(A_{2u}) = 973.2 \text{ cm}^{-1}$, sufficiently close to the experimental values $1582.0 (+ - 1.0) \text{ cm}^{-1}$ and $868.0 (+ - 1.0) \text{ cm}^{-1}$ [55]. These satisfactory tests for diamond and graphite suggest that the potential model may have the ability to describe the dynamical properties of a variety of carbon structures.

Small Carbon Clusters and the Liquid Phase

To further test the transferability of the model to different atomic environments, we have also performed molecular-dynamics (MD) simulations using our TB interatomic potential (see Chapter 5 for details) to study carbon systems in cluster form and in the liquid phase. The time step used in these simulations is $0.7 \times 10^{-15} \text{ s}$.

We discuss our calculations for carbon clusters of size $C_2 - C_{10}$, here paying more attention to the ground state geometries and energy differences. Since the application of the method to a wider range of carbon clusters ($C_2 - C_{60}$) and details of simulation annealing carbon clusters will be the subjects of Chapter 5, we present only results of ground state geometries for $C_2 - C_{10}$ here. From Figure 9, we found for $5 \leq 10$, odd-numbered clusters prefer a linear structure, while even-numbered clusters prefer a ring structure. This result agrees well with the accurate ab-initio calculation result of Raghavachari et al. [54]. For the very small clusters ($n \leq 4$), the linear chain structure is found to be the most stable geometry. We also see an impressive result that the comparisons of bond-length trends and variations in these

Table 3: The values of some elastic coefficients and frequencies for diamond calculated from the current model are compared to values of experiment (Ref. 26) and an empirical model (Ref. 15). Elastic constants are in units of 10^{12}dyn/cm^2 and the normal-mode frequencies are in terahertz.

	Model	Expt.	JT
$c_{11} - c_{12}$	6.22	9.51	9.7
c_{44}^0	5.42		
c_{44}	4.75	5.76	6.4
$\nu_{LTO}(\Gamma)$	37.80	39.90	46.8
$\nu_{TA}(X)$	22.42	24.20	24.1
$\nu_{TO}(X)$	33.75	32.0	33.6
$\nu_{LA}(X)$	34.75	35.5	39.0

 E_{2g_2}

 A_{2u}

Figure 8: Phonons E_{2g_2} and A_{2u} of the two-dimensional graphite.

Figure 9: The ground-state geometries of carbon clusters C_2 – C_{10} from the TB calculation. Bond lengths are in units of angstroms.

structures (except $n=4$) show many similarities.

The tight-binding molecular-dynamics model has also been applied to the simulation of liquid carbon [56] and the results compared well with recent ab-initio molecular-dynamics results using the Car-Parrinello method [4]. The simulation is performed with 64 atoms and with periodic boundary conditions. The density of the sample is chosen to be $2.0\text{g}/\text{cm}^3$ according to Ref. [4] and the MD cell is fixed in a cubic shape. After 20000 MD steps for thermal equilibrium at temperature about 5000K, a statistical average of structural and electronic properties of the liquid is computed over an additional 30000 MD steps (corresponding to 21 ps). In Figure 10 and Figure 11, the results for the radial distribution function $g(r)$ and electronic density of states are presented. The simulation results show that the structure of the liquid carbon is dominated by two-fold ($\sim 38\%$) and three-fold ($\sim 52\%$) coordinated atoms and with an average coordination number of 2.6 Å. A gapless feature in the electronic density of states indicates that the liquid state is metallic. These results are in good agreement with the ab-initio molecular-dynamics results of Galli et al. [4].

Charge Transfer Effects

In the present TB potential model, the tight-binding Hamiltonian H_{TB} is constructed using an orthogonal sp^3 basis,

$$H_{TB}(\{\tilde{r}_i\}) = \sum_i \sum_{\alpha=s,p} \epsilon_\alpha a_{i\alpha}^\dagger a_{i\alpha} + \sum_{i,j} \sum_{\alpha,\beta=s,p} v_{\alpha\beta}(r_{i,j}) a_{i\alpha}^\dagger a_{j\beta}, \quad (4.5)$$

where i, j label ions and α, β denote TB orbitals; ϵ_s and ϵ_p are the on-site energies of s and p orbitals, and $v_{\alpha\beta}(r_{i,j})$ are overlap integrals between orbitals α and β located

Figure 10: Radial distribution function $g(r)$ of liquid carbon.

Figure 11: Electron density of states of liquid carbon.

on site i and j respectively. In doing this, it is assumed that each atom site is neutral, i.e., no charge transfer occurs in the system. The TB potential model would then be questionable if it were applied directly to disordered systems such as clusters and liquids in which charge transfers are likely to occur. This situation can be improved by adding a Hubbard-like term

$$H_u = \frac{1}{2}u(\hat{q}_i - q_i^0)(q_i - q_i^0) \quad (4.6)$$

into H_{TB} . In this equation, q_i is the expectation value of the operator $\hat{q}_i$, $q_i = \langle \hat{q}_i \rangle$ gives the total valence charge at atom site i ; q_i^0 is 4 for sp^3 tight-binding orbitals. Adding this term to H_{TB} makes geometries with large transfer unfavorable. In our calculations we used a value of $u = 4$ eV.

The improved TB model is then used in the MD simulations of carbon clusters. A comparison of the results from the TB model with H_u and from the TB model without H_u showed that charge transfers are significant only for small clusters of size $n \leq 11$. Based on this fact, in Figure 17 of Chapter 5, we use for linear chains and monocyclic rings of $n \leq 20$ the binding energies from calculations with the improved TB model, and for other cases the binding energies from the primary TB model.

In conclusion, our tight-binding approach gives an accurate description of the interatomic potentials of carbon systems, which is able to reproduce the energy-volume curves of accurate LDA calculations, with excellent transferability among the graphite, diamond and linear chain structures. The model's prediction of dynamical and elastic properties of graphite and diamond are also very good compared to the corresponding experimental values. Applications of the model to the MD simulation of cluster and liquid structures yields results which agree well with those from accurate ab-initio calculations. We expect that our model potential will have widespread

applications to complex carbon systems.

CHAPTER 5. CARBON CLUSTERS ($C_2 - C_{60}$)

In this chapter, the structural properties of carbon clusters (C_n , $n = 2 - 60$) are studied using tight-binding molecular-dynamics simulations. The low-energy ground state configurations of the clusters are obtained by annealing and compressing n carbon atoms ($n = 2 - 60$) from the gas phase at high temperatures ($\geq 6000\text{K}$). We observed a transition from one-dimensional linear and cyclic structures to two-dimensional cage structures as the number of atoms in the cluster increases beyond $n=20$.

Introduction

Emerging as a new phase of carbon with a range of structural and chemical properties intermediate between small molecules and bulk phases, carbon clusters have received considerable experimental and theoretical attention over the past decade [47]. Experimentally, most studies have been conducted with mass spectroscopy [50, 57, 58, 59, 60]. Although the mass spectra provide useful information for understanding the relative stability of the clusters, they do not specify the geometries of the clusters. Recent breakthroughs in the synthesis process make it possible to produce C_{60} in sufficient purity and quantity to enable the identification of its structure as a truncated icosahedron. On the theoretical side, attempts have been made

to determine the ground state geometries of carbon clusters through total energy calculations [47, 54, 61, 62, 63, 64] and computer simulations [20]. However, up to now, reliable quantum chemical calculations are practical only for small clusters (up to about $n=10$) [54] and are too time-consuming for establishing a general structural trend. In this chapter, we present a systematic study of the structure of carbon clusters as a function of cluster size using tight-binding molecular-dynamics (TB-MD) simulations.

The TB-MD Scheme

The description of the Newtonian dynamics of an array of atoms requires a Hamiltonian which includes not only the total energy of the electron system moving in the field of relatively static ions, but also the kinetic energy of the ions. We used such a Hamiltonian in the TB-MD scheme [25]

$$H = \sum_i \frac{P_i^2}{2M} + V_{TB}(\{\vec{r}_i\}), \quad (5.1)$$

where $\{\vec{r}_i\}$ denotes the positions of the ions, and P_i and M represent the momentum and the mass of ion i , respectively. The first term gives the kinetic energy of the ions, and the second term presents the potential energy due to the interactions among the atomic system. We modeled V_{TB} here as the TB interatomic potential generated in Chapter 4, i.e.,

$$V_{TB}(\{\vec{r}_i\}) = E_{bs}(\{\vec{r}_i\}) + E_{rep}(\{\vec{r}_i\}). \quad (5.2)$$

In doing this, it is assumed that the electron system is always in its ground state for a given configuration of ions so that the electronic degrees of freedom are not explicitly involved in the dynamics. However, the electronic contribution to the ion-

ion interaction is included in the force calculation due to the employment of the electron band-structure energy E_{bs} in Eq. (5.2).

The tight-binding potential V_{TB} is easily used in the standard molecular-dynamics routine as briefly illustrated in Figure 12. The total force acting on the i th atom of the N -atom system being simulated is $-\nabla_i V_{TB}(\vec{r}_1, \dots, \vec{r}_i, \dots, \vec{r}_n)$, and the atoms move following Newtonian dynamics. The time step Δt is suitably chosen so that it is significantly smaller than the mean collision time of carbon ions moving in the TB potential field. As the atoms move, the total energy of the system, $\sum_i \frac{P_i^2}{2M} + V_{TB}(\{\vec{r}_i\})$, changes accordingly until an energy minimum is reached, and the system is then equilibrated (at a finite temperature).

A Simulation Method

Like most of the empirical interatomic potentials, the V_{TB} describe a finite effective interaction distance between two atoms. Considering the experimental conditions [58] where the carbon clusters are formed in a “highly localized hot region” (i.e., high density and high temperature) we designed for our simulation such a situation that atoms in the system are confined in a hollow sphere with a smooth inner surface and changeable radius r . We assumed that the atoms suffer specular reflections when they collide with the inner surface of the sphere. By setting up the above condition, we expect, that something about the formation of molecular structures due to atomic interactions can be studied for a considerable long time period can be studied, even when the number of atoms is small and the system is at high temperature.

We relate the total energy E of a N -atom system to its temperature T in the conventional way, $E = K + V$, where K is the kinetic energy, $K = \sum_i \frac{1}{2} m \vec{v}_i^2 =$

Figure 12: A brief illustration of empirical tight-binding molecular-dynamics routine.

$3/2Nk_B T$, and V denotes the potential energy. The temperature of the system can then be controlled by scaling the velocities of atoms with a constant factor. And the density condition of the system can be met by adjusting the radius of the sphere. These temperature and volume adjustments are useful in searching for cluster structures of higher stabilities. We set the time step in the annealing process to be $\sim 10^{-15}$ sec.

Formation and Structural Trend of C-Clusters

The reliability of the potential for applications to carbon clusters has been demonstrated, in Chapter 4, by comparing the ground state geometries obtained from our simulation with the results of accurate quantum mechanical calculations for small clusters with $n \leq 11$. For every cluster of a given size, both the linear chain and the monocyclic ring structure are used as the starting configuration for the simulation. After careful annealing, the clusters are found to converge to a unique final structure regardless of initial configuration. In the range $5 \leq n \leq 11$, we found that odd-numbered clusters prefer a linear structure, while even-numbered clusters prefer a ring structure. This result agrees well with the accurate ab-initio calculation result of Raghavachari et al. [54]. For the very small clusters ($n \leq 4$), the linear chain structure is found to be the most stable geometry.

For $n \geq 12$, the clusters can be trapped in local energy minima dependent on the starting configuration. For these clusters, we perform an annealing simulation using the following procedures: first, the system is heated up to 10000K for a few thousand time-steps to randomize their positions. At these temperatures, the carbon atoms are in the gas phase and have to be confined inside a hollow sphere of adjustable radius.

The atoms are subjected to specular reflections when they collide with the inner surface of the sphere. The system is then cooled down gradually to about 6000K, a temperature at which most of the clusters condense. At the same time, the volume of the system is reduced at a slow rate to facilitate the formation of the clusters. In general, we found that as the radius of the sphere is reduced, ring structures will first form and will then change into the more stable cage structures upon further compression. Finally, the system is gradually cooled down to $T=0$ K without any external constraint. For a given cluster size, this procedure can produce several structurally distinct metastable phases depending on the cooling and compressing conditions.

As an example, we present in Figure 13 (a-g) the formation process of a cluster of C_{20} . By cooling down the atoms from the gas-phase (Figure 13 (a)) temperature of 10000K to 6000K, the atomic gas starts to condense, appearing as line sections. The volume is then compressed and the atomic system accordingly experiences a series of structural changes (Figure 13 (b-g)), from line sections to a curled line, and then to a perfect monocyclic ring. Further compression makes twisted rings, and eventually a closed cage which consists of 12 five-member rings. Correspondingly, we recorded the binding energy of the cluster against volume compression in Figure 14. Two maxima occur at $r/a_0=1.17$, where the ring forms, and at $r/a_0=0.62$, where the cage forms, revealing that the monocyclic ring and the cage form are two stable phases of C_{20} (at $T=6000$ K). The zero-temperature geometries of these two phases are obtained by cooling down the system from 6000K to 4000K while keeping the volume constraints for the ring and the cage, respectively, and afterwards relaxing the two structures to 0K. The zero-temperature cage form of C_{20} , with all the atoms

Figure 13: Phases of C_{20} after the equilibrations at the shown temperature T and volume V . (The V is given by r/a_0 , where r is the radius of a hollow sphere, and $a_0 (= 3.548 \text{ \AA})$ is the lattice constant of diamond). Dots are used to represent single atoms and straight lines to connect atom pairs when the interatomic distances are less than $1.8 \text{ \AA}$.

being equivalent, shows very high symmetry. Its binding energy is larger than that of the ring, this is apparent even at $T=6000\text{K}$.

We have also performed molecular-dynamics simulations of the cluster C_{60} . We start the simulation by heating the 60-atom system to very high temperatures (around 10000 K) in a sphere of radius $9.22\text{ \AA}$. The carbon atoms under this condition are found to be gas like. We then gradually reduce the temperature and the radius of the sphere (to simulate the applied pressure) so that the atoms can smoothly condense to a series of phases (see the perspective views in Figure 15). A closed cage of C_{60} (Figure 15 (f)) is formed at $T\approx 6000\text{ K}$ when the radius of the sphere is reduced to $3.832\text{ \AA}$. The structure of the cage is very similar to that of the buckyball, apart from some defects which are probably due to the rapidity of the compression and cooling processes. Further cooling to $T=0\text{ K}$ results in a metastable C_{60} with a binding energy of 7.89 eV .

Similar simulation annealing has been performed for $C_2 - C_{60}$. Our simulations show that monocyclic rings are energetically favorable for the clusters with $12 \leq n \leq 19$, while for clusters with $20 \leq n \leq 60$, the most stable structures are cages made up of mostly 5- and 6-membered rings. Figure 16 shows some cage structures obtained by the above simulation procedure. For even-numbered clusters, the ground state structures are highly symmetric cages while the odd-numbered cages are always found to contain some dangling bonds. For $n \geq 28$, the clusters obtained from the simulations are not structurally perfect, but contain defects such as 4-membered and 7-membered rings, or topological faults in the arrangement of the 5-membered and 6-membered rings. The presence of such defects are probably due to the rapid compression and cooling in the simulation since the larger clusters have

Figure 14: Energy (per atom) of C_{20} vs. volume compression at $T=6000K$. Circles represent instantaneous values of energies after equilibrations. The solid line smoothing the circles shows the energy trend.

Figure 15: C_{60} cage formation process at $T=6000K$. (a), (b), and (c) are the phases after 2.8ps, 4.2ps, and 5.6ps “cooking time” respectively, in a sphere of radius 5.32 Å; and (d), (e), and (f) are the phases when the radius is reduced to 4.61 Å, 3.90 Å, and 3.832 Å, respectively.

more metastable states and require more annealing than smaller clusters [65, 66].

In Figure 17 (a) and Figure 17 (b), we plot the binding energy per atom as a function of cluster size, ranging from $n=2$ to $n=70$ for the linear chain, monocyclic ring, graphitic fragment and cage structures respectively. The energies of the ring structures for $20 \leq n \leq 43$ represent metastable intermediate structures obtained from our simulations.

For graphitic fragments, we investigated clusters of $n=6, 10, 13, 14, 16, 19, 22, 24, 42$ and 54 , (Figure 18 shows their geometries), which have relatively high symmetries and a lower number of dangling-bonds within the range $6 \leq n \leq 60$. The calculations performed for these fragments are geometry-optimized with all bond lengths constrained to be equal. Shown in Figure 17 (open triangles) are also the energies of several "defect-free" cages ($C_{28}, C_{32}, C_{60}, C_{70}$) obtained by relaxing the corresponding structures proposed by Kroto [67] based on geometry considerations. In particular, the relaxed C_{60} is found to be a perfect buckyball which has been verified to be the ground state geometry of the C_{60} cluster.

The energies of the linear chains show odd-even alternations with the odd-numbered clusters being more stable than the even ones, a result similar to the early prediction of Pitzer and Clementi [62]. It is also found that the ring structures are relatively more stable for cluster sizes with $n=10, 14, 18, \dots$. This trend is similar to the previous calculations of Hoffman [61] and Bernholc and Phillips [63]. The underlying physical origin of these behaviors can be attributed to electronic σ -bonding and π -bonding properties of these carbon structures [63, 54]. In each of the clusters, the carbon atoms form one σ and one π bond to each of their neighbors. For the chains, there are $(n-1)\sigma$ bonds and two dangling bonds, either fully occupied or completely

Figure 16: Structures for C_{20} – C_{27} at zero temperature. Arrows mark the position of dangling-bonds.

Figure 17: Binding energy as a function of carbon cluster size for (a) chains, rings, and graphitic fragments with $2 \leq n \leq 20$, and (b) rings, cages, and graphitic fragments with $15 \leq n \leq 60$. See text for details.

Figure 17: continued.

Figure 18: Geometries of some graphitic fragments used in the TB-MD calculation.

empty, leaving $2(n-1)$ (or $2(n+1)$) electrons to fill the π bonds. The odd-numbered chains are preferred, because each of the π levels can accommodate four electrons and the clusters with fully occupied bonds are more stable. For monocyclic rings, the parallel and perpendicular π bonding planes each have a nondegenerate lowest level, followed by doubly degenerate levels. The most stable rings with fully occupied bonds are at $4m+2$ ($m=1, 2, \dots$), because every C atom contributes two π electrons. For the cage structures, we found that the even-numbered clusters are energetically more favorable than the odd-numbered ones. This is because, geometrically, closed cage structures cannot be formed with all the atoms three-fold coordinated when n is odd [68].

The most interesting feature in Figure 17 is the transition from one-dimensional linear chain or ring structures to two-dimensional cage structures when n reaches 20. We found that C_{20} is the smallest closed cage that can be formed in our simulations. For C_{18} and C_{19} when the monocyclic rings are further compressed, metastable multiple ring structures (see Figure 19) are formed instead of cages. As indicated in Figure 17 these structures are less stable than the monocyclic rings.

Discussion

We note the TB-MD scheme used in the MD simulations is a simplified Car-Parrinello (CP) method, which is well known for combining the density functional theory into molecular-dynamics simulations.

The Hamiltonian of an electron-ion system in the CP scheme is expressed as

$$H = \sum_i \frac{1}{2} \mu \int_v d^3r |\dot{\psi}_i|^2 + \sum_I \frac{1}{2} M_I \dot{R}_I^2 + \sum_\nu \frac{1}{2} \mu_\nu \dot{\alpha}_\nu^2 + E[\{\psi_i\}, \{R_I\}, \{\alpha_\nu\}], \quad (5.3)$$

Figure 19: Metastable multiple ring structures for C_{18} and C_{19} when the rings are compressed.

where the first three terms represent the kinetic energy (KE) of the electrons in electronic states ψ_i , the KE of the ions with masses M_I and the KE of possible external constraints α_ν imposed on the system, and the E is the potential energy of the system. The dynamics the equation described includes a fictitious motion of the electrons, so that the Born-Oppenheimer potential energy surface would have a finite thickness. In simulations so defined, each time the ions are displaced from their original position, a simulated annealing is performed in order to bring the electrons to the corresponding ground state. To solve the equations of motion, a large number of plane waves is used to expand the electron wavefunctions and small simulation time steps are chosen in order to appropriately describe the electron motion. The CP scheme has been reported to yield very accurate results when used in many simulation studies. However, it is limited due to the large amount of computational effort required in the associated simulations. On the other hand, the TB-MD scheme is much simpler computationally.

We then discuss the relation between cages with defects and the corresponding perfect ones. Despite the presence of defects, the energies of the cages obtained by cooling and compressing from the gas phase are very close to those of the corresponding relaxed “defect-free” cages. The energy difference between the “cooked” and the relaxed cages are 0.015, 0.0, 0.094 and 0.119 eV/atom respectively for $n=28, 32, 50, 60$. We believe that the general structural trend and transitions obtained from the present simulation will remain the same even if more careful annealings are performed to eliminate the defects.

Finally, we note that the observed abundance of C_{60} molecules cannot be explained solely from its high formation energy. In fact, the formation energy of C_{70}

is even higher than that of C_{60} . We speculate that the abundance of C_{60} is related to its highly symmetric geometry which can lead to a higher survival probability in collisions after formation than other less symmetric clusters. We also note that the formation energy of the C_{60} and C_{70} are still far below the cohesive energy of bulk graphite. This suggests that it is still possible to find even larger clusters with the two-dimensional cage geometry.

In summary, we have developed a tight-binding interatomic potential capable of describing accurately the structures and energetics of small carbon clusters ($n \leq 10$) as well as the bulk crystalline phases of carbon. Using this potential we studied the structure and stability of carbon clusters in the region of $2 \leq n \leq 60$.

CHAPTER 6. CONCLUSIONS

We have developed two tight-binding models and applied them to calculations of properties of Si and C systems. Model 1 (see Chapter 3) was used to study the lattice dynamics, (in particular, anharmonic effect) of diamond-structured Si and C. The model predicts well the thermal expansions of these two materials compared with experimental results. Like most of the TB models, it has described well the electron-phonon interaction which contributes to long-range interactions among ions. The model is also successful in calculations of electronic properties of several other cases. However, it is only good for application to systems close to the diamond structure (i.e., not transferable). The generation of model 2 (Chapter 5) is one step further on the way to a transferable TB potential for carbon. The model was parametrized to some analytic functions which are similar to those of Pettifor's TB model for Si and was fitted to accurate LDA results. It has been adjusted to be transferable to a wide range of carbon coordinations and topologies. The results of a series of tests including the cohesion of carbon polytypes, phonons and elastic constants of diamond and graphite, and the structure and energetics of clusters and liquid phase show very good agreement with the data from the LDA calculations. We think our work of constructing TB interatomic potentials has gone one step further in the direction of modeling covalent systems with semiempirical approaches, which have been playing

the role of bridging the gap between ab-initio density-functional treatments, and the pure classical descriptions. The good behavior of these models in a variety of applications to Si and C shows that future development of TB models for other materials may be fruitful, and applications to complex atomic systems may result in the solution of many interesting problems.

BIBLIOGRAPHY

- [1] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. **148**, A1133 (1965).
- [2] I. Stich, R. Car, and M. Parrinello, Phys. Rev. Lett. **63**, 2240 (1989).
- [3] R. Car and M. Parrinello, Phys. Rev. Lett. **60**, 204 (1988).
- [4] G. Galli, R. M. Martin, R. Car, and M. Parrinello, Phys. Rev. Lett. **63**, 988 (1989).
- [5] G. Galli, R. M. Martin, R. Car, and M. Parrinello, Phys. Rev. Lett. **62**, 555 (1989).
- [6] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).
- [7] M. Born, Ann. Phys. (Leipz.) **44**, 605 (1914).
- [8] B. N. Brockhouse and P. K. Iyengar, Phys. Rev. **111**, 747 (1958).
- [9] W. Cochran, Proc. R. Soc. A **253**, 260 (1959).
- [10] W. Weber, Phys. Rev. Lett. **33**, 371 (1974); Phys. Rev. B **15**, 4789 (1977).
- [11] P. N. Keating, Phys. Rev. **145**, 637 (1966).
- [12] F. H. Stillinger and T. A. Weber, Phys. Rev. B **31**, 5262 (1985).
- [13] R. Biswas and D. R. Hamann, Phys. Rev. Lett. **55**, 2001 (1985).
- [14] J. Tersoff, Phys. Rev. Lett. **56**, 632 (1986); Phys. Rev. B **37**, 6991 (1988).
- [15] J. Tersoff, Phys. Rev. Lett. **61**, 2879 (1988).

- [16] J. R. Chelikowsky, J. C. Phillips, M. Kamal, and M. Strauss, *Phys. Rev. Lett.* **62**, 292 (1989).
- [17] E. R. Cowley, *Phys. Rev. Lett.* **60**, 2379 (1988).
- [18] A. M. Stoneham, V. T. B. Torres, P. M. Masri, and H. R. Schober, *Phil. Mag. A* **58**, 93 (1988); J. D. Broughton and X. P. Li, *Phys. Rev. B* **35**, 9120 (1987).
- [19] R. Biswas and D. R. Hamann, *Phys. Rev. B* **36**, 6434 (1987).
- [20] P. Ballone and P. Milani, *Phys. Rev. B* **42**, 3201 (1990).
- [21] W. A. Harrison and J. C. Phillips, *Phys. Rev. Lett.* **33**, 410 (1974).
- [22] D. J. Chadi, *Phys. Rev. Lett.* **41**, 1062 (1978).
- [23] C. M. Varma and W. Weber, *Phys. Rev. Lett.* **39**, 1094 (1977); *Phys. Rev. B* **19**, 6142 (1979).
- [24] Leif Goodwin, A. J. Skinner, and D. G. Pettifor, *Europhys. Lett.* (Switzerland), **9**, 701 (1989).
- [25] C. Z. Wang, C. T. Chan, and K. M. Ho, *Phys. Rev. B* **39**, 8586 (1989).
- [26] O. Madelung, W. von der Osten, and U. Rössler, *Intrinsic Properties of Group IV Elements and III-V, II-VI, and I-VII Compounds* Vol. 22a, Landolt-Börnstein: Numerical Data and Functional Relationships in Science and Technology, edited by O. Madelung (Springer-Verlag: Berlin 1987); D. Bimberg, R. Blachnik, M. Cardona, P. J. Dean, Th. Grave, G. Harbeke, K. Hübner, U. Kaufmann, W. Kress, O. Madelung, W. von Münch, U. Rössler, J. Schneider, M. Schulz, and M. S. Skolnick, *Physics of Group IV Elements and III-V Compounds* Vol. 17a, Landolt-Börnstein: Numerical Data and Functional Relationships in Science and Technology, edited by O. Madelung (Springer-Verlag: Berlin 1982) and references therein.
- [27] C. A. Swenson, *J. Phys. Chem. Ref. Data* **12** No.2, 179, (1983).
- [28] G. K. White and M. L. Minges, *Thermophysical Properties of Some Key Solids* Pergamon Press, New York 1985.
- [29] M. Okaji, *International Journal of Thermophysics* **9** No.6, 1101 (1988).
- [30] See, for example, T. H. K. Barron, J. G. Collins, and G. K. White, *Advances in Physics* **29**, 609 (1980).

- [31] S. Biernacki and M. Scheffler, Phys. Rev. Lett. **63**, 290 (1989).
- [32] H. Wendel and R. M. Martin, Phys. Rev. B **19**, 5251 (1979).
- [33] M. T. Yin and M. L. Cohen, Phys. Rev. Lett. **45**, 1004 (1980); Phys. Rev. B **26**, 3259 (1982).
- [34] A. Bienenstock and G. Burley, J. Phys. Chem. Solids **24**, 1271 (1963); A. Bienenstock, Phil. Mag. **9**, 755 (1964).
- [35] See, for example, L. L. Boyer, Phys. Rev. Lett. **42**, 584 (1979).
- [36] D. J. Chadi and R. M. Martin, Solid State Commun. **19**, 643 (1976)
- [37] D. J. Chadi, Phys. Rev. B **29**, 785 (1984).
- [38] J. R. Chelikowsky and S. G. Louie, Phys. Rev. B **29**, 3470 (1984).
- [39] Details for the evaluation of the dynamical matrix for tight-binding models are described in O. L. Alerhand and E. J. Mele, Phys. Rev. B **35**, 5533 (1987).
- [40] H. Ibach, Phys. Status Solidi **31**, 625 (1969).
- [41] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt, Rinehart and Winston, New York 1976), 492.
- [42] W. A. Harrison, *Electronic Structure and The Properties of Solids* (W. H. Freeman and Company, San Fransisco, 1980).
- [43] R. Biswas, C. Z. Wang, C. T. Chan, K. M. Ho, and C. M. Soukoulis, Phys. Rev. Lett. **63**, 1491 (1989).
- [44] C. H. Xu, C. Z. Wang, C. T. Chan, and K. M. Ho, Phys. Rev. B **43**, 5024 (1991).
- [45] (a)F. P. Bundy, J. Chem. Phys. **38**, 631 (1963); (b)J. Geophys. Res. **85**, 6930 (1980).
- [46] A. Jayaraman, Rev. Mod. Phys. **55**, 65 (1983).
- [47] W. Weltner Jr. and R. J. Van Zee, Chem. Rev. **89**, 1713 (1989), and references therein.
- [48] See, for example, H. Suzuki, Astrophys. J. **272**, 579 (1983), and H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, Astrophys. J. **314**, 352 (1987).

- [49] W. Kratschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman, *Nature* **347**, 354 (1990).
- [50] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, *Nature (London)* **318**, 162 (1985).
- [51] E. Pennisi, *Science News* **140**, 84 (1991).
- [52] Fang Li and Jeffrey S. Lannin, *Phys. Rev. Lett.* **65**, 1905 (1990).
- [53] S. Fahy and S. G. Louie, *Phys. Rev. B* **36**, 3373 (1987).
- [54] K. Raghavachari and J. S. Binkley, *J. Chem. Phys.* **87**, 2191 (1987).
- [55] M. Cardona, G. Dresselhaus, M. S. Dresselhaus, G. Güntherodt, W. Hayes, M. V. Klein, D. J. Lockwood, J. R. Sandercock, R. G. Ulbrich, and C. Weisbuch, *Light Scattering in Solids III* Vol. 51, Topics in Applied Physics, edited by M. Cardona and G. Güntherodt (Springer-Verlag, Berlin 1982).
- [56] C. H. Xu, C. Z. Wang, C. T. Chan, and K. M. Ho, to be published.
- [57] N. Furstenau and F. Hillenkamp, *Int. J. Mass Spectrom. Ion. Phys.* **37**, 135 (1981).
- [58] E. A. Rohlfing, D. M. Cox, and A. Kaldor, *J. Chem. Phys.* **81**, 3322 (1984).
- [59] L. A. Bloomfield, M. E. Geusic, R. R. Freeman, and W. L. Brown, *Chem. Phys. Lett.* **121**, 33 (1985).
- [60] R. D. Knight, R. A. Walch, S. C. Foster, T. A. Miller, S. L. Mullen, and A. G. Marshall, *Chem. Phys. Lett.* **129**, 331 (1986).
- [61] R. Hoffmann, *Tetrahedron* **22**, 521 (1966).
- [62] K. S. Pitzer and E. Clementi, *J. Am. Chem. Soc.* **81**, 4477 (1959).
- [63] J. Bernholc and J. C. Phillips, *J. Chem. Phys.* **85**, 3258 (1986).
- [64] W. Andreoni, D. Scharf, and P. Giannozzi, *Chem. Phys. Lett.* **173**, 449 (1990).
- [65] R. O. Jones and O. Gunnarsson, *Rev. Mod. Phys.* **61**, 689 (1989).
- [66] H. W. Kroto and K. Mckay, *Nature (London)* **331**, 328 (1988).
- [67] H. W. Kroto, *Nature (London)* **329**, 529 (1987).

- [68] T. G. Schmalz, W. A. Seitz, D. J. Klein, and G. E. Hite, J. Am. Chem. Soc. **110**, 1113 (1988).
- [69] J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1498 (1954).

APPENDIX A: TIGHT-BINDING METHOD

This appendix gives an outline of the Slater-Koster tight-binding method [69].

The tight-binding method or linear combination of atomic orbitals is one of the standard methods for solving the periodic potential problems encountered in theoretical studies of the electronic motions in solids. In solving the one-electron Schrodinger equation $\hbar^2 \nabla^2 \psi_{\vec{k}} = \epsilon \psi_{\vec{k}}$ of wave vector $\vec{k}$, the wave function $\psi_{\vec{k}}$ is expressed as a linear combination of a set of basis functions φ

$$\psi_{\vec{k}} = \sum_n A_n(\vec{k}) \varphi_n(\vec{k}). \quad (1)$$

φ in the TB method is chosen to be the Bloch sums

$$\varphi_n = \frac{1}{\sqrt{N}} \sum_{i=1}^N \exp(i\vec{k} \cdot \vec{R}_i) \phi_n(\vec{r} - \vec{R}_i), \quad (2)$$

where $\phi_n(\vec{r} - \vec{R}_i)$ is an atomic like orbital located on an atom at vector position $\vec{R}_i$, and with quantum numbers n which run over every atomic orbital of an atom, and every atom in the unit cell of the crystal. The sum is to be extended over the atoms in equivalent positions in all the unit cells of the crystal, assuming periodic boundary conditions, the number of unit cells in the repeating region is N . A wave function chosen in this way also diagonalizes the translational symmetry operations of the crystal.

We now find matrix components of the energy among all these Bloch sums φ_n , and shall have a secular problem whose order equals that of the total number of atomic orbitals concerned, for a general $\vec{k}$ point. If h is the one-electron Hamiltonian operator, the matrix component between two Bloch sums φ_n and φ_m is clearly

$$N^{-1} \sum_{i,j} \exp(i\vec{k} \cdot (\vec{R}_j - \vec{R}_i)) \int \phi_n^*(\vec{r} - \vec{R}_i) h \phi_m(\vec{r} - \vec{R}_j) dv. \quad (3)$$

The sum is over the N unit cells. We notice that one of the summations in the double sum of Eq. (3) can be eliminated, for it merely amounts to multiplying the single summation by N , which cancels the factor N^{-1} . If the summation over $\vec{R}_i$ is eliminated, then we have, in place of Eq. (3)

$$\sum_j \exp(i\vec{k} \cdot (\vec{R}_j - \vec{R}_i)) \int \phi_n^*(\vec{r} - \vec{R}_i) h \phi_m(\vec{r} - \vec{R}_j) dv. \quad (4)$$

In this formula, $\vec{R}_j - \vec{R}_i$ is the vector displacement from the atom on which the orbital ϕ_n is located to one of its neighbors on which an orbital ϕ_m is located.

Rigorous calculation of the matrix components of the energy is very tedious. This is not only because the individual terms are difficult to work out, but also because there are so many of them which are combined in such complicated ways. Although eventually some methods will be developed to do this work by means of high-speed computers, it is certainly not the goal we pursue.

So simplifications are necessary. This is done by arbitrarily discarding many of the terms which make trouble in an accurate calculation, but retaining those which are necessary to give qualitative correctness to the method. The following simplifications are usually made:

i) Nearest-neighbor approximation. This is based on the fact that the integral in Eq. (4) will decrease fairly rapidly as the interatomic distance increases because the overlap of the two atomic like orbitals gets smaller as the atoms in question get farther apart. We can use only nearest neighbors, or only nearest and second-nearest neighbors, and so on, according to the calculation capability.

ii) Selecting orbitals. In this simplification we consider only atomic orbitals whose energy is somewhere near that of the energy bands we are interested in. Serious errors with this simplification are unlikely to happen if parameters are chosen so as to fit certain accurately determined energies.

iii) Using crystal symmetry. Many of the integrals in Eq. (4) must be related through the symmetry operations (rotation, inversion etc.) of the crystal.

iv) Two-center approximation. If we treat the potential energy in h as being the sum of spherical potentials located on the various atoms and disregard three-center integrals, then the only part of the potential we retain in Eq. (4) is the sum of spherical potentials located on the two atoms on which the atomic orbitals are located.

Solving the above secular problem will result in eigenvalues $\epsilon_{\vec{k}}$ and eigenstates for vector $\varphi_{\vec{k}}$.

Although the use of the above simplifications reduces various integrals appearing in Eq. (4) to a relatively small number, the calculation of remaining terms, each of which involves the integration of two atomic like orbitals located at $\vec{R}_i$ and $\vec{R}_j$ multiplying the spherical potentials centered on the $\vec{R}_i$ and $\vec{R}_j$ (two-center integrals) is still appreciable because there may be many combinations of atomic orbitals and the displacement vector $(\vec{R}_j - \vec{R}_i)$ may vary over a wide range. Slater and Koster

showed that the energy integrals in Eq. (4) can be written as a sum of products, each of which consists of a $(\vec{R}_j - \vec{R}_i)$ direction-dependent part and a two-center integral $V_{ll'}(r)$ involving space quantized functions l located at $\vec{R}_i$ and l' located at $\vec{R}_j$. Slater and Koster then made tables of energy integrals in Eq. (4) for crystals in terms of such expressions.

In many TB models, the $V_{ll'}(r)$ is written as $V_{ll'}(r_0)s(r)$, where r_0 is the nearest neighbor distance of the equilibrium diamond-structure of the material concerned, and $s(r)$ is a r -dependent scaling function. $V_{ll'}(r_0)$ is often called a "TB parameter".

APPENDIX B: A FITTING SCHEME

The fitting scheme used in generating the TB interatomic potential for carbon includes mainly the following steps.

First, calculate the electronic band structure energy $E_{bs}^\alpha(r)$ vs. nearest-neighbor distance r for a set of crystalline phases: diamond, graphite, linear chain, simple cubic (sc), and face-centered cubic (fcc), represented by α . Given a set of sp^3 parameters and those defined in the function $s(r)$, the $E_{bs}^\alpha(r)$ for structure α with nearest-neighbor distance r can be obtained by solving the TB Hamiltonian matrix equation

$$H_{\vec{k}}^\alpha \psi_{n\vec{k}} = \epsilon_{n\vec{k}}^\alpha \psi_{n\vec{k}}, \quad (1)$$

and summing the eigenvalues $\epsilon_{n\vec{k}}^\alpha$ over the N lowest occupied eigenstates, i.e.,

$$E_{bs}^\alpha = 2 \sum_{n\vec{k}} \epsilon_{n\vec{k}}^\alpha. \quad (2)$$

Sufficient $\vec{k}$ -points in the irreducible Brillouin zone of reciprocal space of the lattice α are chosen (diamond 10, graphite 36, linear chain 20, sc,120, fcc 110) so that convergence is reached for each $E_{bs}^\alpha(r)$.

Secondly, we define a fitting residue as

$$\Delta = \sum_{\alpha i} [(E_{tot}^\alpha(r_{\alpha i}) - E_{bs}^\alpha(r_{\alpha i}))^2 - U^\alpha(r_{\alpha i})^2] \omega_{\alpha i}, \quad (3)$$

where i runs from 1, to N^α , the number of energy vs. distance data-pair chosen for structure α , and $\omega_{\alpha i}$ are weighting factors which are chosen to favor lower-energy structures (graphite, diamond, and linear chain). The $E_{bs}^\alpha(r_i)$ obtained from the first step are subtracted from the total energy $E_{tot}^\alpha(r_{\alpha i})$ of accurate first-principles LDA calculations, which are read in as input data, and the energy differences are compared with the term $U^\alpha(r_i)$, which equals to $\sum_j f(\sum_k \phi(r_{jk}))$. By adjusting the parameters of function $\phi(r)$, $\Delta = \Delta_{min}$ can be obtained, which is a sufficient condition to have a better phase diagram (i.e., a set of energy vs. nearest-neighbor distance curves).

The above fitting procedures are performed as many times as we chose the set of sp^3 parameters and the parameters in the $s(r)$, and the results of the minimized Δ 's give us the range within which good phase diagrams can be chosen and thus satisfactory TB parameters can be determined.

END

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