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Dynamical Studies of Periodic and Disordered Systems

by

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Dynamical studies of periodic and

disordered systems

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The time evolution of two classes of systems is studied with real time molecular dynamics simulations. The first consists of a coupled electron-lattice system. For a periodic system, we present results for the time evolution of a one-dimensional system consisting of an electron, described by a tight-binding Hamiltonian, and a harmonic lattice, coupled by a deformation-type potential. We solve numerically the nonlinear system of equations of motion for this model in order to study the effects of varying the electronic effective mass for several initial conditions and coupling strengths. A large effective mass favors localized polaron formation for initially localized electrons. For initially extended electronic states, increasing the effective mass of an electron initially close to the bottom of the band makes localization more difficult, while for an initially highly excited electron, localized polaron formation is possible only when the electronic effective mass and the atomic masses of the lattice become of the same order. For a small parameter range, we find an impressive recurrence, a periodic and a complete exchange between the electronic and vibrational degrees of freedom of a small part of the initial electronic energy. The disordered case, described by a tight-binding model exhibiting metal-insulator transition (the diagonal matrix elements having a spatial variation incommensurate with the lattice), demonstrates the combined effects of disorder and electron-phonon interaction. The el-ph interaction

has profound effects, especially on one-electron extended states just above the mobility edge, where the electronic states change from extended to localized. Polaron formation is facilitated close to the mobility edge and, in most cases, the localization length (l_c) decreases upon increasing the disorder or el-ph coupling, as expected. However, for strongly localized states due to disorder or el-ph interaction, increase of el-ph coupling or disorder, respectively, results in an increase of l_c . This increase is due to phonon assisted hopping. The second class of systems studied consists of carbon and hydrogen. We calculate phonon anharmonic effects in diamond and graphite using a tight-binding molecular dynamics scheme. Using one-phonon spectral intensities that have been calculated through the Fourier transform of the velocity-velocity correlation function, we study the temperature dependence of the phonon frequency shift and phonon linewidth. In the case of the zone-center optical mode of diamond where experimental data are available, our results are in good agreement with experiment. A tight-binding model for carbon-hydrogen interaction is developed and used in molecular dynamics simulations. The parameters are obtained by fitting to the electronic and vibrational properties of methane. The results obtained for hydrocarbon molecules are in good agreement with experimental data and first-principles results. Interstitial hydrogen in diamond is also studied with this model and the results are compared with available experimental and *ab initio* results. The case of hydrogenated amorphous carbon is considered as well.

CHAPTER 1. GENERAL INTRODUCTION

The study of the electronic and vibrational properties of solids plays a central role in condensed matter physics. Understanding and predicting such properties on the atomic scale requires appropriate modeling of the electrons, the ions, and their interactions, as well as methods of calculation of meaningful physical quantities. An “appropriate” model sometimes translates to a simplified model, which captures the necessary essentials and exhibits universal behaviors, without necessarily corresponding to any real material. The insight gained from simple models can then be applied to investigate more complex systems and explain the diversity and systematic trends in the behavior of real materials. There are other situations where a model is “appropriate” if it includes every possible effect, reproduces accurately the properties of a specific system, explains complex phenomena, and results in quantitative predictions subject to direct experimental verification. In recent years, both of these aspects of condensed matter theory have grown due to the enormous increase in computational power. The availability of large computational resources provided new tools for the solution of problems in traditional many-body theory, opened the way for the study of disordered systems [1], and it became possible to calculate properties of real materials with remarkable accuracy, by means of powerful *ab initio* (first principles) total energy calculation methods, such as the density functional theory [2]. The bulk

of the work is focused on the ground state properties of solids. In the case of *ab initio* techniques, for instance, calculations of ground state properties include the equilibrium structure of a solid, the total energy, the electronic band structure, the stability of different phases at zero temperature, and changes in the presence of static external influences. Furthermore, under the adiabatic approximation, i.e., when the ionic motions are considered to be on a much slower time scale than the electronic excitations and the electrons are always in their ground state for every configuration of the ions, a lot of low temperature phonon properties are obtained.

Still, there is a plethora of interesting physical phenomena away from equilibrium and the transient behavior can be very interesting itself. The powerful modern computers have also made it possible to study the dynamics of periodic and non-periodic systems. This is done by numerical solution of the equations of motion for the particles constituting the system for long equilibration times. The general term used to describe these approaches is Molecular Dynamics (MD) [3]. Using MD, it is now possible to monitor the time evolution of systems with detail and accuracy that cannot be achieved with experiment, even in conditions where it may be impossible to carry out experiments. In addition, MD provides macroscopic properties of experimental interest derived from the microscopic properties of the system. In this sense, MD not only connects theoretical models with experiments, but it can be a powerful investigatory tool on its own right. A point where MD may be difficult to simulate reality, in some problems, is the simulation time comparing to the time scales involved in physical phenomena (sometimes simulations times are orders of magnitude smaller than the time scales involved in real experiments).

In this thesis, we use MD to study two different types of systems. One of

them is based on a simple, general model for a single electron interacting with a harmonic lattice. It is employed in order to understand general features of electron-phonon systems covering all the relevant parameter space and initial conditions, and to study the interplay of disorder and nonlinearity introduced by the electron-lattice interaction. The other type is real carbon and carbon-hydrogen systems. The model used is more complicated and attempts to incorporate the most important structural, electronic, and vibrational properties of these specific systems.

Electron-phonon Interaction and Localization in Periodic and Disordered Systems

The first part of the thesis covers the topic of electron-phonon (el-ph) interaction, localization, and polaron formation in periodic systems (Chapter 2) [4, 5] and disordered systems (Chapter 3) [6]. This problem has been the subject of extensive studies over the last decades and, traditionally, it is treated within the framework of many-body theory for periodic systems [7]. In the case of a single electron interacting with vibrational degrees of freedom via a short-range interaction, these studies have shown that the ground state of the coupled electron-lattice system is either an extended Bloch-like solution (if the el-ph coupling is smaller than a critical value) or a self-trapped localized solution (if the coupling is larger than the critical value). The state consisting of the electron and its induced lattice deformation is referred to as a polaron. Depending on the parameters range and the dimensionality, large polarons (with spatial extend that far exceeds lattice spacing) or small polarons (localized in a few atomic sites) are formed. Small polarons can move from site to site by thermally activated hopping (small polaronic transport) and may be immobilized

at low temperatures, especially in the presence of (even a small amount of) disorder. Although the question of el-ph interaction and polaron formation has been well studied, a lot of questions remain unanswered. Some very interesting regions of the parameter space (el-ph coupling, adiabatic parameter) have not been fully explored due to the limitations of several approximations (only the cases of weak and strong coupling are fairly well understood). Besides the fact that the intermediate regime remains poorly understood, some important aspects of the problem have not been adequately addressed. The time evolution of an electron photoexcited or injected in an otherwise empty band as it interacts with the lattice is of great interest. Within traditional treatments it is assumed that the electron reaches the bottom of the band in a short period of time and the ground state solutions are immediately applicable. The possibility, though, that long-lived metastable states may be reached could have significant physical consequences. Another very important issue is the combined effects of disorder and el-ph interaction. In the absence of disorder and lattice vibrations, the electrons are moving in a perfect periodic potential and are described by Bloch states (plane waves). The very existence of a finite electronic conductivity is due to disorder and phonons (lattice thermal vibrations). As we mentioned earlier, a lot of work has been devoted to the study of el-ph interactions, without disorder. The same is true for the study of disordered systems without el-ph interaction; it is now well established that in a random system (i.e, when the potential takes any value within a certain range and with a certain probability), electronic states are always localized in strictly one and two dimensional systems, and a phase (metal-insulator) transition from extended to localized states exists in three dimensions (Anderson localization) [1]. The wavefunction of localized states decays exponentially with dis-

tance and is characterized by the localization length (l_c). The energy where electronic states change from extended to localized is called mobility edge. Much less has been done in the case of the simultaneous presence of these two basic sources of electronic localization. Cohen, Economou, and Soukoulis have studied the behavior of a disordered el-ph system near the mobility edge with scaling theory [8] and they found that localized polarons are formed in the vicinity of the mobility edge even for very weak short range el-ph interaction. This effectively shifts the mobility edge into the region of extended states and changes the metal-insulator transition from a power law to a discontinuity for the conductivity, thus supporting the concept of a minimum metallic conductivity.

A more extensive review of the problems described above, as well as a discussion of our approach, which is similar to the one used in the field of nonlinear physics, can be found in the introductions of Chapters 2 and 3 of the thesis and the references therein. We studied these problems through real-time numerical simulations of the dynamics of the coupled system of an electron in a linear chain, described by a tight-binding model that exhibits metal-insulator transition (the diagonal matrix elements having a spatial variation incommensurate with the lattice), as it interacts with a harmonic lattice via a deformation potential (Fröhlich-type model). The numerical solution of the system of nonlinear equations of motion for this model is non-trivial due to the long time required for the system to reach a steady state (typical runs include 300-600 atoms and 10^8 iterations) and massively parallel computers were used. In this case, our MD simulations explicitly include the electronic degrees of freedom, thus requiring a small time step. We obtained different types of localized and extended states with novel features that are absent from the traditional polaronic states

and depend very strongly on the initial electronic configuration and electronic effective mass (adiabatic parameter), m^* . Even in the absence of disorder, the transient behavior for the periodic electron-lattice system is of great interest and Chapter 2 deals with this case. The expected ground state behavior is recovered in the adiabatic and weak coupling (soliton-like, large polaron solutions) and in the nonadiabatic and strong coupling (small polaron) regimes, but for initially highly excited electrons, an "anti-thermodynamic" behavior is observed (the transfer of electronic energy to the lattice seems to stop on the average without the electron reaching the bottom of the band), with most impressive the recurrence phenomenon [4]. A large m^* (a case relevant to narrow-band materials) favors localized polaron formation for initially localized electrons, but this is not always the case for initially extended electronic states. In the latter case, increasing m^* of an electron initially close to the bottom of the band makes localization more difficult while for initially highly excited electrons, localized polaron formation is possible only when m^* becomes of the order of the atomic mass. We explain these results with a resonance type condition that matches the effective velocity of the electron with the speed of the lattice vibrations, for initially extended electronic states (localized in momentum space), and with the small polaron formation criterion, for initially localized (in real space) electrons [5].

In the disordered (quasiperiodic) system, which is treated in Chapter 3, the el-ph interaction has profound effects, especially on one-electron extended states just above the mobility edge, where the electronic states change from extended to localized. Polaron formation is facilitated close to the mobility edge and, in most cases, the localization length (l_c) decreases upon increasing the disorder or el-ph coupling, as expected. However, some of our results confirm speculative ideas based on scaling

arguments concerning transport in disordered systems: for strongly localized states due to disorder or el-ph interaction, increase of el-ph coupling or disorder, respectively, results in an increase of l_c . This increase is due to phonon assisted hopping and suggests that the mobility of a strongly localized system increases rather than decreasing with temperature [6].

The results of our extensive simulations of the dynamical behavior of the system, determine the role of all parameters involved in this nonlinear, discrete, coupled electron-lattice model and show how strongly the final state depends on the electronic effective mass (adiabatic parameter), the initial electronic configuration, the strength of the el-ph coupling, and disorder.

Tight-Binding Molecular Dynamics Studies of Carbon and Carbon-Hydrogen Systems

The second part of the thesis deals with phonon anharmonic effects in diamond and graphite (Chapter 4) and with the simulation of carbon-hydrogen systems (Chapter 5). Carbon is a very interesting element both from the fundamental and the technological point of view due to its unique ability to form strong covalent bonds with several coordination numbers resulting to many different bondings and configurations. Hydrogen and carbon is a combination of elements that occurs in abundance in nature and has received attention recently in many technological applications. The method used is Tight-Binding Molecular Dynamics (TBMD) [10]. Within usual MD the interatomic interactions are derived from empirical interatomic potentials fitted to properties of crystalline structures obtained by first-principles techniques or experiments [3]. This type of simulations can handle a large number of atoms and

for long simulation times but fail to describe accurately phenomena where quantum mechanical effects are essential. One of the breakthroughs in the field of MD was the development of *ab initio* MD, such as the Car-Parrinello method [9] which is MD within the Local Density Approximation (LDA) functional theory. *Ab initio* MD methods are the most accurate but they are limited to relatively small systems and short time scales. TBMD incorporates electronic structure effects into MD through an empirical tight-binding Hamiltonian. The interatomic interactions are determined at the microscopic level by first-principles calculations without resorting to fitting experimental data. It can handle a relatively large number of atoms for long simulation times with similar computational cost for different elements. A potential setback of the TBMD approach is the determination of the tight-binding parameters that guarantee accuracy and transferability, a process that can prove very tedious.

The TBMD technique has given accurate description of various structural, dynamical, and electronic properties of covalent systems. Following the early versions of tight-binding models of Harrison [11] and Chadi [12], subsequent transferable models were developed for silicon and carbon that describe well the energy-versus-volume phase diagrams for different atomic coordinations [13]. For silicon, the model developed by Kwon, Biswas, Wang, Ho, and Soukoulis [14] gives accurate energy-versus-volume diagrams for high-coordinated metallic structures as well as the diamond structure. The model developed by Xu, Wang, Chan, and Ho (XWCH model)[15, 16] for carbon has been very successful in describing carbon in different atomic environments. Liquid carbon was found to be metallic and dominated by twofold and threefold atoms at low densities, while at high densities diamond-like tetrahedral arrangements were obtained. Comparisons with *ab initio* MD results were satisfactory

[17]. In the case of amorphous carbon ($a-C$), TBMD helped clarified the microscopic picture by showing that sp^3 bonding concentration increases when $a-C$ samples are generated under higher densities. The results showed that the first peak of the radial distribution function shifts towards larger distances with increasing density, in agreement with neutron scattering experiments [18]. The XWCH model also predicted the ground state structures of every even-numbered carbon cluster from C_{20} to C_{102} and the energy ordering of buckyballs isomers (in the case of C_{84} before experiment) [19].

Using this model for the carbon-carbon interactions, we study anharmonic properties of diamond and graphite. MD is the method of choice for studying such properties, provided that the model used for the calculation of the interatomic interactions is accurate. The achievements of the XWCH model for carbon briefly described, guarantee such an accurate calculation. Phonon properties of solids are usually calculated with the harmonic or the quasiharmonic approximation. Within the harmonic approximation, only the leading nonvanishing term in the expansion of the ionic interaction about its equilibrium value is retained. The observed phonon peaks should be very sharp at the energies allowed by the conservation laws of one-phonon processes. However, these peaks have a measurable width because the eigenstates of the harmonic Hamiltonian are not true stationary states of the crystal due to the anharmonicity inherent in the ionic interactions. Thus, the linewidth of the one-phonon peaks is a measure of the anharmonicity. In addition, in a harmonic solid, the phonon frequencies would not depend on equilibrium volume, which implies that the thermal expansion coefficient should vanish. It is clear that harmonic approximation is inadequate to describe real solids. The quasiharmonic approximation takes into account

that phonon frequencies do depend on the equilibrium volume, but it attributes their temperature dependence entirely to the change of force constants due to thermal expansion. The absence of explicit phonon interactions in this approximation leads to an underestimate of frequency shifts and does not predict linewidths. There are perturbative approaches, but they are restricted to lowest orders, due to the complexity of the calculations, becoming unsatisfactory for strongly anharmonic systems, or for systems at high temperatures. TBMD provides a very good alternative for the calculation of anharmonic effects and our results for diamond and graphite (Chapter 4) are in excellent agreement with the available experimental data.

The TBMD study of carbon-hydrogen systems of Chapter 5 is based on the XWCH model for the carbon-carbon interactions, while for the carbon-hydrogen interactions a tight-binding model is developed in the present work [20]. The parameters involved are obtained by fitting to the electronic and vibrational properties of methane obtained by LDA. Our TBMD results for the structural, electronic, and vibrational properties of hydrocarbon molecules are in very good agreement with experimental and *ab initio* results. In the case of interstitial hydrogen in diamond, the agreement with available data is not always good. The lowest energy configuration is found to be hydrogen at the bond-center site, but the energy of the tetrahedral interstitial site is much higher than expected. Using this model, we obtain results for hydrogenated amorphous carbon ($a-C:H$) that are in good agreement with *ab initio* MD and experimental data.

Dissertation Organization

This dissertation includes papers submitted or to be submitted to scholarly journals. The research in all parts was suggested by Prof. C.M. Soukoulis and performed under his supervision.

The first part, which deals with electron-phonon interaction and localization in periodic and disordered systems, consists of Chapters 2 and 3. In Chapter 2, the question of polaron formation in periodic systems is treated, with emphasis on the role of the electronic effective mass (adiabatic parameter) and initial conditions in the final outcome. In Chapter 3, the combined effects of disorder and electron-phonon interaction are examined.

The second part, which deals with tight-binding molecular dynamics of carbon and carbon-hydrogen systems, consists of Chapters 4 and 5. Chapter 4 is about phonon anharmonic effects in carbon and graphite, and Chapter 5 describes a tight-binding model for carbon-hydrogen interactions with applications in hydrocarbon molecules, hydrogen in diamond, and diamond-like hydrogenated amorphous carbon.

We conclude in Chapter 6 with a brief summary of our results and their implications for future work.

In the Appendix, we describe the tight-binding molecular dynamics algorithm and the XWCH tight-binding model for carbon.

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CHAPTER 6. CONCLUDING REMARKS

In what follows we briefly summarize our basic results and point to some directions for future work that will complement and extend the present approaches.

We studied through real time numerical simulations a simple model for the interactions of electrons and lattice vibrations in periodic and disordered systems, and several electronic and vibrational properties of carbon and carbon-hydrogen systems using more sophisticated tight-binding models.

Our results for coupled electron-phonon systems show that "heavy" electrons are not always more localized than "light" electrons. This is always true if the electronic excitation is initially localized in real space, i.e., if it is a superposition of electronic modes. In this situation, a small electronic effective mass (adiabatic case) allows for the spreading of the electronic wavefunction before the "slow" lattice can respond and the formation of localized polarons is impossible for any realistic value of the el-ph coupling. When the effective mass becomes larger (nonadiabatic case) and the electronic time scale is of the order of (or larger than) the lattice time scale, a localized polaron is formed, even for weak coupling. If the initial electronic state is extended, one electronic mode interacts with the lattice vibrations and self-trapping occurs when the effective speed of the electron matches the speed of the lattice vibrations. Consequently, initial extended configurations at (or close to) the ground

state end up localized much easier for "light" electrons, while initial highly excited states localize when the electronic and ionic masses are of the same order. Long-lived metastable states have been found, contrary to the common assumption that the electron and the lattice always thermalize, with most impressive example a very canonical exchange of energy between electronic and vibrational modes (recurrence). The combined effects of disorder and electron-lattice interaction were studied. The same electron-lattice model was used with the addition of an electronic potential with spatial variation incommensurate with the lattice (thus exhibiting metal-insulator transition and simulating a three dimensional system). Under the same initial conditions and parameters range as the periodic case, the behavior outlined above persisted for weak disorder. For strong disorder, as the mobility edge was approached, localized polaron formation was always facilitated. A very interesting phenomenon was demonstrated in the case of strongly localized states due to disorder: introduction of el-ph interaction resulted in an increase of the localization length (phonon-assisted hopping). Similarly, disorder in strongly localized systems due to el-ph interaction, increased the localization length (by fragmentation of the wave function).

There are a lot of very interesting remaining questions, that can be answered immediately with the methodology and computational tools already in place, and we briefly mention some of them.

Throughout our treatment, at no point we resort to the adiabatic approximation (our approach fully includes lattice vibrations). However, within the adiabatic approximation, our coupled model reduces to a nonlinear Schrödinger equation, which is well studied in nonlinear physics. Thus, comparison of the time evolution for the two models is of fundamental importance.

Our approach can be extended immediately to the two-electron problem, thus allowing an accurate and detailed treatment of bipolaron formation, especially in the poorly understood case of electronic effective mass comparable to the atomic masses or in the case of anharmonic vibrations. This may be relevant to narrow-band high critical temperature (high- T_c) superconductors or to fullerenes.

The question of how the behavior observed in one-dimension is modified in higher dimensions is a very important one. For instance, the two-dimensional bipolaron problem for narrow-band systems can prove crucial in understanding high- T_c superconductivity.

The dynamical simulations of the response of polarons and bipolarons to an external field would be of great interest.

In order to determine the conditions under which the phenomena discovered can be observed in real systems, it is necessary to examine how temperature affects our system's behavior. Preliminary results indicate that this behavior changes significantly with increasing temperature. It is important to further study these effects and extract relevant critical temperatures.

Our approach allows systematic corrections when some of the quantum mechanical aspects of the lattice motion are taken into account. It would be desirable to devise a method of full quantum mechanical treatment of the lattice and at the same time obtain an accurate time evolution of a highly excited state of the system, a task beyond the current state of the art but not completely out of reach with the available computational resources.

Throughout the second part of the thesis we performed realistic molecular dynamics simulations using the tight-binding scheme. The tight-binding molecular dy-

namics studies of anharmonic effects in diamond and graphite showed how this technique provides a tool for temperature dependent studies of realistic systems. The overall agreement with experiments for the zone-center phonon mode of diamond was good and predictions were made in the case of graphite. We also developed a tight-binding model for the carbon-hydrogen interaction by fitting to first-principles results for the electronic and vibrational properties of methane. The model reproduces accurately the geometric, electronic, and vibrational structure and the energies of hydrocarbon molecules. It gives a qualitatively correct picture of the energy landscape of hydrogen in diamond and results that compare well with experimental data for hydrogenated amorphous carbon.

Further work to check and improve the transferability of the carbon-hydrogen model is needed. The environment dependence has to be taken into account in a way that the model will remain efficient for molecular dynamics simulations.

The carbon-hydrogen model can be used in molecular dynamics of systems that range from molecules to amorphous solids.

APPENDIX: TIGHT-BINDING MOLECULAR DYNAMICS MODEL FOR CARBON

Transferable Tight-Binding Model for Carbon

The binding energy of a system in the tight-binding approximation is given by

$$E_{binding} = E_{bs} + E_{rep} \quad (A.1)$$

The first term in the right-hand side is the electronic band structure energy

$$E_{bs} = \sum_n \langle \psi_n | H_{TB} | \psi_n \rangle \quad (A.2)$$

i.e., the sum of the eigenvalues over all occupied electronic states. The electronic eigenvalues are obtained by solving the empirical tight-binding Hamiltonian, H_{TB} . The matrix elements of H_{TB} are adjustable parameters that are determined by fitting to *ab initio* results. The off-diagonal elements are two-center hopping parameters, scaled with the interatomic separation, r , with a specific functional form. The second term in the right-hand side of Eq. (1) is the repulsive term, E_{rep} , which is also described by short-ranged functions of the interatomic distance.

By following Goodwin et al [1], who developed a tight-binding model for silicon, Xu et al [2] obtained a set of parameters for carbon that guarantee transferability

of the model, i.e., they fit simultaneously to first-principles Local Density Approximation (LDA) results of energy-versus-volume curves of an infinite linear chain of C, graphite, diamond, simple cubic and face-centered cubic structures, with an emphasis on the diamond, graphite, and linear chain structures. Unlike in the Goodwin et al model, two distinct functions of the same form were used to scale the off-diagonal matrix elements, $s(r)$, and the pairwise repulsive potential, $\phi(r)$:

$$s(r) = \left(\frac{r_0}{r}\right)^n \exp\left(n\left[-\left(\frac{r}{r_c}\right)^{n_c} + \left(\frac{r_0}{r_c}\right)^{n_c}\right]\right) \quad (\text{A.3})$$

$$\phi(r) = \phi_0 \left(\frac{d_0}{r}\right)^m \exp\left(m\left[-\left(\frac{r}{d_c}\right)^{m_c} + \left(\frac{d_0}{d_c}\right)^{m_c}\right]\right) \quad (\text{A.4})$$

where r_0 is the nearest neighbor atomic distance in diamond and n , n_c , r_c , ϕ_0 , m , d_c , and m_c are parameters determined by the fit (table A.1) [2]. The functions $s(r)$ and $\phi(r)$ go smoothly to zero at a cut-off distance $r_m = d_m = 2.6 \text{ \AA}$ by using a third order polynomial, $t_s(r - r_1)$ and $t_\phi(r - d_1)$, respectively, whose coefficients are determined by requiring the connection of $s(r)$ and $t_s(r)$ at $r_1 = 2.45 \text{ \AA}$, and $\phi(r)$ and $t_\phi(r)$ at $d_1 = 2.57 \text{ \AA}$ and their first derivatives and that $t_s(r)$ and $t_\phi(r)$ and their first derivatives are zero at $r_m = d_m$ (table A.2). [2].

The sp^3 TB parameters E_s , E_p for the on-site matrix elements and $V_{ss\sigma}$, $V_{sp\sigma}$, $V_{pp\sigma}$, $V_{pp\pi}$ for the hopping matrix elements are shown in table A.1.

The carbon-carbon repulsions in this scheme are described by:

$$E_{rep,c-c} = \sum_i f\left(\sum_j \phi(r_{ij})\right) \quad (\text{A.5})$$

where $\phi(r_{ij})$ is the pairwise potential between carbon atoms i and j given by (A.4), and f is a fourth order polynomial with argument $\sum_j \phi(r_{ij})$ and coefficients given in table A.2 [2].

This model reproduces accurately the energy-versus-volume diagram of carbon polytypes as well as properties that do not enter explicitly into the fitting procedure, such as the phonon properties and elastic constants for carbon in the diamond and graphite structures, and has been used successfully in molecular dynamics studies of different atomic environments (small carbon microclusters [2], liquid phase [3], amorphous carbon [4, 5, 6, 7], fullerenes [8]).

Tight-Binding Molecular Dynamics Algorithm

Within the tight-binding molecular dynamics (TBMD) scheme, the system is described by the Hamiltonian:

$$H = \sum_i \frac{p_i^2}{2m_i} + \sum_n \langle \psi_n | H_{TB} | \psi_n \rangle + E_{rep} \quad (\text{A.6})$$

The first term in (A.6) is the kinetic energy of the atoms ($i = 1, \dots, N$) with momentum, p_i , and mass, m_i , the second term is the electronic band structure energy, and the third term includes all the repulsive energies as described in the previous section. The Hamiltonian (A.6) is easily inserted into the molecular dynamics algorithm (Fig. A.1). The interatomic forces are calculated from (A.6) as a sum of the contributions from the repulsive forces obtained from E_{rep} and the ones coming from the band structure energy (Hellmann-Feynman forces). One then solves the equations of motion for the N atoms:

$$m_l \frac{d^2 r_l}{dt^2} = F_l^{bs} + F_l^{rep} \quad (\text{A.7})$$

In the present scheme of TBMD using standard diagonalization, the band structure forces are easy to calculate. The band structure force acting on an atom l is

$$F_l^{bs} = - \sum_n \langle \psi_n | \frac{\partial H_{TB}}{\partial r_l} | \psi_n \rangle \quad (\text{A.8})$$

where the sum is over occupied levels ϵ_n with eigenvectors ψ_n . The eigenfunctions can be written in terms of the basis functions φ_{la}

$$|\psi_n\rangle = \sum_{l,a} c_{nla} |\varphi_{la}\rangle \quad (\text{A.9})$$

where a runs over all orbital types. Then the electronic force can be written

$$F_l^{bs} = - \sum_{l'} \sum_n \sum_a \sum_{a'} c_{nla}^* c_{nl'a'} \frac{\partial H_{la,l'a'}}{\partial r_l} \quad (\text{A.10})$$

with

$$H_{la,l'a'} = \langle \varphi_{l'a'} | H_{TB} | \varphi_{la} \rangle \quad (\text{A.11})$$

or

$$F_l^{bs} = \sum_{l'} F_{ll'} \quad (\text{A.12})$$

with

$$F_{ll'} = - \sum_n \sum_a \sum_{a'} c_{nla}^* c_{nl'a'} \frac{\partial H_{la,l'a'}}{\partial r_l} \quad (\text{A.13})$$

The integration in time of the equations of motion (A.7) for each atom l is performed with the Gear fifth-order predictor-corrector algorithm. An estimate of the first five derivatives of the position at time $t + \Delta t$ is obtained by Taylor expansion about time t :

$$\frac{d^n}{dt^n} r_l^p(t + \Delta t) = \sum_{k=0}^{5-n} \frac{(\Delta t)^k}{k!} \frac{d^k}{dt^k} r_l(t), \quad \forall n = 0, 1, 2, 3, 4, 5 \quad (\text{A.14})$$

The superscript on the position vector indicates that these are the "predicted" values of the derivatives. From the "predicted" position r_l^p , the force at time $t + \Delta t$ is evaluated, and hence the "corrected" acceleration a_l^c

$$a_l^c(t + \Delta t) \equiv \frac{d^2}{dt^2} r_l^c(t + \Delta t) = \frac{F_l(t + \Delta t)}{m_l} \quad (\text{A.15})$$

which is compared with the predicted acceleration from (A.8)

$$a_l^p(t + \Delta t) \equiv \frac{d^2}{dt^2} r_l^p(t + \Delta t) \quad (\text{A.16})$$

in order to estimate the error in the prediction step:

$$\Delta r_l(t + \Delta t) = \frac{1}{2}(\Delta t)^2 [a_l^c(t + \Delta t) - a_l^p(t + \Delta t)] \quad (\text{A.17})$$

This error is used in the corrector step:

$$\frac{d^n}{dt^n} r_l^c(t + \Delta t) = \frac{d^n}{dt^n} r_l^p(t + \Delta t) + \frac{n!}{(\Delta t)^n} C_n \Delta r_l(t + \Delta t) \quad (\text{A.18})$$

where the so-called Gear coefficients are $C_0 = 3/16$, $C_1 = 251/360$, $C_3 = 1$, $C_4 = 1/6$, $C_5 = 1/60$. The superscript (c) now indicates the "corrected" positions. This predictor-corrector procedure is iterated during the simulation.

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Table A.1: sp^3 TB parameters and parameters for $s(r)$ and $\phi(r)$.

E_s (eV)	E_p (eV)	$V_{ss\sigma}$ (eV)	$V_{sp\sigma}$ (eV)	$V_{pp\sigma}$ (eV)	$V_{pp\pi}$ (eV)
-2.99	3.71	-5.0	4.7	5.5	-1.55
	n	n_c	r_c (Å)	r_0 (Å)	r_1 (Å)
	2.0	6.5	2.18	1.536329	2.45
ϕ (eV)	m	m_c	d_c (Å)	d_0 (Å)	d_1 (Å)
8.18555	3.30304	8.6655	2.1052	1.64	2.57

Table A.2: Coefficients for $t_s(r - r_1)$, $t_\phi(r - d_1)$, and $f(\sum_j \phi(r_{ij}))$.

	$t_s(r - r_1)$	$t_\phi(r - d_1)$	$f(\sum_j \phi(r_{ij}))$
c_0	$6.7392620074314 \times 10^{-3}$	$2.2504290109 \times 10^{-8}$	-2.5909765118191
c_1	$-8.1885359517898 \times 10^{-2}$	$-1.4408640561 \times 10^{-6}$	0.5721151498619
c_2	0.1932365259144	$2.1043303374 \times 10^{-5}$	$-1.7896349903996 \times 10^{-3}$
c_3	0.3542874332380	$6.6024390226 \times 10^{-5}$	$2.3539221516757 \times 10^{-5}$
c_4			$-1.24251169551587 \times 10^{-7}$

Figure A.1: Schematic representation of the TBMD algorithm.