

**Graphitic Nanocarbon Supports For
Molecular Transport, Sensing, and Catalysis**

BY

JOHN RUSSELL

B.A. (Washington University in St. Louis) 2002

THESIS

Submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy in Chemistry
in the Graduate College of the
University of Illinois at Chicago, 2012

Chicago, Illinois

Defense Committee:

Petr Kral, Advisor and Chair
Michael Trenary,
Preston Snee,
Scott Shippy
Peter Zapol, Argonne National Laboratory

Elementis Regamus Proelium!

ACKNOWLEDGMENTS

I would like thank my UIC and Argonne advisors Prof. Petr Král, Dr. Peter Zapol and Dr. Larry Curtiss for their advice, guidance, insight, and numerous contributions to my research. I would like to acknowledge the generous support of the Department of Defense through the National Defense Science and Engineering Graduate Fellowship and the support of Argonne National Laboratory through the Guest Graduate program.

Several people contributed greatly to my studies at UIC and I would like to acknowledge their support. I would like to thank my committee: Professors Michael Trenary, Preston Snee, and Scott Shippy. In addition I would like to thank Prof. Tim Keiderling and Prof. Robert Gordon. Ms. Pat Ratajczyk, Ms. Silvia Solis, and Ms. Rhonda Staudohar and the Chemistry Department staff were invaluable for their practical knowledge and an endless source of encouragement. I am very proud to have had the opportunity to work with such excellent faculty and staff that serve as public employees of a state institution, tirelessly creating opportunities in historically underserved communities for the benefit of all.

I would also like to thank my fellow graduate students, Dr. Boyang Wang and Dr. Alexey Titov for teaching me the practical aspects of modeling chemical systems and the fundamentals of FORTRAN programming. Lela Vukovic, Niladri Patra, Artem Baskin, Irena Yzerei, and Dominic Esan contributed greatly to a positive academic environment of curiosity and learning, and I very much appreciate their many insightful comments on modeling nanoscale phenomena. Lastly I would like to thank our undergraduate researchers, Kyaw "Joe" Sint, Liz Vokac, Neil

ACKNOWLEDGMENTS (Continued)

Shah, Ryan Pearson, Antonett Madriaga, Wai Yip Lo, Alan T. Tang, and Mena Poonaki for their many contributions to the lab and making it a more fun place to work.

I also have many colleagues at Argonne National Laboratory that were essential to making this thesis possible. I would like to thank Dr. Rajeev Assary for his help with DL-POLY, NWChem and G09 software packages, Dr. Faisal Mehmood for advice on spin in metallic clusters, and Dr. Kah Chun Lau for his help with DL-POLY and many molecular dynamics problems. I greatly appreciate Dr. Haiying He for her insight into crystal structure problems and also Dr. Lei Cheng for advice on dispersion effects in quantum calculations. Dr. Paul Redfern had great advice regarding non-Kekule graphitic materials, and I am grateful for the many conversation with Dr. Glen Ferguson regarding periodic electronic structure problems. I also would like to thank Dr. Hakim Iddir and Dr. Weronika Walkosz for their many excellent suggestions on mathematics and physics problems of strings and membranes. I also appreciate the great conversations with Mr. Alejandro Rebola.

I would be remiss not to mention our scientific spiritual leaders, Dr. Dieter Gruen and Dr. Marvin Tetenbaum. Dieter and Marv both worked on the Manhattan Project, and regaled us with tales of radioactive experiments and walking around with uranium. Dieter has worked at Argonne for 65 years and remembered Enrico Fermi at the University of Chicago. We are all greatly benefited by their service, and I greatly appreciate them for sharing their wisdom, experience, and scientific insight with the group at lunch.

Finally, I would like to thank my wife Dr. Beth Russell for her unwaivering, cheerful support, and my family: Ralph and Marilee Russell, Robert Russell, Prof. Joellen Russell, Mary Russell,

ACKNOWLEDGMENTS (Continued)

Cecilia Russell, Dr. Les and Connie Goldsmith, Kate Goldsmith, and the old man himself, Rob Russell, 101 years old and still going strong.

TABLE OF CONTENTS

<u>CHAPTER</u>		<u>PAGE</u>
1	INTRODUCTION	1
2	MODELING METHODS	3
2.1	First Principles Methods	3
2.1.1	Density Functional Theory	7
2.1.2	Density Functional Tight Binding	15
2.2	Classical Molecular Dynamics	17
2.2.1	Fixed Bond Force Fields (non-reactive)	17
2.2.2	Long Range Nonbonded Interactions	21
2.2.3	Electrostatics	21
2.2.4	Dispersion	23
2.2.5	Many-Body Force Fields	24
2.2.6	Embedded Atom Method	26
2.2.7	Tersoff Potential	27
2.2.8	Reactive Bond Order Methods	31
2.2.9	Dispersion and Many-Body Force Fields	35
2.2.10	Integration schemes for molecular dynamics	37
2.2.11	Ensembles in MD simulations	39
3	METHANE BOND ACTIVATION BY PT AND PD SUB-NANOMETER CLUSTERS SUPPORTED ON GRAPHENE AND CARBON NANOTUBES	42
3.1	Introduction	42
3.2	Methods	43
3.3	Results	47
3.3.1	Cluster-Nanotube Binding	47
3.4	Methane Activation by Unsupported Clusters	49
3.5	Reaction Energies, Islands of Stability and Instability	51
3.6	C-H Bond Activation in Methane	54
3.7	Conclusions	56
4	CONFIGURATION-SENSITIVE MOLECULAR SENSING ON DOPED GRAPHENE SHEETS	58
4.1	Introduction	58
4.2	Design of the molecular nest	60
4.3	Simulation of selective molecular docking	65

TABLE OF CONTENTS (Continued)

<u>CHAPTER</u>		<u>PAGE</u>
4.4	Simulation of molecular sensing	68
4.5	Results and discussions	71
4.6	Conclusions	77
5	NANODROPLET TRANSPORT ON VIBRATED NANOTUBES	78
5.1	Introduction	78
5.2	Model System	79
5.3	Nanodroplet transport by linearly polarized waves	81
5.4	Nanodroplet transport by circularly polarized waves	85
5.5	Temperature effects	92
5.6	Conclusions	92
6	GRAPHITIZATION BY THERMAL ANNEALING	93
6.1	Introduction	93
6.2	Buckling in Graphene Monolayers	94
6.3	Interlayer Repulsion in Buckled Graphene Bilayers	96
6.4	Diamond to Graphite Phase Transition	102
6.5	Diamond Nanowire Graphitization	105
6.6	Conclusions	111
7	SHIFTED-SPLINED ELECTROSTATICS METHODS	115
7.1	Introduction	115
7.2	Spline Cutoff Functions	116
7.3	Splined Electrostatics	119
7.4	Applications to UO_2	122
7.5	Thermal Conductivity	125
7.6	Conclusions	128
8	CONCLUDING REMARKS	130
	CITED LITERATURE	132

LIST OF TABLES

<u>TABLE</u>		<u>PAGE</u>
I	GRAPHENE BILAYER COORDINATES AND VECTORS	100
II	DIAMOND TO GRAPHITE COORDINATES AND VECTORS . .	104
III	POTENTIAL PARAMETERS	124
IV	THERMAL CONDUCTIVITY	127

LIST OF FIGURES

<u>FIGURE</u>		<u>PAGE</u>
1	The development of modelling techniques is shown from the most computationally expensive first principles methods (top) to the moderately expensive semi-empirical methods (middle) to the least expensive empirical modelling methods (bottom).	4
2	The heritage of empirical methods from the tight binding approximation is shown. Most modern reactive potentials are derived from the Tersoff many-body potential, which is in turn derived from tight-binding. . . .	5
3	Calculated structures of a methane molecule reacting with a palladium tetramer (top row), supported on a (7,0) CNT represented by a finite model: a) molecular adsorption, b) transition state, c) dissociative adsorption. A methane molecule reacting with a platinum tetramer using the same model (bottom row, truncated) shows hydrogen adsorption on a single Pt atom rather than occupying a bridge site as for the Pd tetramer.	44
4	Calculated Pd ₄ /Pt ₄ cluster binding energy E_B^M to the CNT support shown by CNT curvature and chirality: a) armchair including (10,10), (8,8), (5,5), (4,4) and b) zigzag including (15,0), (10,0), (8,0), (7,0). The number of surface bonds from the cluster to the support are shown next to each point. Inset: a Pd ₄ cluster with 1 surface bond to graphene (left) and a Pt ₄ cluster with 2 surface bonds to graphene (right).	48
5	Adsorption energies and reaction barriers of C-H bond breaking which proceeds from the separated methane and unsupported Pd(Pt) tetramers, to molecular adsorption (MA) of the methane, to the transition state (TS) of C-H bond insertion, and finally to dissociative adsorption (DA). Inset spin density plots of the Pd tetramer shows very little contribution of spin density from the methane throughout the reaction. All energies are relative to $M_4 + CH_4$ and spin density ($\alpha - \beta$) isosurface contour values are $0.003 e^-/\alpha_0^3$	50
6	Energies of molecular adsorption (MA, E_{MA}^M , and dissociative adsorption (DA), E_{DA}^M , for tetramer clusters where M is Pd (straight) or Pt (dashed), as a function of support curvature and chirality, including graphene ($r^{-1} = 0.0 \text{ \AA}$), zigzag (open circles) and armchair (filled circles) CNTs. The C-H bond insertion reaction is exothermic if $E_{DA}^M < E_{MA}^M$.	53

LIST OF FIGURES (Continued)

<u>FIGURE</u>		<u>PAGE</u>
7	Calculated apparent barriers, E_a^M , for CH bonds with (a) $M = \text{Pd}_4$ and (b) $M = \text{Pt}_4$ catalysts on supports by curvature and chirality, including graphene ($r^{-1} = 0.0 \text{ \AA}$), armchair, and zigzag CNTs. Barriers are reduced for Pd clusters by CNT supports and increased for Pt clusters relative to gas phase (shown in Figure 5).	55
8	(top) The (M) enantiomer of the 2,2',4,4',6,6'-Hexanitrostilbene molecule. The electrostatic potential distribution formed $\approx 1.0 \text{ \AA}$ above (left) and below (right) the HNS molecule.	61
9	(left) The doping pattern of the nest designed for the (M)-HNS enantiomer docked above the sheet. (bottom) The electrostatic potential distribution formed above (or below) the doped graphene sheet (complementary to that in Figure 8 (bottom right)).	64
10	(top) (M)-HNS enantiomer docked in the nest on the graphene sheet designed for it. (bottom) However, (M)-HNS enantiomer does not bind to the nest at the bottom of the graphene sheet, because this nest (with vertically mirrored electric field) matches the opposite (P)-HNS enantiomer.	66
11	(left) The frequency dependent values of the projected amplitude of the axial vibration mode ($T = 75 \text{ K}$). We display the vibrations of the free sheet, the sheet with the HNS bound at the top and bottom, respectively. (inset) The atom displacements in the reference frame of the axial vibration mode in the clamped graphene sheet ($T = 5 \text{ K}$).	74
12	(left) The frequency dependent values of the projected amplitude of the edge vibration mode ($T = 75 \text{ K}$). We display the vibrations of the free sheet, the sheet with the HNS bound at the top and bottom, respectively. (inset) The atom displacements in the reference frame of the edge vibration mode in the clamped graphene sheet ($T = 5 \text{ K}$).	75
13	Nanodroplets of a) $N_w = 10,000$ and b) $N_w = 1,000$ waters adsorbed on the (10,0) CNT and dragged by the linearly polarized TA vibrational wave with the amplitude of $A = 1.2$ ($T = 300 \text{ K}$). c) A nanodroplet of $N_w = 1,000$ adsorbed on the same CNT is dragged by a circularly polarized vibrational wave of $A = 0.75 \text{ nm}$	80

LIST OF FIGURES (Continued)

<u>FIGURE</u>		<u>PAGE</u>
14	The drag velocity of nanodroplets with $N_w = 1,000$ and $10,000$ waters in dependence on the amplitude, A , of the linearly polarized wave, with the frequency of $\omega = 208$ GHz. (inset) The adsorbed nanodroplets viewed in the CNT axis.	84
15	The average translational v and angular ω_d velocities of water nanodroplets with $N_w = 1,000$ and $2,000$, in dependence on the wave amplitude, A , when driven by circularly polarized waves.	86
16	Time dependent angle of rotation (top), position (middle), and height (bottom) of the $N_w = 1,000$ droplet center of mass above the local CNT center of mass as the CNT is driven by circularly polarized waves of $\omega = 208$ GHz at amplitudes ranging from $A = 0.21$ nm to $A = 0.75$ nm. Tangents between vertical lines indicate regions of surfing where the nanodroplet slides down the CNT surface.	89
17	Temperature dependent translational velocities, v , of the $N_w = 1,000$ and $10,000$ droplets dragged by linearly polarized vibrational waves of $\omega = 208$ GHz and $A = 1.2$ nm. (inset) The temperature dependence of the effective nanodroplet density.	91
18	Graphitic carbon (C-C), silicon (Si-Si), silicon-carbide (Si-C) and boron-nitride (B-N) monolayers are bent out of plane at constant bond length.	95
19	Electronic repulsion between layers of graphite (A) is due to the anti-symmetry of the HOMO in separate layers. This is not the case for graphitic silicon carbide (B) but is true for graphitic silicon (C).	98
20	The buckling of a graphitic bilayer can be modeled parametrically with dependence on three variables: bond length (B), buckling angle (θ), and interlayer separation (Z). The x-y plane of a single layer of graphene is shown (left) with translation vectors, and the z plane of an AA stacked bilayer is shown (right) with interlayer separation ∂Z	99
21	The total energy of a buckled graphene bilayer with respect to buckling angle at constant interlayer separation of $2 \text{ \AA}$ of an AA stacked graphene bilayer is shown in (upper left) and of an AB stacked graphene bilayer in (upper right). Likewise the total energy of a buckled graphene bilayer with respect to interlayer separation at constant optimal unbuckled graphene bond length is shown (bottom left) and (bottom right).	101

LIST OF FIGURES (Continued)

<u>FIGURE</u>		<u>PAGE</u>
22	Graphitization of diamond can be modeled as a linear interpolation of bond length, buckling angle, and interlayer separation. Here a 12-atom unit cell of diamond (left) moves through intermediate states (center) with a final state of rhombohedral graphite (right).	103
23	Graphitization of diamond can be modeled as a linear interpolation of bond length, buckling angle, and interlayer separation. A 12-atom unit cell of diamond is interpolated on a grid of one percent per step using DFT, DFTB, and MD methods.	106
24	The top row shows pristine (A) cuboctahedron, (B) hexagon, and (C) diamond shaped nanowires. The bottom row shows the graphitized nanowires after $\approx 2ns$ of thermal annealing. The nanowires are oriented to run lengthwise along the $\langle 110 \rangle$ direction with surfaces labeled on the top row.	108
25	Diamond nanowires are shown in order of size. A method of identifying the width of the wire is shown whereby the number of rings is counted from the center to the outside edge.	109
26	The sp^2 fraction of cuboctahedron shaped diamond nanowires is shown by temperature after 2ns of thermal annealing. Inset is a figure of the initial configuration. The wires have $\langle 100 \rangle$ and $\langle 110 \rangle$ surfaces that are extremely slow to graphitize. Small wires can graphitize suddenly leading to a jump in sp^2 fraction.	110
27	The sp^2 fraction of diamond shaped diamond nanowires is shown by temperature after 2ns of thermal annealing. Inset is a figure of the initial configuration. The wires consist only of $\langle 111 \rangle$ surfaces and therefore graphitize very easily. Larger wires graphitize more slowly than smaller wires.	113
28	The sp^2 fraction of hexagon shaped diamond nanowires is shown by temperature after 2ns of thermal annealing. Inset is a figure of the initial configuration. The wires have $\langle 100 \rangle$ surfaces that are extremely slow to graphitize. Small wires can graphitize suddenly leading to a jump in sp^2 fraction.	114

LIST OF FIGURES (Continued)

<u>FIGURE</u>		<u>PAGE</u>
29	The electrostatic potential between two arbitrary particles is shown for the real, shifted, and shifted-splined variants. Inset is the electrostatic force in the splined region. Splines introduce large bumps in forces unless the potential is also shifted. All constants are set to 1 and the splined region is between 10 – 12 Å. The shifted potential is modified by a constant such that $V_{shift} = V_{coul}(10) - V'_{coul}(10)$	120
30	Configuration of 25 nm fluorite UO ₂ blocks modeled by (A) PPPM electrostatics method, (B) shifted-splined method with 12 Å and 15 Å inner and outer cutoffs, and (C) shifted-splined method with 10 Å and 12 Å inner and outer cutoffs. The (C) method has too short a cut off and gives incorrect results.	123
31	Radial distribution function of fluorite UO ₂ model with PPPM and shifted-spline model using 12 Å and 15 Å inner and outer cutoffs. . . .	126

LIST OF ABBREVIATIONS

AM1	Austin Model 1
B3LYP	Becke 3-Parameter Lee-Yang-Parr Functional
CNT	Carbon Nanotube
DFT	Density Functional Theory
DFTB	Density Functional Tight Binding
GGA	Generalized Gradient Approximation
HF	Hartree-Fock
HOCO	Highest Occupied Crystal Orbital
HSE	Heyd-Scuseria-Ernezhof Functional
LDA	Local Density Approximation
LSDA	Local Spin Density Approximation
MINDO	Modified Intermediate Neglect of Differential Overlap
MD	Molecular Dynamics
PBE	Perdew-Burke-Ernezhof Functional
PME	Particle-Mesh Ewald
PM3	Parameterized Model 3

LIST OF ABBREVIATIONS (Continued)

PM6	Parameterized Model 6
PPPM	Particle-Particle Particle-Mesh
Qeq	Charge Equilibration Method
REBO	Reactive Bond Order
SCF	Self-Consistent Field
SWNT	Single Wall Carbon Nanotube
vdW	van der Waals

SUMMARY

Energy production is a critical problem impacting both economic and national security interests. The history of energy production, research and development in the United States is inseparable from the history of national security decisions. The greatest example of this is the agreement aboard the USS Quincy in 1944 where President Roosevelt provided security guarantees to King Ibn Saud of Saudi Arabia in exchange for oil concessions, with the consequences of that agreement reaching into modern day conflicts. The human and environmental costs of energy production are not small. Whaling in the nineteenth century for lamp oil was both a dangerous occupation and led to overfishing. Present day coal mining has led to numerous fatal accidents and coal combustion contributes greatly to air pollution. The recent Fukushima daiichi accident has demonstrated the risks of nuclear power for energy production. It is important to remember that energy research has often had dual-use for both energy and weapons applications. Nuclear power and nuclear weapons are the most obvious example, but it must be remembered that the scientific advances in catalysis such as the Haber process also led to mass production of explosives and chemical warfare during the first world war. Fortunately, new sources and methods of energy production have fewer human and environmental costs and fewer national security risks. Catalytic conversion of domestically abundant natural gas and renewable energy strategies harnessing wind, solar, and biomass do not have the same drawbacks as traditional energy sources, and improved nuclear fuels might reduce the risk of future meltdowns. National investment in basic and applied research is not just important for

SUMMARY (Continued)

the economic concerns of today but it is also critically important for the security concerns of tomorrow.

Advanced materials are needed to support development of next generation technologies for energy and security applications. Experimental successes at the manipulation of materials at the nanoscale have led to an unprecedented control of physical and chemical processes. Concurrent development of *ab initio* and molecular dynamics theory has resulted in unprecedented insight into these nanoscale reactions and processes. The predictive power of computational methods assists experimental efforts to discover new materials by suggesting chemical trends and reducing trial and error. The motivation of this thesis is to use the materials by design concept to select functional requirement and then computationally predict materials that might fit the required properties.

The thesis is structured to introduce the topic of graphitic nanocarbon supports for various applications including molecular transport, sensing and catalysis. The discoveries of graphitic carbon nanomaterials including fullerenes, nanotubes, and graphene monolayers has created new opportunities in the fields of energy and nanotechnology. The ambition of this thesis is to explore a tiny portion of what might be possible with graphitic nanocarbon materials and contribute to the greater body of scientific knowledge in service of the goal of a brighter tomorrow.

CHAPTER 1

INTRODUCTION

Recent discoveries of ultrananocrystalline diamond (1), diamond nanoparticles (2), and carbon spheres (3) demonstrate exciting properties such as remarkable resistance to wear and chemical stability (4). Applications have been wide ranging including use as a drug delivery vehicles (5). Diamond has been a hot research topic for many years both theoretically and experimentally, and current research has looked closely at the connection between graphite and diamond. Graphitic materials such as fullerenes (6), carbon nanotubes (7), and graphene (8) have been used in a wide variety of applications from electronic devices (9) to fabrics (10). Carbon chemistry is a very rich topic with deep connections to many important research areas including hydrocarbon chemistry, proteins, and nanotechnology.

The purpose of this thesis is to study the role of the graphitic nanocarbon supports for applications in molecular transport, sensing, and catalysis. Theoretical methods will be discussed in the second chapter, including first principles, semi-empirical, and molecular dynamics. The research strategy used throughout the thesis will be to use these methods to explore physical and chemical properties of graphitic nanocarbon supports. The third chapter will explore how a graphite support might affect catalytic reactions on supported metal subnanometer clusters. The fourth chapter will develop a model of an electrostatic nest to optimally bind a molecule of interest on a doped graphene sheet and explore vibrations as a method of sensing the bound molecule. The fifth chapter will model transport of water nanodroplets of different sizes on

a coherently vibrated carbon nanotube. The sixth chapter will discuss graphitization of carbon nanomaterials including diamond nanowires. The seventh chapter will introduce modeling methods for electrostatics with application to uranium oxide materials. The eighth chapter will conclude the thesis with a brief summary.

CHAPTER 2

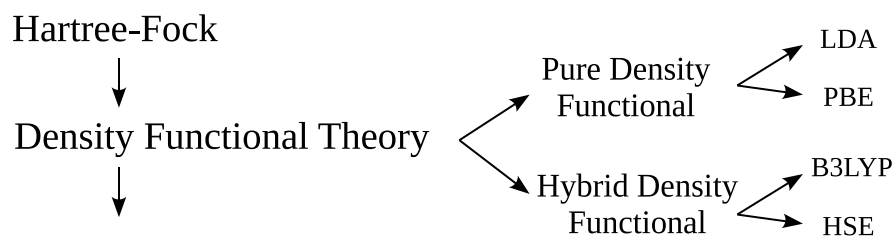
MODELING METHODS

Modeling methods will be introduced from the most computationally expensive with the greatest accuracy to the least computationally expensive with the least accuracy. Density Functional Theory (DFT) methods are fully self-consistent electron models, Density Functional Tight Binding (DFTB) methods account for electrons but use the two-center approximation of Slater and Koster, and classical molecular dynamics methods do not take into account electrons explicitly. The first two sections will discuss the motivations for development and use of DFT to model chemical problems. The third section will introduce the roots, uses, and limitations of DFTB methods. The last sections will discuss different classical molecular dynamics techniques. For the reader's convenience, two diagrams are provided, the first of which shows the lineage of techniques from first principles in Figure 1 and a second extended chart that shows the heritage of empirical models to tight binding, and by extension, first principles in Figure 2.

2.1 First Principles Methods

Hartree performed the first quantum calculations of chemical systems when he modeled the ionization energies of atoms in 1928 (11), well before the dawn of computers and automated calculations. Hartree's father was a retired engineer who famously helped Hartree perform the laborious calculations of the self-consistent field (SCF) method (12).

First Principles $O(N^4)$



Semi-Empirical $O(N^3)$

Neglect of Differential Overlap → MINDO, AM1, PM6

Tight Binding → Density Functional Tight Binding

Empirical $O(N)$

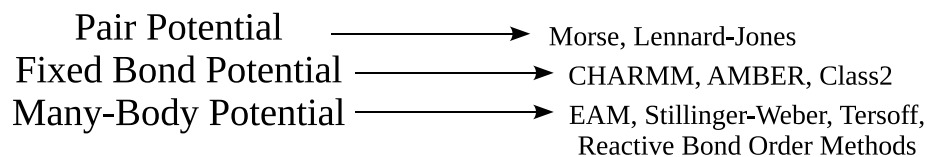


Figure 1. The development of modelling techniques is shown from the most computationally expensive first principles methods (top) to the moderately expensive semi-empirical methods (middle) to the least expensive empirical modelling methods (bottom).

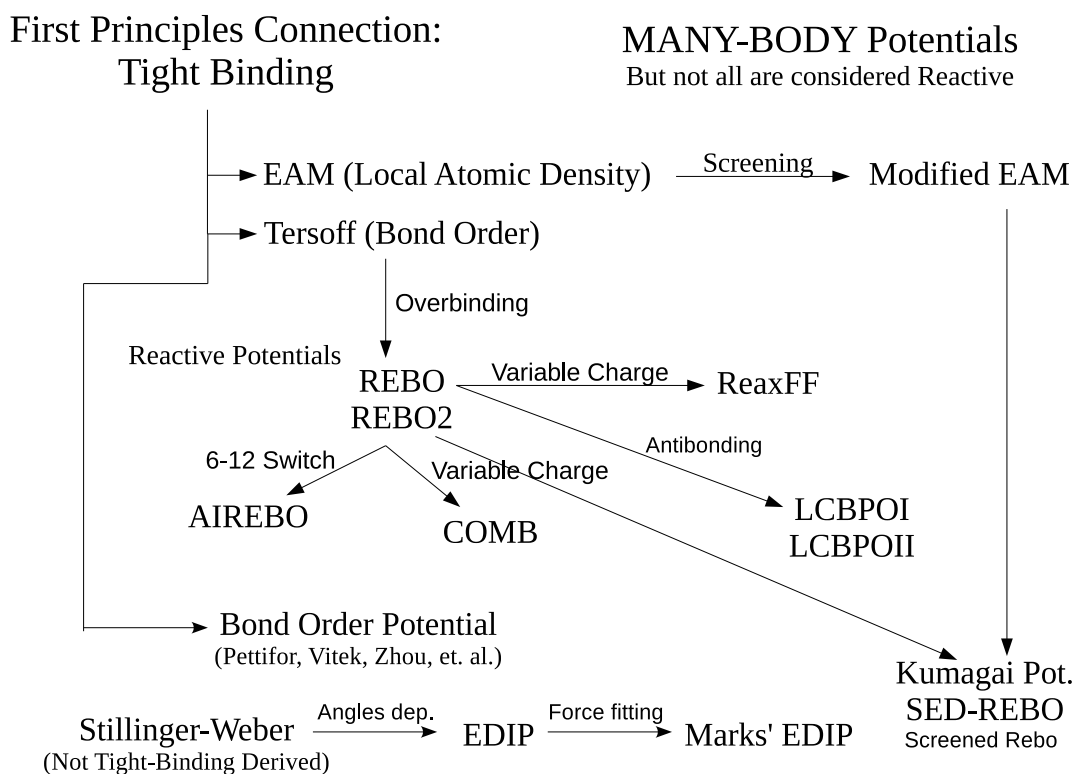


Figure 2. The heritage of empirical methods from the tight binding approximation is shown. Most modern reactive potentials are derived from the Tersoff many-body potential, which is in turn derived from tight-binding.

Modern day computational chemistry methods and tools have gone far beyond these humble beginnings to predict structure and properties of molecules and materials with atoms in the thousands. Total energies calculated by the Hartree-Fock method achieve results on order of one percent of the actual values. Unfortunately, that one percent error is where all the chemistry occurs, with quantities such as excitation energies and molecular binding energies evaluated as differences in total energies (13). Total energies are extensive quantities, but the excitation and molecular binding energies are intensive quantities several orders of magnitude smaller than the total energies from which they are derived (14). As the number of atoms increases for larger systems sizes, the chemically interesting intensive quantities become a mere fraction of the total energy, requiring highly accurate, numerically stable modeling. An important goal of modern quantum chemistry is to develop computationally efficient methods which can reduce the missing one percent error to chemical accuracy, within $1 - 2$ kcal/mole of experimental values (15).

The source of error in the Hartree-Fock method is electron correlation (16). The Hartree-Fock method is a time-independent variational procedure based on the clamped-nuclei Born-Oppenheimer approximation which uses a single Slater-determinant and treats electron-electron repulsion as a mean field (17). Because the electron coupling is treated in an average way, the actual interactions of electrons are missing from the Hartree-Fock treatment. These additive interactions are called correlations (18), which Löwdin defined as the difference between the exact nonrelativistic energy and the energy

predicted by the Hartree-Fock method. Dynamic correlation arises from electron-electron repulsion which at short range can be quite different from a mean field. Static correlation results from the use of a single Slater determinant, whereas in reality, many Slater determinant configurations may be nearly equal in energy. This situation can require a multi-reference treatment for accurate energy and structural predictions. Many post-Hartree Fock approaches have been developed, with the added accuracy at a high computational cost. DFT is one of the most widely used methods in computational chemistry due to its accuracy and relatively low cost scaling with system size compared with other methods, particularly for metals which can have large static correlation due to many nearly degenerate states from unfilled d-electron orbitals (19).

2.1.1 Density Functional Theory

The following is a brief review of DFT following Kolt and Holthausen (17) with a practical discussion of several density functionals (20; 21; 22; 23) as applied to modeling chemical problems. We neglect fundamental constants in the equations that follow. DFT reduces the problem of a N-electron antisymmetric wavefunction with $3N$ degrees of freedom into a 3 dimensional electron density (19; 24; 25). The probability of finding an electron in a given volume is given by,

$$|\Psi(x_1, x_2 \dots x_N)|^2 dx_1, dx_2 \dots dx_N \quad (2.1)$$

where Ψ is the wavefunction with $x_i = (r_i, s_i)$. Here, r_i and s_i are the 3N cartesian coordinates and spin of the electrons which we identify with the collective variable x_i for total number of electrons N . Likewise, the ground state density of the N-electron antisymmetric wave function can be shown as,

$$\rho(\vec{r}_1) = \int \dots \int |\Psi(x_2 \dots x_N)|^2 dx_2 \dots dx_N \quad (2.2)$$

where ρ is the ground state electron density and the other variables defined as before. We can treat the density in a non-interacting reference system, just as in the Hartree-Fock method, where the Hamiltonian for this non-interacting system can be shown as,

$$H = -\frac{1}{2} \sum_i^N \nabla_i^2 + \sum_i^N V_S(\vec{r}_i) \quad (2.3)$$

where ∇_i is the Laplacian differential operator and V_s is the new effective local mean-field potential. The density is based on the N-electron anti-symmetric wavefunction which can be written as a Slater determinant,

$$\Psi(x_1, x_2, \dots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(x_1) & \varphi_2(x_1) & \cdots & \varphi_N(x_1) \\ \varphi_1(x_2) & \varphi_2(x_2) & \cdots & \varphi_N(x_2) \\ \vdots & \vdots & & \vdots \\ \varphi_1(x_N) & \varphi_2(x_N) & \cdots & \varphi_N(x_N) \end{vmatrix} \quad (2.4)$$

where φ are Kohn-Sham spin-orbitals. Although this looks very similar to the Hartree-Fock method, it should be emphasized that the density from the Kohn-Sham approach is in principle exact, but the density obtained from the Hartree-Fock method is approximate (17). The spin orbitals can be determined by,

$$\begin{aligned} f^{KS} &= -\frac{1}{2} \sum_i^N \nabla_i^2 + V_s(\vec{r}_i) \\ f^{KS} \varphi_i &= \epsilon_i \varphi_i, \end{aligned} \tag{2.5}$$

where the one-electron Hamiltonian is given by f^{KS} , V_s is the effective potential, ϵ_i are the Kohn-Sham orbital energies, and φ_i are the Kohn-Sham orbitals. The total energy of the system can then be expressed as a functional of the density (17; 26),

$$\begin{aligned} E[\rho(\vec{r})] &= E^T[\rho] + E^V[\rho] + E^J[\rho] + E^{XC}[\rho] \\ &= E^T[\rho(\vec{r})] + \int V_{Ne} \rho(\vec{r}) d\vec{r} + \frac{1}{2} \int \int \frac{\rho(\vec{r}_1) \rho(\vec{r}_2)}{r_{12}} + E_{XC}[\rho], \\ &= -\frac{1}{2} \sum_i^N \langle \varphi_i | \nabla^2 | \varphi_i \rangle - \sum_i^N \int \sum_A^M \frac{Z_A}{r_{1A}} |\varphi(\vec{r}_1)|^2 d\vec{r}_1 \\ &\quad + \frac{1}{2} \sum_i^N \sum_j^N \int \int |\varphi_i(\vec{r}_1)|^2 \frac{1}{r_{12}} |\varphi_j(\vec{r}_2)|^2 d\vec{r}_1 d\vec{r}_2 + E_{XC}[\rho(\vec{r})] \end{aligned} \tag{2.6}$$

where E^T is the kinetic energy, E^V is the electron-nuclear interaction energy, E^J is the Coulomb integral, and E^{XC} is the electron exchange-correlation energy. The nuclei-electron attraction is V_{Ne} which is identified by nuclear charge Z of atom index A through M , where M is the number of nuclei. The exchange-correlation energy must be approxi-

mated as the true function is unknown. The variational principle can then be applied to the Kohn-Sham orbitals where the effective potential V_s is defined as,

$$\begin{aligned}
 f^{KS}\varphi_i &= \epsilon_i\varphi_i, \\
 f^{KS}\varphi_i &= \left(-\frac{1}{2}\nabla_i^2 + \left[\int \frac{\varphi(\vec{r}_2)}{r_{12}} d\vec{r}_2 - \sum_{A=1}^M \frac{Z_A}{r_{iA}} + V_{XC}(\vec{r}_1) \right] \right) \varphi_i \\
 f^{KS}\varphi_i &= \left(-\frac{1}{2}\nabla_i^2 + V_s(\vec{r}_i) \right) \varphi_i = \epsilon_i\varphi_i,
 \end{aligned} \tag{2.7}$$

where the definitions are as before and the V_{XC} is the exchange-correlation potential.

The exchange-correlation potential is given as,

$$V_{XC} = \frac{\delta E^{XC}}{\delta \rho} \tag{2.8}$$

where V_{XC} is a functional derivative of E_{XC} with respect to the electron density is also an approximation where the true form is unknown.

In principle, the Kohn-Sham equations can provide the exact ground state energy but, in practice, the functional form of the E^{XC} is unknown and must be approximated. The local spin density approximation (LSDA) is the first and simplest spin-polarized approximation to the exchange-correlation energy and the lowest rung of Perdew's Jacobs ladder of density functional approximations to the exchange-correlation energy (22). It is the spin-polarized version of the local density approximation (LDA) which is modeled after jellium, a uniform electron gas. This can be shown as (27),

$$E_{XC}^{LSDA}(n \uparrow, n \downarrow) = \int d^3r \, n \epsilon_{XC}^{unif}(n \uparrow, n \downarrow), \quad (2.9)$$

where $n \uparrow$ and $n \downarrow$ are the spin densities and ϵ_{XC}^{unif} is the exchange-correlation energy per particle of a uniform electron gas (28). The LSDA has been widely tested and performs remarkably well for the simplicity of the method. However, LSDA predictions tend to “overbind” where lattice parameters are underestimated and where cohesive energies, phonon frequencies, and elastic moduli are overestimated (29). Generalized gradient approximations (GGA) attempt to correct for the shortcomings of the LSDA, shown here as,

$$E_{XC}^{GGA}(n \uparrow, n \downarrow) = \int d^3r \, f(n \uparrow, n \downarrow, \nabla n \uparrow, \nabla n \downarrow), \quad (2.10)$$

where f is an approximate parameterized analytic function (27). The main idea is to correct the homogenous gas density in the jellium model (27; 17). Many GGA approximations have been developed with various functional forms, and one of the most popular is the Perdew-Burke-Ernzerhof (PBE) functional. The authors of PBE use a second-order gradient expansion of the exchange-correlation hole surrounding the electron in a slowly varying electron gas, truncating longer range contributions to enforce normalization. As the forms of f can be quite involved and parameterizations are inherently non-unique, we will not pursue those details further and focus on applications of the method. GGA functionals improve cohesive energies over the LSDA functional, with occasional over-

correction, and are widely used for modeling chemical systems. GGA methods are the second rung of Perdew’s Jacob’s ladder of density functional approximations, where reasonable predictive accuracy is possible at reasonable computational cost (30). Better approximations will provide more accuracy, but the additional accuracy may not be worth the additional computational cost as scaling becomes increasingly unfavorable at higher levels of theory.

Another approach to approximating the exchange-correlation energy is to mix in exact exchange (20). Exact exchange for DFT has different meaning than Hartree-Fock exchange despite similar equations. In DFT exact exchange is over Kohn-Sham orbitals whereas Hartree-Fock exchange is calculated over Hartree-Fock orbitals. The distinction is that the square of the ground state wavefunction from Hartree-Fock orbitals does not give the true ground state charge density, but in principle the Kohn-Sham ground state charge density should be exact (17). Functionals that take this approach are termed hybrid functionals because they mix exact and local exchange. They use empirical parameters that are fit to a test set rather than using an analytical form derived entirely from first principles, as in pure functionals. B3LYP is one of the most successful hybrid functionals, a combination proposed by Stephens et al. (31) of Becke’s exchange formulation (20) and correlation function of Lee, Yang, and Parr (LYP) (21). B3LYP can be shown as (17),

$$E_{XC}^{B3LYP} = (1 - a)E_X^{LSDA} + aE_X^{exact} + bE_X^{B88} + cE_C^{LYP} + (1 - c)E_C^{LSDA} \quad (2.11)$$

where E_X^{LSDA} , E_X^{exact} , and E_X^B are LSDA exchange, exact exchange, and Becke’s 1988 exchange functional (32) respectively and E_C^{LSDA} and E_C^{LYP} are LSDA correlation and LYP correlation. The parameters $a = 0.20$, $b = 0.72$, and $c = 0.81$ are unchanged from Becke’s original parameterization. B3LYP has been extremely successful for the G2 test set, with unsigned error of just over 2 kcal/mole (17; 33). The G2 test set is a benchmark set of experimentally well established reaction energies used to evaluate the accuracy of the G2 composite method and also as a measure of relative quality of other quantum chemical methods.

Research on hybrid functionals continues with special emphasis on improving accuracy and transferability, especially for long range interactions. Modern screened hybrid functionals are a powerful method for metallic systems, particularly for calculations using periodic Gaussian basis sets (34). Screened hybrid functionals divide the Coulomb r_{12}^{-1} operator into a short and long component applying exact exchange at short range and smoothing exact exchange to zero at long range. This can be shown as,

$$\frac{1}{r_{12}} = \frac{\text{erfc}(\omega r_{12})}{r_{12}} + \frac{\text{erf}(\omega r_{12})}{r_{12}} \tag{2.12}$$

where erfc and erf are the complimentary error function and error function, respectively, the short range and long range components are on the right hand side of the equation and ω is a scaling parameter. The Heyd-Scuseria-Ernzerhof (HSE) functional (23) has

been particularly successful at treating graphitic systems using periodic Gaussian basis sets (35). For the HSE functional, the exchange-correlation energy can be shown as (36),

$$E_{XC}^{HSE} = E_{XC}^{PBE} - \frac{1}{4}(E_X^{exact,SR} - E_X^{PBE,SR}) \quad (2.13)$$

where E_{XC}^{PBE} is the previously discussed PBE functional (27) and the $\frac{1}{4}$ prefactor was determined by perturbation (37). This greatly benefits periodic Gaussian basis set calculations where slow convergence of exact exchange at large distances can make Hartree-Fock and B3LYP calculations all but impossible.

The transferability of DFT to a wide variety of chemical problems is one of the greatest achievements of the method. However, the transferability and generality of the method comes at the price of a high computational cost. By introducing empirical parameters, semi-empirical and molecular dynamics force fields can perform calculations much more cheaply. The cost of an empirical approach is that the method is only clearly valid for the test set for which it was parameterized with no guarantee of validity for other problems. Overparameterization is a potential danger for empirical methods where only the test set is well fit and model systems outside of the test set can gain substantial error. A much more insidious problem with empirical methods is that they are typically only parameterized for minima on the potential energy surface. This can introduce substantial error in transition state calculations where transition states were not part of the test set.

Nevertheless a degree of empiricism may be required depending on the problem and high quality parameterized methods can provide good results.

2.1.2 Density Functional Tight Binding

Large system size can require a much computationally cheaper method. Semi-empirical methods are an intermediate level of theory in-between first principles methods and empirical methods which may not consider electrons at all. The essential idea of semi-empirical methods is to replace the most costly integrals in a Hartree-Fock or DFT calculation with parameters in order to speed up the calculation. Two historically very important and currently very widely used methods are tight binding and neglect of differential overlap.

The family of semi-empirical methods that are based on various forms of neglect of differential overlap include MINDO, AM1, and PM6 (38; 39; 40). These methods are parameterized heavily with spectroscopic data but are much faster than Hartree-Fock or DFT because overlap integrals $S_{ij} = \langle \varphi_i | \varphi_j \rangle$ are set to unity drastically simplifying the secular equation from $|H - ES| = 0$ to the much easier to compute $|H - E| = 0$ (41). A frequent criticism of these semi-empirical methods is that they have empirical parameters that are fit to match experimental values. However semi-empirical methods have two primary advantages over empirical methods. First, they account for electrons explicitly and therefore can perform spin-polarized calculations. Second, they are often more accurate than fully empirical models. The disadvantages include the lack

of available parameters, the lack of transferability to problems other than for what the model was parameterized, and scaling on order of N^3 due to matrix diagonalization where molecular dynamics models typically have linear scaling.

In the tight binding family of semi-empirical methods, the two-center approximation of Slater-Koster (42) is the starting point. The idea is to calculate a parameterized Hamiltonian based on overlap of atomic orbitals centered on each atom pair (43). That means that the orbitals in the calculation will only come from two atoms at a time, and this gets rid of the costly four center integrals. Later it was realized that such a scheme could be derived directly from density-functional theory (44). DFTB began as a tight binding variant with parameters calculated from LDA calculations rather than experimental results (45). It is for this reason that the authors of DFTB claim that the method is not truly semi-empirical because the method does not rely on experimentally derived parameters. However, it is not parameter free, and due to the fitting of the parameters to LDA, the method inherits all of the problems of LDA as well. Nevertheless, DFTB has achieved remarkable results with improvements including parallel implementations, self-consistent charge, spin polarization, dispersion, calculation of optical properties in time-dependent DFT framework, and electron transport (46; 47; 48; 49; 50).

DFTB has a number of advantages that make it very useful as important modeling tool when combined with levels of theory both above and below it. DFT calculations can often be very difficult to converge if the initial configuration is far from the minima. A cheap

method like DFTB can often optimize a bad initial configuration into a configuration very close to the DFT minima in a fraction of the time that a full DFT calculation would take. At the other end of the scale, DFTB may be too expensive to model systems of thousands of atoms or for very long trajectories. However, DFTB is often much more accurate than a comparable molecular dynamics model. Small sections of the larger system might be optimized in DFTB and compared to results from molecular dynamics. This can be a very useful sanity check to identify simulation artifacts.

2.2 Classical Molecular Dynamics

This section will discuss a wide variety of classical molecular dynamics modeling techniques and the problems for which they might be used. This section will cover fixed bond molecular dynamics, long range nonbonded interactions, many-body potentials, statistical ensembles, and integration techniques. The nomenclature used to describe all force fields will follow that of W. Smith and DL-POLY in order to most closely match implementation in DL-POLY and LAMMPS codes. Exceptions will be noted in the text.

2.2.1 Fixed Bond Force Fields (non-reactive)

Molecular dynamics in its modern form was developed by A. Rahman (51) to simulate an 864 atom model of liquid argon with a Lennard-Jones potential at Argonne National Laboratory in 1964. Previous work by Alder and Wainright (52) had introduced computer simulations of hard spheres. The idea is to numerically integrate Newton's equations of motion for a system of N particles with an initial position r_i and velocity v_i . The

potential energy and forces between interacting particles is defined by a force field, with parameters determined from experimental values or ab initio calculations. Force fields can be simple pair potentials where interactions are calculated between pairs of atoms, fixed bond potentials where bonds, angles, and dihedrals are predefined and static throughout the simulation, and many-body potentials where the force field depends on more than two atoms.

There are many flavors of fixed bond molecular dynamics including AMBER, CHARMM, and Class2 potentials. Here we will use the CHARMM force field as an example of fixed bond force fields, referring to the CHARMM version implemented in the NAMD molecular dynamics package. In fixed bond molecular dynamics methods (53; 54), the energy of an interatomic bond can be treated as a harmonic spring with characteristic equilibrium bond distance r_0 and spring constant k . The bond is not broken throughout the simulation, even if the atoms are stretched far beyond the equilibrium bond length. The spring constant is parameterized for the atom types. Because the bond is harmonic, the restoring force and resulting velocities can easily destabilize model systems by loss of energy conservation if the bond is stretched too far. This can occur due to large time steps, which can be greater than 2.0 fs per step in NAMD for example (53) (different methods will have different timestep thresholds where energy begins to drift), very high temperatures, or an initial simulation configuration that is far from equilibrium. The CHARMM27 parameters used in the NAMD code are carefully parameterized for bio-

logical conditions with temperatures near 300 K and pressures near 1 atm. Therefore simulations run outside these conditions should be carefully compared to available experimental and first principles results to determine the suitability of the force field for the specific problem. Transferable parameterizations are exceedingly rare. The functional forms of molecular dynamics are approximations of first principles methods, and the price of computationally efficient parameterized methods is the loss of generality.

The potential energy of a harmonic bond is given as,

$$V(r_{ij}) = \frac{1}{2}k(r_{ij} - r_0)^2, \quad (2.14)$$

Here the interatomic distance r_{ij} is the distance between atoms i and j . This quantity is calculated by

$$r_{ij} = |\underline{r}_j - \underline{r}_i|, \quad (2.15)$$

where the position vector to atom l is given as $\underline{r}_l$.

The potential energy for deformation of angles is given as,

$$V(\theta_{jik}) = \frac{1}{2}k(\theta_{jik} - \theta_0)^2 \quad (2.16)$$

where θ_{jik} is the angle between vectors r_{ij} and r_{ik} , which can be given as,

$$\theta_{jik} = \cos^{-1} \left(\frac{\underline{r}_{ij} \cdot \underline{r}_{ik}}{|\underline{r}_{ij}| |\underline{r}_{ik}|} \right), \quad (2.17)$$

This formulation of the angular potential energy function is harmonic with spring constant and equilibrium angle determined by the atom types of each atom i , j , and k . For example, the angle potential energy function for atoms C-C-C in an alkane chain would be different than for atoms C-C-C in graphite because atoms in the alkane chain are sp^3 hybridized (saturated) and atoms in graphite are sp^2 hybridized (unsaturated). All angles are defined as part of the simulation input, and cannot be changed during the simulation. This is substantially different than the case of many-body potentials in which angular energy contributions are calculated on the fly by determining atomic coordination from periodically updated neighbor lists. Many body potentials will be discussed later.

Dihedral angles are the angles between two planes formed by atoms $i - j - k$ and $j - k - n$ in a four atom, three bond chain, $i - j - k - n$. The dihedral potential energy function reflects the torsional energy of molecules and solid materials, and is very important for description of steric effects. This function is given as,

$$\phi_{ijkn} = \cos^{-1} \left(\frac{(r_{ij} \times r_{jk}) \cdot (r_{jk} \times r_{kn})}{|r_{ij} \times r_{jk}| |r_{jk} \times r_{kn}|} \right) \quad (2.18)$$

Here the normal of each plane is given as a cross product, $(r_{ij} \times r_{jk})$ and $(r_{jk} \times r_{kn})$ respectively. The dihedral angle is derived from the dot product of these normal vectors. As in angle potential energy functions, the dot product returns the cosine of the vectors. It is often more computationally efficient to treat angles as $\cos \theta$ and $\cos \phi$ rather than θ

and ϕ due to the fact that the derivative $\cos^{-1} \theta$ is equal to $\frac{-1}{\sin(\cos^{-1}(\theta))}$. This can create an inconvenient divide by zero problem for small angles. Improper dihedral angles are also possible as a method of constraining geometry to conserve chirality and are treated in the same way as regular dihedral angles.

2.2.2 Long Range Nonbonded Interactions

Long range nonbonded interactions consist of electrostatic interactions due to atomic charges from ionic bonds and unequal sharing of electrons in covalent bonds and dispersion interactions from atomic multipoles. The potential energy function for electrostatic interactions is given as,

$$V_{coul}(r_{ij}) = \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}} \quad (2.19)$$

where q_i and q_j are the charges on atoms i and j and ϵ_0 is the vacuum permittivity. Treatment of electrostatic interactions requires a great deal of care, however, due to the $1/r$ slow decay of the potential energy with distance. In periodic systems, several strategies have been developed to reduce both the computational cost of calculating electrostatics and improve the accuracy in periodic systems.

2.2.3 Electrostatics

In molecular dynamics simulations, we often need to approximate the electrostatic potential because it decays very slowly with distance. Truncation of the potential, even at ranges up to 25 Å, may result in artifacts (55). More advanced shifted methods can improve energy conservation and reduce artifacts in molecular dynamics simulations. In

a shifted-energy scheme (E-shift), a constant is introduced to reduce the electrostatic interaction to zero at the cutoff distance. Similarly, in a shifted-force scheme (F-shift), a constant is introduced to reduce the forces to zero at the cutoff distance. This can be shown as,

$$\begin{aligned} V(r_{ij}^{E-shift}) &= \begin{cases} V_{coul}(r_{ij}) - V_{coul}(r_c), & r_{ij} < r_c, \\ 0, & r_c < r_{ij}, \end{cases} \\ V(r_{ij}^{F-shift}) &= \begin{cases} V_{coul}(r_{ij}) - (r_{ij} - r_c)V'_{coul}(r_c) - V_{coul}(r_c), & r_{ij} < r_c, \\ 0, & r_c < r_{ij}, \end{cases} \end{aligned} \quad (2.20)$$

where $V_{coul}(r_c)$ and $V'_{coul}(r_c)$ are constants at the cutoff r_c , and $V_{coul}(r_c)$ is the same as in Equation 2.19. This can be continued to second derivative of the potential (56) for improved energy conservation in strongly ionic systems. Shifted force potentials continue to be an active area of research due to the low computational cost (57).

Beyond truncation and shifted potentials, the Ewald summation (58) is the gold standard for electrostatics but it scales poorly with system size on order of N^2 for direct calculation. The Ewald approach calculates a short-range pairwise interaction inside a cutoff distance and then calculates a long range contribution to the electrostatic interaction by solving in k-space. Modern order $N \log N$ methods such as particle-particle particle-mesh (PPPM) (59; 60) is implemented in the LAMMPS molecular dynamics package, and particle-mesh Ewald (PME) (61) is implemented in the NAMD package as

standard methods. A drawback to these methods is the cost of the fast-Fourier transforms (FFT) required to transform the potential back into real space. Accuracy can also be a consideration due to artificially induced periodicity (53).

The Wolf summation (62) is an important alternative to Ewald methods implemented as a pairwise additive potential where image charges are placed on the surface of a cutoff sphere to ensure charge neutrality and a damping parameter is introduced to improve convergence (63). Wolf summation methods are used to predict the energies of crystals, scale computationally as pair potentials and are an active area of research (57; 64).

2.2.4 Dispersion

Long range van der Waals (vdW) contributions can be included in simulations by several methods including 6 – 12 potentials, shifted 6 – 12 potentials (65), splined 6 – 12 potentials (66), and by the dispersion-correction methods of Grimme (67; 68; 69). Also called London dispersion these weak interactions originate in electron correlations (70). The 6 – 12 potential is given as,

$$V_{LJ}(r_{ij}) = \epsilon_{ij} \left[\left(\frac{R_{min,ij}}{r_{ij}} \right)^{12} - 2 \left(\frac{R_{min,ij}}{r_{ij}} \right)^6 \right]. \quad (2.21)$$

Here, ϵ is the well-depth and R_{min} is the radial interatomic distance to the minima of the potential well. R_{min} is related to the radial interatomic distance at which the potential is zero σ where $R_{min} = 2^{1/6}\sigma$. The 6 – 12 potential is appropriate for fixed-bond simulations which require a hard-wall repulsion to correctly model physisorption and

other non-bonded interactions between molecules. The r^6 interaction provides the long range attraction between atoms and the r^{12} term approximates electronic repulsion which prevents atoms in different molecules from getting too close. The electronic repulsion in Lennard-Jones models is due to the Pauli principle and the overlap of occupied orbitals.

2.2.5 Many-Body Force Fields

Many-body force fields in the context of molecular dynamics means a potential energy function that depends on positions of more than two atoms at a time. The many-body potential energy function can be expanded as a series and truncated for efficiency. Interactions typically included are between atomic pairs, triplets, and quartets due to the increasing complexity of analytic functions required to describe larger groups of atoms. Lennard-Jones force fields and Morse potentials are properly pair potentials dependent only on the distance between pairs of atoms. In contradistinction, many body force fields require dependence on triples or larger groups of atoms in order to distinguish between atomic configurations and evaluate energies. To understand this requires going back to the tight binding method (43) where the Slater-Koster rules (42) require a two-center approximation previously discussed in the semi-empirical section. Some force fields may also use the two-center approximation and can have functional forms inspired directly from tight binding. Pair potentials can then be reasonable approximations to the tight binding method, except that an analytical function is used to approximate the energy based on atomic position rather than explicitly accounting for electrons. It should be

noted, however, that many-body potentials do not require an explicit relationship to quantum mechanics and functional forms can be achieved with purely empirical parameters from experimental data and with symmetry arguments. Symmetry is extremely important to the development, and parameter fitting in particular, of molecular dynamics potentials. Consider that different crystal structures such as Wurtzite, β -tin, and simple cubic can all have different densities and unique energies for each configuration and material. Force fields are fit to these crystal structure configurations using lattice parameters and energies obtained from either first principles calculations or experimental data. An empirical potential such as the Embedded Atom Method, which will be discussed next, needs only this symmetry information and the empirical energies from experiment to arrive at very high quality metal molecular dynamics potentials.

The Embedded Atom Method has a density dependent component, the Stillinger-Weber potential consists of a two body pair potential and a three body angular potential, and the Tersoff potential in essence combines the two ideas with a pair potential and a density dependent angular function. Although these methods have been developed over the past 30 years, the functional forms are still very robust and very high quality parameterizations are available. The key idea is that a more complicated functional form does not necessarily give better results. For well defined problems such as crack propagation in metals and thermal conductivity simple many-body potentials are more than adequate. More complex problems such as chemical reactions, variable charge systems,

or phase transitions that involve making and breaking covalent bonds requires a more complicated functional form as in Reactive Bond Order potentials.

2.2.6 Embedded Atom Method

The embedded atom method of Baskes (71; 72) was developed for the modeling of metallic systems and incorporated the concept of electronic density of DFT into a many-body molecular dynamics force field. The main idea was to modify a pairwise potential energy function between metal atoms by adding a bulk density dependent term. By calculating the local density of atoms, the lattice structure can be inferred. In this way the energy of known lattice structures could be determined from DFT and implemented into molecular dynamics with interpolation between intermediate states. The EAM potential energy function can be shown as,

$$V_{EAM}(r_{ij}) = \frac{1}{2} \sum_{i=1}^N \sum_{i \neq j}^N V_{ij}(r_{ij}) + \sum_{i=1}^N F(\rho_i) \quad (2.22)$$

Here the V_{ij} term is a distant dependent pair potential and $F(\rho_i)$ is the embedding function. The embedding function can be shown as,

$$F(\rho_i) = \sum_{j=1, j \neq i}^N \rho_{ij}(r_{ij}) \quad (2.23)$$

Here the embedding function is shown to be a sum of atom pairs and reflects the local atomic density. The value of ρ_i can have a tabulated form in the case of EAM or an

analytic form for EAM variants including Finnis-Sinclair (73), Sutton-Chen (74), and Gupta potentials (75).

2.2.7 Tersoff Potential

A very important many-body potential was developed by Tersoff (76) in 1986 which had the unique feature of flexible angular dependence so that more than one phase could be modeled. The Tersoff potential could model more than one phase of silicon and carbon which was a very important improvement. The Stillinger-Weber potential (77) was also designed to accomodate three-body angles, however it lacked transferability and could only be tuned for a single material phase at a time. The success of the Tersoff potential was bolstered by important developments from chemical pseudopotential theory.

In 1984, G. C. Abell published a seminal paper on the environmental dependence of bonds (78). Previous work had demonstrated the universality of diatomic and metallic bonds sharing the same potential energy surface, and that physisorption and chemisorption on surfaces had the same quantum mechanical basis (79; 80; 81). Based on this information, Abell argued that all bonds can essentially be approximated as Morse potentials, and that the well depth and equilibrium bond length of the potential energy functions depended on the local coordination of each atom. Abell used a Bethe lattice to prove the point that bond strength depended on neighbor coordination. He compared his results to configuration interaction (CI) models with good results. More recent

derivations of chemical environment dependent interatomic potentials similar to Tersoff potentials rely more explicitly on tight binding theory. (82).

J. Tersoff expanded on Abell's theory development by developing an interatomic potential that could change bond strengths based on local coordination of each atom. This approach was applied to silicon materials (76) where atoms could be three coordinated with sp^2 hybridized bonds or four coordinated with sp^3 hybridized bonds. Tersoff also extended this method to carbon (83) and silicon-carbide (84) materials. However, certain drawbacks began to appear in the method.

The Tersoff potential is the sum of a repulsive and an attractive exponential function. The well-depth for a carbon-carbon bond is $6.0eV$ in the case of a carbon dimer. The well depth is reduced if the coordination is increased. For example, the double bond between two three-coordinated sp^2 carbon atoms is stronger than the single bond between two four-coordinated sp^3 carbon atoms. The Tersoff potential accounts for this by a bond order term b_{ij} that scales the attractive term, V_a . Recent high quality Tersoff parameterizations (85) use the strategy of fitting the pairwise dimer parameters first and then fitting angular parameters to high symmetry bulk configurations (86). This is based on the Pauling relation,

$$E_b = -D_0 \exp[-\beta\sqrt{2S}(r_b - r_0)] \quad (2.24)$$

where the energy per bond, E_b , is related to the equilibrium bond distance of a given high symmetry bulk configuration, r_b , and the bond distance of the dimer is r_0 . The slope of the Pauling plot gives the S parameter. The dimer well depth is D_0 and the parameter β can be derived as,

$$\beta = k \frac{2\pi c}{\sqrt{2D_0/\mu}} \quad (2.25)$$

where k is the wave number and μ is the reduced mass of the dimer.

Using the nomenclature of Albe, we can show the Tersoff potential as,

$$V_{Tersoff}(r_{ij}) = \sum_{i>j}^N \left[V_R(r_{ij}) - \frac{b_{ij} + b_{ji}}{2} V_A(r_{ij}) \right] \quad (2.26)$$

where V_R and V_A are the repulsive and attractive contributions and b_{ij} is the bond order.

The repulsive function and attractive functions are given by,

$$\begin{aligned} V_R(r_{ij}) &= \frac{D_0}{S-1} \exp[-\beta\sqrt{2S}(r_{ij} - r_0)], \\ V_A(r_{ij}) &= \frac{SD_0}{S-1} \exp[-\beta\sqrt{2/S}(r_{ij} - r_0)], \end{aligned} \quad (2.27)$$

where the variables are as before. The cutoff function f_C can be shown as,

$$f_C(r) = \begin{cases} 1, & r < R - D \\ \frac{1}{2} - \frac{1}{2} \sin\left(\frac{\pi}{2} \frac{r - R}{D}\right), & |R - r| \leq D \\ 0, & R + D < r \end{cases} \quad (2.28)$$

where the parameters R and D of the cutoff f_C sets the radial distance at which an atom pair are considered first neighbors. The cutoff function allows for fractional neighbors by reducing the value of f_C from 1 to 0 inside the smoothing region. The effect of the cut off function is to create a large "bump" in the force profile of the force field when an atom enters into a radial distance inside this smoothing region. This is entirely an artifact of the simulation but it is unavoidable because the Tersoff potential artificially drops interaction energies to zero outside the first neighbor radius. Atoms interact at much longer range and additional long range corrections are required to improve the force field.

The bond order term of the Tersoff potential depends on the value of χ which can be shown as,

$$b_{ij} = (1 + \chi_{ij})^{-1/2} \quad (2.29)$$

$$\chi_{ij} = \sum_{k \neq i, j}^N f_C(r_{ik}) \exp[2\mu(r_{ij} - r_{ik})] g(\theta_{ijk})$$

where χ is a sum over neighboring atoms k , the parameter 2μ is a bond length difference term, and $g(\theta_{ijk})$ is an angular function. The number of neighbors will define the preferred angle. The angular function can be shown as,

$$g(\theta) = \gamma \left(1 + \frac{c^2}{d^2} - \frac{c^2}{d^2 + [h + \cos \theta]^2} \right) \quad (2.30)$$

where γ , c , d , and h are parameters which define the shape of the angular function. The angular function is fit to high symmetry bulk configurations such as rhombohedral graphite, diamond, simple cubic, and linear chain where experimental values or DFT calculated values are known.

2.2.8 Reactive Bond Order Methods

Reactive bond order methods systematically improve the Tersoff potential by adding additional terms to distinguish between bonding configurations. Reactive bond order potentials beyond the Tersoff potential have grown rapidly for the past twenty years, largely beginning with the important contribution of D. W. Brenner in the modeling of carbon deposition and the growth of thin films in 1990 (87). He also demonstrated explicitly the relationship of Tersoff potentials to the Embedded Atom Method of Baskes (88) which are both derived from the second-moment approximation of tight-binding (82). The key contribution of Brenner was the inclusion of an overbinding term F in a Tersoff potential to improve bond breaking characteristics. The essential idea was to modify the bond strength between two bonded atoms based on the coordination number

of each atom. For example, two carbon atoms would share a double bond if both carbon atoms had coordination numbers of 3. However, if one carbon atom was 3-coordinated and the other 4-coordinated, the bond between the two atoms would be a single bond. In this way Brenner was able to describe conjugated carbon molecules. Modern interatomic potentials all use some form of this method to differentiate between different kinds of bonds and bond strengths.

More recent developments in reactive bond order potentials have grown from different families with different core approaches to modeling. The EAM family of molecular dynamics has focused on modeling metallic systems with recent improvements in the addition of many-body screening in the Modified Embedded Atom Method (MEAM) (89; 90), inclusion of second-row elements (91), and charge transfer in the Embedded Ion Method (EIM) (92). The Brenner family of potentials has improved by including environmental dependent vdW contributions (93), improved conjugation and fitting in second generation REBO (94), silicon materials (95; 96), and most recently extended into variable-charge methods, including Yasukawa (97; 98) and split-charge equilibration (99).

The environment-dependent interatomic potential (EDIP) was developed by Bazant for modeling Si materials (100) in 1997 and later extended to carbon materials by Marks (101) in 2000. The functional form of EDIP is closer to Stillinger-Weber potentials than to Tersoff potentials, and the method retains the superior cut off functions of Stillinger-

Weber. Marks added a major improvement to the EDIP carbon potentials by explicitly accounting for interlayer repulsion in graphitic materials, a feature lacking in the original EDIP, Tersoff and both versions of the Brenner potentials. More recent parameterizations of EDIP for silicon-carbide have been published (102), however they do not retain sp^2 repulsion corrections by Marks.

Long range bond order corrected methods of Los and Fasolino developed two advanced methods for treating carbon. In the long range bond order corrected potential (LCBPOI) (103), the first key advance was the treatment of interlayer repulsion by adding a repulsive term to all carbons and then stiffening the short range Tersoff-like potential to make up for repulsion between second nearest neighbors in a graphite sheet. The second key advance was the inclusion of bond length difference term. Overbinding was very similar to Brenner's term but with a different interpolation strategy. The improved long range bond order corrected potential (LCBPOII) (104) added additional corrections including small angle corrections, and improved overbinding term, addition of an antibonding term, and an additional correction for dangling bonds.

Reax force field developed by van Duin and Chenoweth (105; 106) takes the approach of adding a term for every possible chemical interaction. The advantage is that parameterizations for chemical reactions can be achieved at this level of theory, with successes in the modeling of shock propagation in explosive materials (107). The drawback is the lack of transferability due to the 'overparameterization' that results from the large number of

parameters. Nevertheless a major strength of the method is the ability to model charge transfer using Goddard’s charge equilibration (Qeq) method (108). The Qeq method is a variable charge model based on equalization of electronegativity.

Finally, an important bond order method by Pettifor (109; 110) is just now reaching maturity, with application to hydrocarbons (111) and to modeling multiple phases of CdTe materials (112). It has been developed to have an analytical functional form for molecular dynamics derived explicitly from tight-binding theory (113) to include many-body screening (114), an idea originally conceived as a purely empirical correction for tight binding (115). It should be noted that many-body screening as a correction to tight binding was developed in 1996. However, the empirical screening method of Baskes (116) was developed two years earlier in 1994. This screening method is still used in MEAM (89), screened first generation Brenner potential (117), and screened second generation Brenner potential (118). This was the second time that Baskes provided elegant empirical solutions to molecular dynamics problems before more sophisticated tight binding derived methods were proposed (71; 73; 116; 115; 114).

New and exciting developments in the world of interatomic potentials are combinations of the various families of potentials. Most recently, the combination of many-body screening formalism of Baskes and Lee has been combined with the AIREBO potential (118). The SED-REBO potential and LCBPOII potentials have been used to model shock propagation in diamond (119). Blended functional forms have had excellent per-

formance, and this approach seems to be an area of growing interest in many-body force field molecular dynamics research.

2.2.9 Dispersion and Many-Body Force Fields

In the Lennard-Jones potential, the r^{12} term is not appropriate for reactive potentials which allows making and breaking bonds because a hard-wall repulsion would prevent bond formation by preventing atoms from getting within reaction distance, typically less than 2 Å for carbon atoms.

Three approaches are typically used to eliminate the problem of the hard-wall of a 6 – 12 potential when combined with a reactive potential. The first approach is to use a cubic spline to reduce the 6 – 12 potential energy to zero in the region where the reactive potential describes covalent bonding. A splined 6 – 12 potential can be given as (66),

$$V_{noncov}(r_{ij}) = \begin{cases} 0, & r \leq r_s \\ c_{3,k}(r_{ij} - r_k)^3 \\ + c_{2,k}(r_{ij} - r_k)^2, & r_s \leq r_{ij} \leq r_m \\ \epsilon_{ij} \left[\left(\frac{R_{min,ij}}{r_{ij}} \right)^{12} - 2 \left(\frac{R_{min,ij}}{r_{ij}} \right)^6 \right], & r_m \leq r_{ij} \leq r_b \end{cases} \quad (2.31)$$

where $c_{n,k}$ are cubic spline coefficients, r_s is the inner cutoff radius where the potential goes to zero, r_m is the switching radius where the cubic spline begins, and r_b is the outer cutoff radius for dispersion in a truncated 6 – 12 potential. This is the method used by D. W. Brenner in his second generation REBO potential code (94). This effectively

creates a double well potential with a large potential well for covalent interactions and a much smaller well for nonbonding interactions. Since the total energy is a sum of two potentials each with a minima, the combined potential will have two wells. A drawback to this approach is that the potential energy may be greater than zero depending on the radius of the inner cutoff, which is clearly unphysical.

A second approach to eliminating hard-wall repulsion is to include environment dependent switching functions, which is the method implemented in the popular AIREBO potential (93). The idea is that electronic repulsion should occur in intermolecular interactions but not in between atoms in the same molecule. This is achieved by disallowing 6 – 12 interactions between first, second, and third neighbors in a bonded network. A drawback to this approach is the added computational cost of determining bond connectivity of the local environment over a long range, where the number of neighbors to loop over increases volumetrically.

A third approach by Grimme is to include a pairwise r^6 dispersion contribution with an exponential damping function, which smooths the potential energy to zero in the short-range region of covalent bonding(67). This method originally implemented as a method of including dispersion in DFT calculations can also be applied in molecular

dynamics, particularly if the molecular dynamics potential was fit to DFT results rather than experiment. Grimme’s DFT-D2 correction can be shown as,

$$V_{disp}(r_{ij}) = -s_6 \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{C_6^{ij}}{r_{ij}^6} f_{dmp}(r_{ij}) \quad (2.32)$$

where s_6 is a scaling factor, C_6^{ij} is the dispersion coefficient for atom pair C_6^{ij} , and f_{dmp} is the exponential damping function. The damping function is given as,

$$f_{dmp}(r_{ij}) = \frac{1}{1 + e^{-\alpha(r_{ij}/r_0-1)}} \quad (2.33)$$

where α is a parameter which determines the steepness of the exponential and r_0 is the sum of vdW radii of atoms i and j . The clear advantage of this approach is that it is an all-attractive potential. Because dispersion corrections are very small relative to covalent bonding, the repulsive force resulting from a potential rising from its minima to zero is considered too small for concern (69).

2.2.10 Integration schemes for molecular dynamics

In order to evolve a molecular dynamics system in time, molecular dynamics simulations require a method to integrate forces at each time step. Many different methods of integration have been developed and implemented including velocity Verlet, leapfrog Verlet, and third order Nordiesek predictor-corrector algorithms. Velocity Verlet is commonly used for its efficiency, energy conservation, and time-reversible properties. Velocity

Verlet is implemented in LAMMPS, NAMD, and DL-POLY. Leapfrog Verlet is implemented in DL-POLY and third order Nordiesek predictor-corrector algorithms are used in the serial Brenner code.

The velocity Verlet (120) algorithm is a two step process where the time step is divided in half with initial forces, velocity and position recalculated in the second step (121; 53).

The first step can be shown as,

$$\begin{aligned}\underline{v}(t + \frac{1}{2}\Delta t) &= \underline{v}(t) + \frac{\Delta t}{2} \frac{\underline{f}(t)}{m}, \\ \underline{r}(t + \Delta t) &= \underline{r}(t) + \Delta t \underline{v}(t + \frac{1}{2}\Delta t),\end{aligned}\tag{2.34}$$

where $\underline{f}, \underline{v}, \underline{r}$ are force, velocity, and radius respectively, m is the mass, and Δt is the time step. The position vector from the origin to atom l is $\underline{r}_l$. The second step recalculates the velocity by integrating force at the new position. This can be shown as,

$$\begin{aligned}\underline{f}(t + \Delta t) &\leftarrow \underline{f}(t), \\ \underline{v}(t + \Delta t) &\leftarrow \underline{v}(t + \frac{1}{2}\Delta t) + \frac{\Delta t}{2} \frac{\underline{f}(t + \Delta t)}{m},\end{aligned}\tag{2.35}$$

As a result, position can be updated time reversibly and while conserving energy. This method is appropriate for microcanonical ensembles which require temperature stability due to the lack of thermostating. Leap frog Verlet and Nordiesek methods do not have the same numerical stability and are therefore not appropriate for long trajectory microcanonical simulations.

2.2.11 Ensembles in MD simulations

The microcanonical ensemble is modeled as a NVE system in molecular dynamics. The (N) means that the number of atoms is fixed through the simulation, (V) means constant volume, and (E) means constant energy. This is the simplest method where dynamics are evolved without any control of temperature. Total energy can drift due to numerical errors, too large a timestep, or bad initial conditions where atoms are far from the minima. NVE simulations are very important for calculations such as thermal conductivity.

In the NVT ensemble the meaning of (N) and (V) are the same as before, however here (T) means a constant temperature. For molecular dynamics NVT is the canonical ensemble because the addition of a thermostat keeps the temperature constant as per the nomenclature (T). However, this means that the energy is not a conserved quantity and it can fluctuate in order to maintain a specified temperature. Care has to be taken when using this method because the energies calculated are essentially the Helmholtz potential and not the Gibbs free energy. Thermostat strategies must be carefully considered. In a Langevin thermostat, random kicks are applied stochastically to control temperature (122). If the kicks are applied pairwise to atoms in the simulation in equal and opposite directions, the center of mass will not move during the simulation. This modeling approach is often called Brownian dynamics. However, the Langevin thermostat method is not time reversible because the direction and magnitude of the kicks are

determined in the simulation by a random number generator. A Nose-Hoover thermostat (123; 124) on the other hand, is time reversible meaning that trajectories, in principle, are completely deterministic given knowledge of initial conditions and complete numerical accuracy. The system is connected to a heat bath as an extra degree of freedom with a connection of a specified relaxation time. This requires some care as the Nose-Hoover is second order and can create large fluctuations if not carefully thermalized. Finally, the Berendsen thermostat (125) is essentially a velocity rescaling method with connection to a heat bath. Gently increasing a simulation temperature is easily done with a Berendsen thermostat, however it can also lead to the “flying ice cube” effect where the thermostat dumps kinetic energy into collective translational motion.

The NPT ensemble in molecular dynamics is the isobaric-isothermal ensemble and the energy calculated in this ensemble corresponds to the Gibbs energy. Here the volume is allowed to change by means of a barostat. Barostats are commonly either of the Nose-Hoover or Berendsen type. Pressure changes are achieved by maintaining the position of each atom in a fractional coordinate system while allowing the cell dimensions to fluctuate in order to maintain a particular pressure. Pressure is calculated by tallying force contributions to the total virial (126). However, pressure can also be calculated as the negative stress per atom (127) which is extremely important for error checking. Virial contributions from many-body interatomic potentials on a per atom basis have

been shown to work very well for spatial decomposition and with the LAMMPS molecular dynamics package in particular (128).

Grand canonical ensemble depends on the chemical potential and is an active area of research. Single core methods and approximate methods have been accomplished. However, parallel grand canonical modeling has not been achieved in a robust way, at least in LAMMPS.

CHAPTER 3

METHANE BOND ACTIVATION BY PT AND PD SUB-NANOMETER CLUSTERS SUPPORTED ON GRAPHENE AND CARBON NANOTUBES

Activation of the C-H bond is important for hydrocarbon catalysis with applications in energy technology such as production of synthetic fuels. Subnanometer clusters show great promise for catalytic activities potentially much greater than monolith. Using density functional theory, we investigate in this chapter C-H bond breaking, an important step of the conversion reaction of methane to liquid fuels, on Pt and Pd subnanometer clusters with graphene and carbon nanotubes as supports.

3.1 Introduction

The activation of alkanes is an important challenge due to limited fossil fuel reserves and increasing global demand for petrochemicals (129). Renewable energy sources in the future may still require that energy be stored as liquid fuels for transportation. Highly selective, efficient and robust catalysts are therefore important to meet this challenge, and are an active area of research. C-H bond activation in CH₄ provides a good model chemistry for similar bond activation in other alkanes.

Subnanometer Pt clusters on Al₂O₃ show great promise with catalytic activities much greater than Pt monolith (130) due to undercoordination of Pt atoms and high surface

area to volume ratio in the clusters. Carbon nanotubes (CNTs) and graphene have also been proposed as supports for transition metal catalysts (131; 132; 133), including palladium (134) and platinum tetramers (135), due to their high surface area and capability to stabilize these clusters (136). Recent experimental advances in the separation of single chirality CNTs (137; 138) raise the possibility of matching catalytic materials such as subnanometer clusters to select CNT supports to improve catalytic potential of the combined system. A key question is whether the adsorption on a support will modify the catalytic activity of subnanometer clusters due to the formation of cluster-support bonds which increases coordination of the cluster atoms. We investigate the role of CNT curvature and chirality for methane C-H bond activation on CNT-supported Pt and Pd tetramers using first principles methods.

3.2 Methods

Methane activation by supported Pt and Pd tetramers was investigated with a first-principles approach using DFT with the B3LYP hybrid functional (139; 21) as implemented in the Gaussian 09 software package (140). A generalized (5*d*, 7*f*) 6-31G* basis set was used for carbon and hydrogen atoms in the methane and support structure, while Stuttgart "SDD" effective core potentials and corresponding basis sets were used for Pt and Pd atoms of the clusters. The support was represented by a 66-carbon atom graphene model with edges terminated by 22 hydrogen atoms, either flat or bent to CNT curvature, the latter being shown in Figure 3 for a (7,0) CNT. We investigated nine

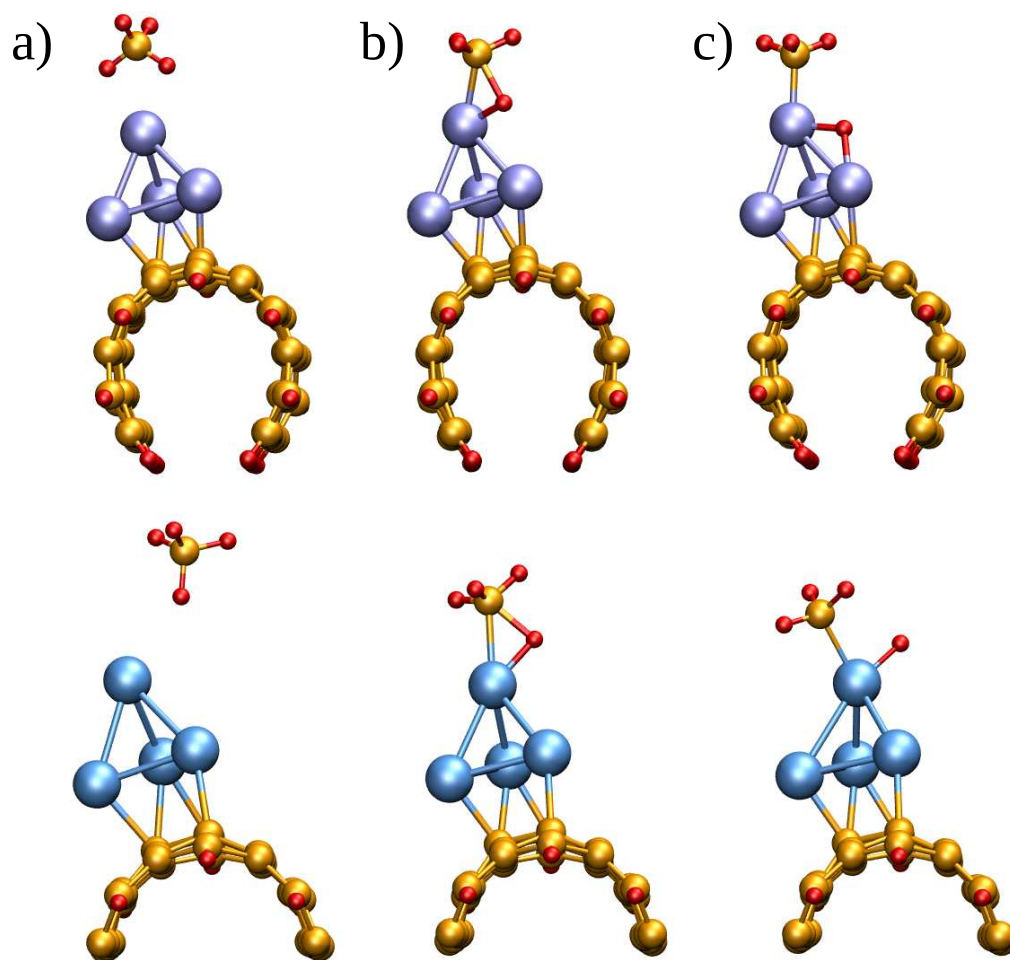


Figure 3. Calculated structures of a methane molecule reacting with a palladium tetramer (top row), supported on a (7,0) CNT represented by a finite model: a) molecular adsorption, b) transition state, c) dissociative adsorption. A methane molecule reacting with a platinum tetramer using the same model (bottom row, truncated) shows hydrogen adsorption on a single Pt atom rather than occupying a bridge site as for the Pd tetramer.

support structures including graphene, (10-10), (15-0), (8-8), (10-0), (5-5), (8-0), (7-0), and (4-4) CNTs in order of increasing curvature.

The support structure for a given curvature r^{-1} was produced by a linear transformation which mapped the planar graphene to a cylinder of radius r such that

$x_2 = r \cos\left(\frac{x}{r}\right)$, $y_2 = y_1$, and $z_2 = r \sin\left(\frac{x}{r}\right)$. The radius r is given as,

$$r = \sigma \frac{\sqrt{3(n^2 + nm + m^2)}}{2\pi}, \quad (3.1)$$

where n and m are the lattice vectors and σ is the carbon-carbon covalent bond length ($\sigma = 1.41 \text{ \AA}$) (141). We studied CNTs of both zigzag ($n,0$) and armchair (n,n) chiralities, where the graphene is rotated by 90 degrees before bending. The geometry was then optimized with the hydrogen atoms fixed to hold the curvature, and the carbon atoms were allowed to relax. The optimized structures were calculated with unrestricted spin, however the lowest energy spin configurations were closed shell singlet in all cases. The energy required to bend the support to the shape of the CNT has quadratic dependence on r , as expected. The relative energy of bending where $\Delta E = E_b - E_{flat}(\text{eV})$ can be fit such that $\Delta E = 127.666 r^{-2}(\text{\AA}^{-2})$ with RMS deviation of 0.068 eV.

The optimized support structure was then combined with the metal clusters to find the binding energies of the cluster to the support. All cluster-support structures were

optimized in both singlet and in triplet states. Cluster stability on the CNT support was evaluated by calculating the binding energy, E_B :

$$E_B^M = E_{(M_4-CNT)} - E_{M_4} - E_{CNT}, \quad (3.2)$$

where metal M is Pd or Pt, $E_{(M_4-CNT)}$ is the total energy of the combined cluster-support system, E_{M_4} is the energy of the (triplet) cluster, and E_{CNT} is the energy of the (singlet) support. Negative E_B energies are exothermic. We did not consider basis set superposition error in this study.

Next, methane was added to the lowest-energy singlet and triplet configurations of the cluster-support systems and then optimized to find both molecular adsorption (MA) and dissociative adsorption (DA) of the methane on the supported cluster. The energy of adsorption, $E_{MA(DA)}$, was calculated by,

$$E_{MA(DA)}^M = E_{(CH_4-M_4-CNT)}^{MA(DA)} - E_{(M_4-CNT)} - E_{CH_4}, \quad (3.3)$$

where $E_{(CH_4-M_4-CNT)}^{MA(DA)}$ is the total energy of the combined methane-cluster-support system in the configuration corresponding to either MA or DA, and E_{CH_4} is the total energy of the methane. Negative $E_{MA(DA)}$ energies are exothermic.

Finally, the transition state (TS) was found by optimization using the Berny Algorithm (142). The apparent barrier, E_a^M is given as,

$$E_a^M = E_{TS}^M - E_{(M_4-CNT)} - E_{CH_4}, \quad (3.4)$$

where E_{TS}^M is the total energy in the transition state. Negative E_a^M energies are possible provided that $E_{TS}^M > E_{MA}^M$, which indicates no apparent barrier.

3.3 Results

3.3.1 Cluster-Nanotube Binding

The cluster binding energies to the support, E_B , are shown in Figure 4. The trend is that E_B increases with CNT curvature for both Pd and Pt. Additionally, optimized geometries show a trend in which the number of cluster-support bonds increases with curvature. This is not surprising due to the greater reactivity of small CNTs which are highly strained (143; 144). Our results show that for triplet Pd₄-CNT systems, clusters bind more strongly to zigzag CNT supports than to armchair CNT supports with the exception of the (10,0) CNT. The opposite result is obtained with singlet Pd₄-CNT systems. In contrast, in triplet Pt₄-CNT systems, clusters bind more strongly to armchair CNT supports than to zigzag supports except at very high curvature of $r^{-1} > 0.3 \text{ \AA}^{-1}$. But in singlet Pt₄-CNT systems, clusters bind more strongly to zigzag CNT supports than to armchair CNT supports. This shows that electronic effects of the support play

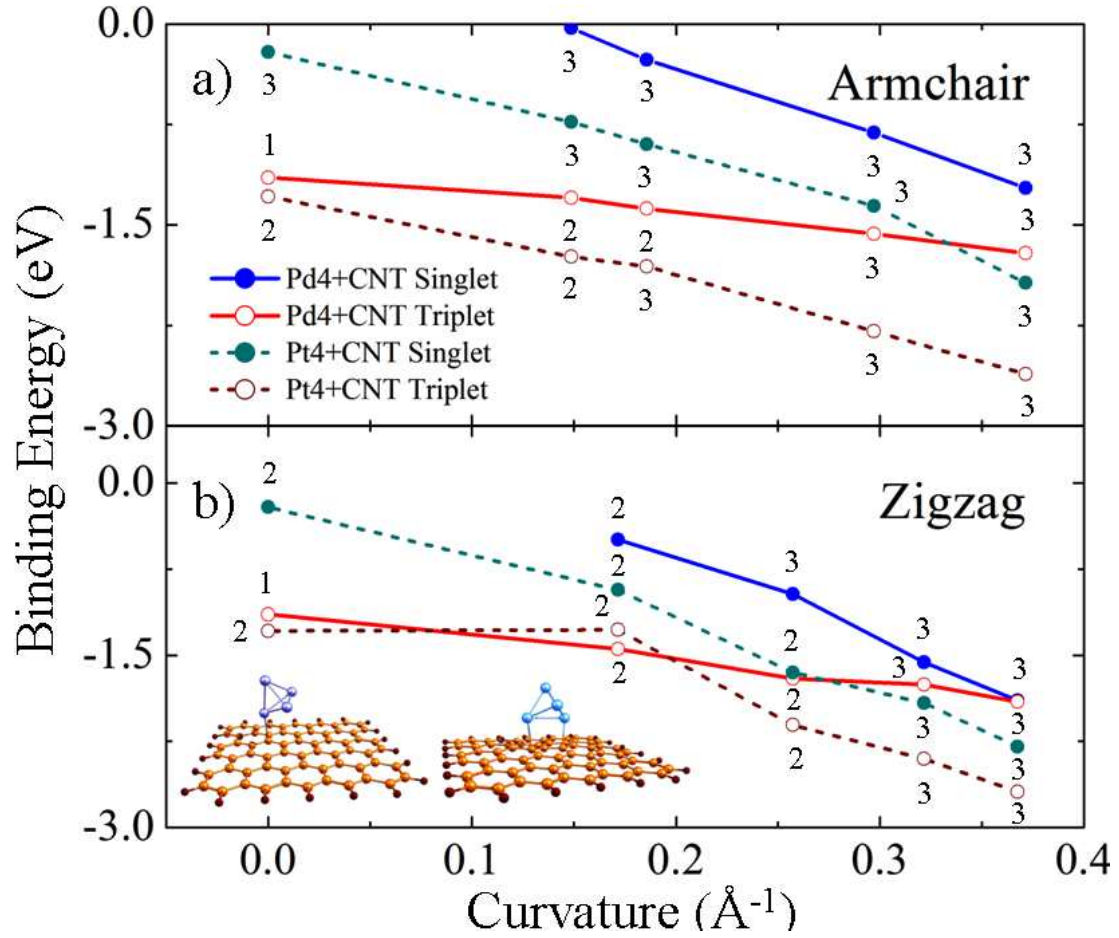


Figure 4. Calculated Pd₄/Pt₄ cluster binding energy E_B^M to the CNT support shown by CNT curvature and chirality: a) armchair including (10,10), (8,8), (5,5), (4,4) and b) zigzag including (15,0), (10,0), (8,0), (7,0). The number of surface bonds from the cluster to the support are shown next to each point. Inset: a Pd₄ cluster with 1 surface bond to graphene (left) and a Pt₄ cluster with 2 surface bonds to graphene (right).

a role in the binding properties of the cluster as armchair CNTs are metallic and zigzag CNTs are mostly semiconducting (145).

Our results using the B3LYP hybrid functional show that Pd_4 and Pt_4 cluster-CNT systems have stronger binding energies in the triplet state than in the singlet state. These results are in agreement with previous DFT studies with the GGA-PBE functional (135) that showed Pt_4 stability on (10,0) CNTs with binding of 2.31 eV and on graphene with binding of 1.35 eV, both in singlet states. The lowest energy Pt_4 binding configuration calculated with the GGA-PBE functional has 3 surface bonds to either (10,0) CNT or graphene supports, which is similar to that found with the B3LYP hybrid functional.

3.4 Methane Activation by Unsupported Clusters

We use the gas phase Pd_4 and Pt_4 clusters as a reference for comparison with the clusters supported on CNTs shown in Figure 3. The comparison is appropriate to determine the effect of the support on catalytic activity because the additional bonds from the cluster to the support may reduce the undercoordination that is characteristic of subnanometer cluster activity.

The lowest energy configurations of unsupported Pd_4 and Pt_4 gas phase clusters are trigonal pyramids in triplet states. In Figure 5, we show the spin density of Pd_4 reacting with methane. The reaction starts with methane and the cluster separated, and proceeds from MA, to the C-H bond insertion TS, and finally to DA. The unpaired spin density

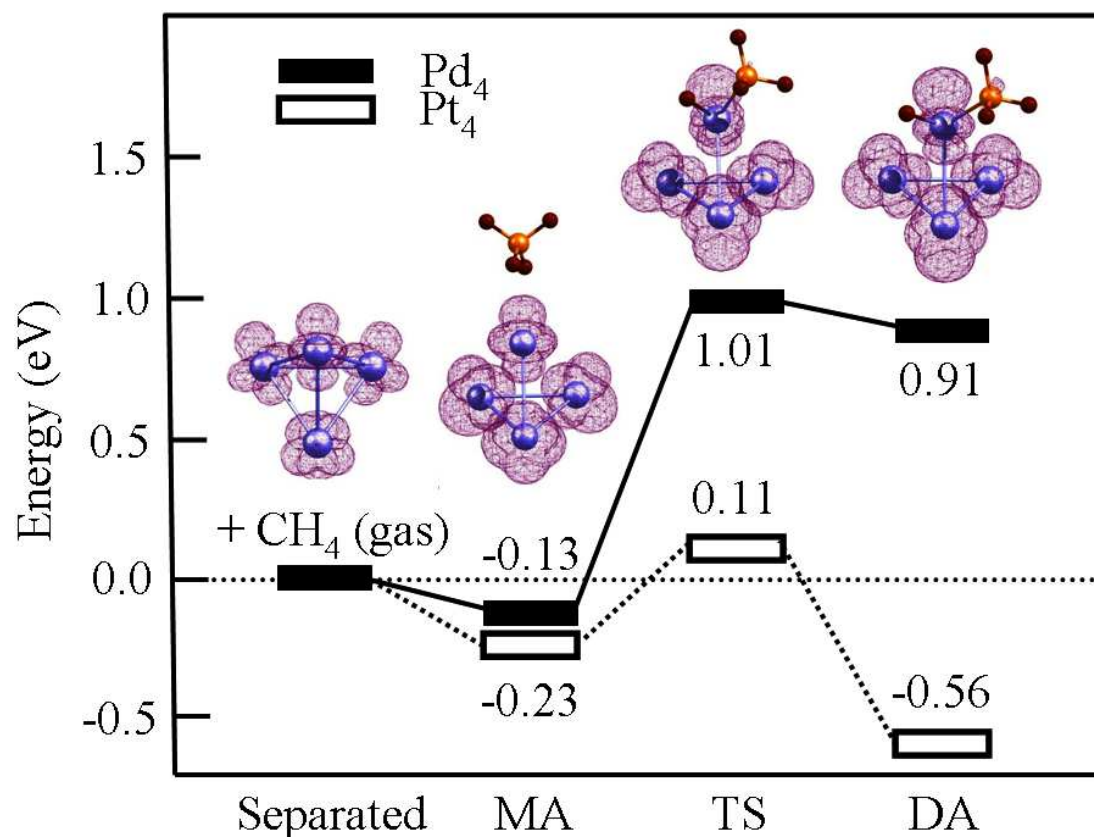


Figure 5. Adsorption energies and reaction barriers of C-H bond breaking which proceeds from the separated methane and unsupported Pd(Pt) tetramers, to molecular adsorption (MA) of the methane, to the transition state (TS) of C-H bond insertion, and finally to dissociative adsorption (DA). Inset spin density plots of the Pd tetramer shows very little contribution of spin density from the methane throughout the reaction. All energies are relative to $M_4 + CH_4$ and spin density $(\alpha - \beta)$ isosurface contour values are $0.003 e^-/\alpha_0^3$.

resides on the cluster throughout the reaction with very little contribution from the carbon atom.

The C-H bond breaking reaction is endothermic on Pd_4 clusters but is exothermic on a Pt_4 cluster as shown in Figure 5. The apparent barrier for breaking the C-H bond in methane adsorbed on a Pd_4 is 1.0 eV, and the dissociation is endothermic, by 0.9 eV. Conversely, the apparent barrier to C-H bond insertion on Pt_4 is much lower at 0.1 eV, and the dissociation is exothermic, by -0.56 eV. In comparison, other studies have found barriers for C-H bond breaking in methane to be 0.66 eV on a $\text{Pd}(111)$ surface (146) and 0.74 eV on a $\text{Pt}(111)$ surface (147). Overall, this shows that Pt_4 has a higher activity than Pd_4 for C-H bond breaking of methane.

3.5 Reaction Energies, Islands of Stability and Instability

The size and chirality of the support can strongly effect the adsorption and dissociation of methane on subnanometer clusters. The energies of adsorption, E_{MA}^M and E_{DA}^M , are shown as a function of curvature in Figure 6, for methane adsorbed on Pd_4 and Pt_4 clusters supported by armchair and zigzag CNTs and graphene. In all cases the reaction on Pd is endothermic because $E_{DA}^{Pd} > E_{MA}^{Pd}$. However, the trend of the reaction energy is less endothermic for small diameter CNTs for both zigzag and armchair chiralities as the difference between E_{DA}^{Pd} and E_{MA}^{Pd} decreases with curvature, though not monotonically. In contrast, the reaction on Pt is exothermic for graphene and CNTs of large diameter where $E_{DA}^{Pt} < E_{MA}^{Pt}$.

The trends in adsorption energies, E_{MA}^M and E_{DA}^M , for Pd and Pt clusters are related to the cluster binding energy to the support, E_B^M . Cluster binding energy E_B^{Pd} ranges from -1.1 to -1.9 and E_B^{Pt} ranges from -1.3 eV to -2.7 eV for graphene to (7,0) CNT supports as shown in Figure 4. The least endothermic Pd₄ reaction occurs when the Pd cluster is strongly bound (-1.5 eV to -1.75 eV) to a small diameter CNT support. Conversely, the most exothermic Pt₄ reaction occurs when the Pt cluster is weakly bound (-1.7 eV and -1.8 eV) to a large diameter CNT support.

Moreover, the reaction is more exothermic on CNTs of particular sizes and chiralities, which might be understood as islands of stability. For Pd, the least endothermic reaction is for sizes that are tightly curved (5,5) armchair and (7,0) zigzag CNTs. Likewise for Pt, the most favorable sizes are (10,10) and (8,8) armchair CNTs. The least favorable size and chirality, an island of instability, for methane C-H bond insertion reactions on Pt are (15,0) CNTs.

We postulate that the reason some supports have lower or higher adsorption energies is due to geometric distortion and electronic effects of carbon atoms in the support that have been displaced from the optimal (bare) configuration. The bond energy of the metal-CNT bond increases with curvature. However, the increased metal-CNT bond energy is off-set by distortion of the CNT and the cluster away from an optimal geometry in order to fit multiple binding sites on the support. We define the distortion energy as the difference in energy between the support (cluster) optimized in the reaction steps and

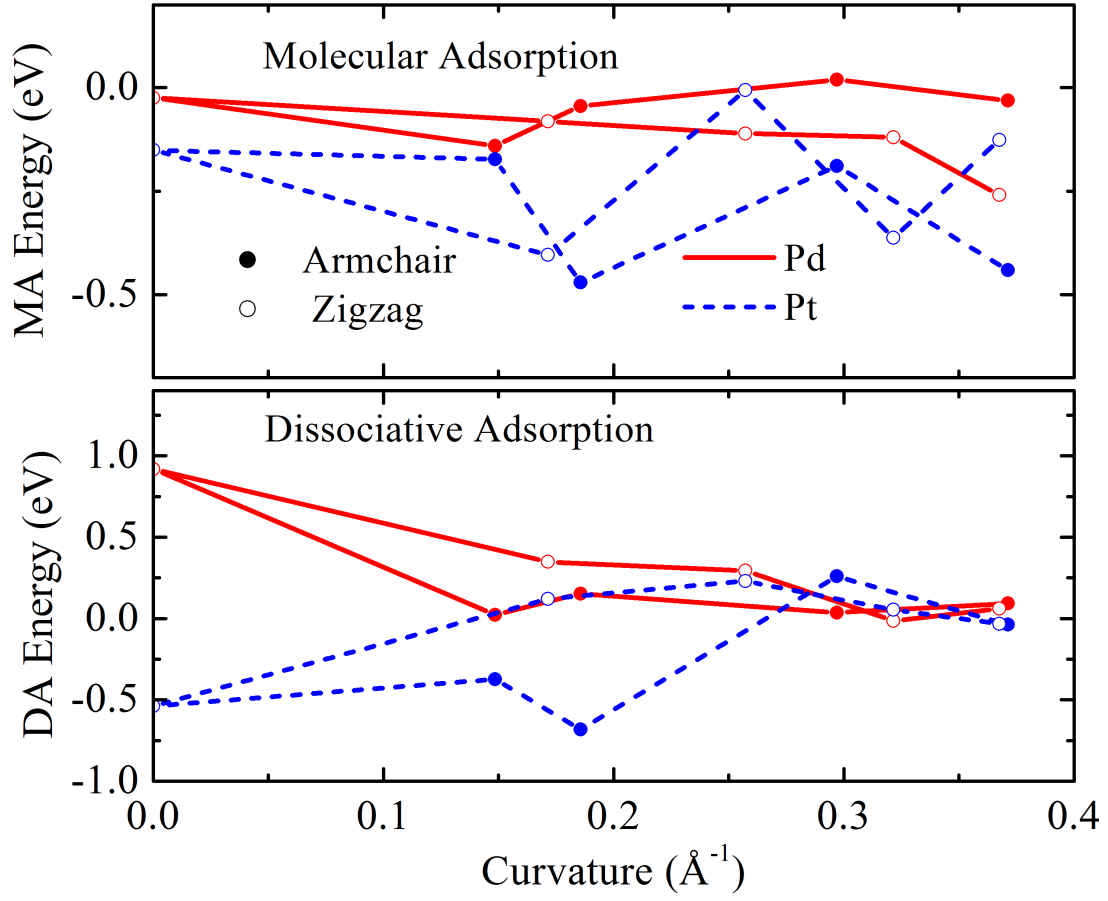


Figure 6. Energies of molecular adsorption (MA, E_{MA}^M , and dissociative adsorption (DA), E_{DA}^M , for tetramer clusters where M is Pd (straight) or Pt (dashed), as a function of support curvature and chirality, including graphene ($r^{-1} = 0.0$ Å), zigzag (open circles) and armchair (filled circles) CNTs. The C-H bond insertion reaction is exothermic if $E_{DA}^M < E_{MA}^M$.

the initial relaxed configuration. For both Pd_4 and Pt_4 clusters, the distortion energy for the support was inversely proportional to the support radius. Distortion energies ranged from 0.049 to -0.494 eV for triplet Pd_4 barriers and from 0.242 to -0.877 eV for triplet Pt_4 barriers, with graphene having the least distortion and (7,0) CNTs having the greatest distortion. A qualitative description of the calculated distortion energies is that cluster and CNT distortion is greater for adsorption on zigzag CNTs than on armchair CNTs.

3.6 C-H Bond Activation in Methane

The apparent barrier, E_a^M , for methane C-H bond insertion on supported Pd_4 and Pt_4 clusters is shown as a function of support curvature and chirality in Figure 7. The trends in the apparent barrier, E_a^M , can be compared to those of the cluster-support binding energies, E_B^M , as shown in Figure 4. For Pd, the apparent barrier E_a^{Pd} has, approximately, a direct relationship to the binding energy E_B^{Pd} . A strongly bound (-1.9 eV) Pd_4 on a high curvature (4,4) CNT has an apparent barrier of 0.5 eV, which is half the apparent barrier of an unsupported Pd_4 cluster as shown in Figure 5. The trend in Pd apparent barrier, E_a^{Pd} , with chirality is less clear. Armchair CNTs have lower barriers at curvature below $0.18 \text{ \AA}^{-1}$ and zigzag CNTs have lower apparent barriers otherwise.

In contrast, the trend in the Pt apparent barriers, E_a^{Pt} with curvature is roughly opposite with barrier energies E_a^{Pt} decreasing with binding energies E_B^{Pt} . However, the trend is not linear and the Pt_4 cluster on a large curvature (8,8) CNT with relatively

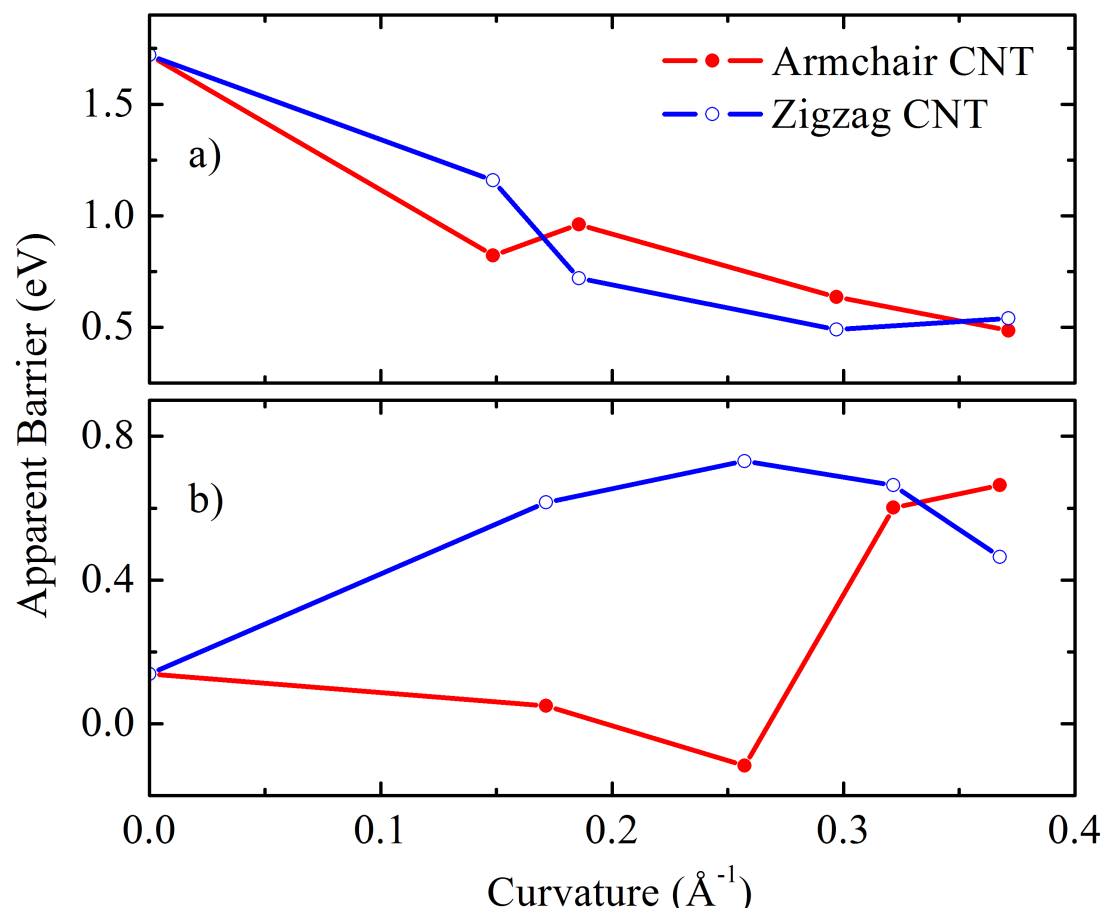


Figure 7. Calculated apparent barriers, E_a^M , for CH bonds with (a) $M = \text{Pd}_4$ and (b) $M = \text{Pt}_4$ catalysts on supports by curvature and chirality, including graphene ($r^{-1} = 0.0 \text{ \AA}$), armchair, and zigzag CNTs. Barriers are reduced for Pd clusters by CNT supports and increased for Pt clusters relative to gas phase (shown in Figure 5).

weaker binding (-1.8 eV) has the lowest apparent barrier of -0.1 eV, which is better than the unsupported Pt_4 cluster with an apparent barrier of 0.1 eV. Apparent barriers for Pt C-H bond activation E_a^{Pt} , are lower for armchair CNTs than for zigzag CNTs except at very high curvature above $0.3 \text{ \AA}^{-1}$. The trends for reaction barriers with chirality are similar to the trends in adsorption energies, E_{MA}^{Pt} and E_{DA}^{Pt} with chirality.

3.7 Conclusions

Both Pt and Pd subnanometer clusters are stable on CNT supports with binding energies for Pt higher than for Pd. In the triplet state, Pt and Pd have opposite ordering of binding energies relative to the chirality of the support, with armchair supports having lowest energy for Pt_4 and with zigzag supports having lowest energy for Pd_4 . This pattern is reversed in the higher energy singlet state. Reaction energies for CH_4 dissociation on supported Pd clusters are more exothermic relative to gas phase Pd_4 while reaction energies on supported Pt clusters are less exothermic relative to gas phase Pt_4 . When compared to an initial state of a bound cluster-support system with a separated methane, all reactions on supported Pd_4 are endothermic and all reactions on supported Pt_4 are endothermic except for highly curved armchair supports. In all cases, triplet states for products are preferred. For Pd clusters, barriers for C-H bond activation decrease with increasing CNT curvature, while the trend is opposite for Pt clusters. Certain CNT sizes and chiralities result in lower barriers than the overall trend. Our results show that CNT

supports can be selected by size and chirality to provide stable support for subnanometer Pt and Pd clusters and tailor their catalytic activity.

CHAPTER 4

CONFIGURATION-SENSITIVE MOLECULAR SENSING ON DOPED GRAPHENE SHEETS

We show by non-reactive classical molecular dynamics simulations that configuration-sensitive molecular spectroscopy could be realized on optimally doped and vibrated graphene sheets. High selectivity of the spectroscopy is achieved by maximizing Coulombic binding between the detected molecule and a specific nest, formed for this molecule on the graphene sheet by substituting selected carbon atoms with boron and nitrogen dopants. One can detect binding of different isomers to the nest from the frequency shifts of selected vibrational modes of the combined system. As an illustrative example, we simulate detection of hexanitrostilbene enantiomers in chiral nests formed on graphene.

4.1 Introduction

Selective molecular sensing is important in numerous life areas, such as military (148), fire sensing (149), wine tasting (150), and cancer detection (151). Recent advances in nanotechnology brought new possibilities to develop accurate, reliable, and portable chemical sensors, which would benefit a broad range of industries (152; 153). Among numerous tested systems, carbon nanostructures (154; 155) and, in particular, carbon nanotubes (CNT) allow the preparation of highly sensitive sensors (156; 157; 158; 159; 160; 161; 162; 163). The molecules adsorbed on the CNT surfaces are sensed via changes

of the CNT quasi-one-dimensional conductivity (164), but the approach is usually less specific, due to the nonspecific character of molecular binding to CNTs.

Molecular sensing could also be realized with vibrating microstructures which measure the mass of adsorbed molecules (165). CNTs have been tested as vibrational sensors of attached molecules (166; 167), where the molecules can be sensed with Raman scattering (168; 169). Suspended and vibrated graphene monolayers may also be used for this purpose (170; 171). Although CNT and graphene-based sensors might be highly sensitive, they can not easily distinguish between isomers.

In this work, we describe highly selective graphene-based vibrational sensors that can detect molecules in different isomeric states. Our idea is to form selective nests for polar molecules on small graphene sheets by selectively replacing carbon atoms with boron and nitrogen dopants (172). The dopants are positioned to create an electrostatic field above the graphene that is complementary to that of the detected (attached) molecule, so that their Coulombic binding is maximized. Once attached in the nest, the molecule can be recognized from its other isomers by the frequency shifts of the normal vibrational modes of the combined graphene-molecule system.

Several approaches might be potentially used to experimentally realize such nests. For example, scanning tunneling microscopy (STM) has been shown to induce local reactions (173). The STM might be used to reactively replace selected C atoms with B and N atoms in the graphene. Alternatively, STM might form the nests by attaching

charged (polar) atomistic (174; 175; 176) and molecular ligands (177; 178) to different regions of the graphene (179; 180). One could also externally synthesize molecules that are complementary to the tested molecules, attach them covalently to the graphene, and vibrate the combined system (181).

Although selective doping patterns might not be feasible experimentally today, several strategies might be employed to generate electrostatic nests in the future. One such strategy might be to dope the edges of several graphene flakes and allow them to self assemble on a surface, with the goal of creating a selective doping pattern in the joined flake (179; 180). Another approach might be to synthesize a nest by organic chemistry and attaching the flake to the graphene sheet (181). Scanning tunneling microscopy (STM) might also be used to push dopants into position. We consider boron and nitrogen as the simplest case to demonstrate the principle, however larger assemblies, such as ligands or molecular switches, might also be used to create the nest.

4.2 Design of the molecular nest

We demonstrate these ideas on a hexanitrostilbene (HNS) sensor. First, we calculate the electronic structure and optimized geometry of HNS using Gaussian03 (182) at the B3LYP/STO-3G level. The atomic charges are calculated using the natural bond order (NBO) approach. As shown in Figure 8 (up), HNS is composed of two trinitrobenzyl groups connected via a trans double bond. In the ground state, the HNS is chiral since

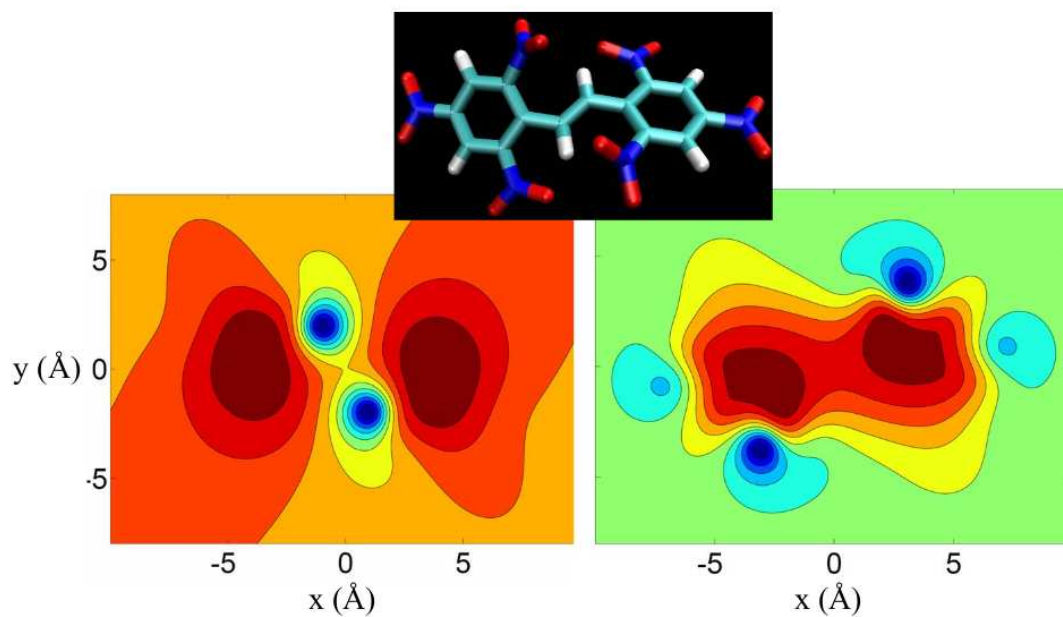


Figure 8. (top) The (M) enantiomer of the 2,2',4,4',6,6'-Hexanitrostilbene molecule. The electrostatic potential distribution formed ≈ 1.0 Å above (left) and below (right) the HNS molecule.

these two groups are twisted one with respect to the other, like the blades of a molecular propeller (183).

In Figure 8 (top) the calculated electrostatic potential of HNS is presented in the (x, y) plane with a fixed distance ($z = 3.15 \text{ \AA}$ and $-2.35 \text{ \AA}$) above (left) and below (right) the geometric center of the molecule, which is located at $z \approx -0.166 \text{ \AA}$ below the central C-C double bond. Slight (ground-state) bending of the HNS in the central region and related reorganization of the $-\text{NO}_2$ groups cause that the HNS has C_2 symmetry along the z axis but not along the x or y axis. Therefore, the two charged profiles shown in Figure 8 (top) are not mirror images of each other. The six highly polar $-\text{NO}_2$ groups provide useful sites for recognition. Distinct arrangement of charges in the chiral HNS might in principle be used to distinguish between its two enantiomers (184), with mirror imaged charges.

We design a selective molecular nest on doped graphene for the chosen (M)-HNS enantiomer. We position the molecule above the center of the graphene sheet ($\approx 39.5 \times 24 \text{ \AA}^2$) at a typical binding distance of $z = 3.35 \text{ \AA}$. Then, we start to form the nest under the (M)-HNS by modifying the graphene sheet and considering that each of its C atom is a potential candidate for replacement by boron or nitrogen. Two B or two N atoms are not allowed to be neighbors, and the edge of graphene is left open and without doping. The doping B and N atoms in the sheet have the charge of $Q_B \approx 0.55 \text{ e}$ and $Q_N \approx -0.55 \text{ e}$, which is approximately (exactly in the model) neutralized by the charges on the three

neighboring C atoms. We can find the energies associated with the substitutions of C with B and N atoms from the formula $\Delta E_{B(N)} = E_{doped} + E_C - E_{undoped} - E_{B(N)}$. Both reactions are endothermic and (in 78 C atoms flake) require $\Delta E_B = 4.58$ eV and $\Delta E_N = 2.53$ eV. The NBO charges and substitution energies are obtained using the B3LYP density-functional and 6-31G* basis set within Gaussian03 (182).

When we test for B or N doping of a particular site, we calculate the change of potential energy due to Coulombic coupling between the molecule and the neutral cluster formed by the charged dopant and its three oppositely charged neighbors (172). This change of potential energy is

$$E_{B(N)} = Q_{B(N)} \sum_{i=1}^n \frac{Q_i}{4\pi\epsilon_0} \left(\frac{1}{r_{i0}} - \sum_{j=1}^3 \frac{1}{3r_{ij}} \right), \quad (4.1)$$

where r_{i0} is the distance between the i th atom in the molecule, with the charge Q_i , and the dopant with the charge $Q_{B(N)}$, r_{ij} is the distance between this i th atom and the j th neighbor of the dopant, with the charge $\approx -Q_{B(N)}/3$, and ϵ_0 is the dielectric constant. We decide for doping a particular site when the change of the Coulombic potential energy decreases at least by the value of $\Delta E = -0.02$ eV.

In Figure 9 (top), we show the nest formed by doping the graphene sheet under the (M)-HNS. The doping pattern complements the electrostatic fields under the molecule (Figure 8 - right) and copies its C_2 symmetry; the exact C_2 symmetry is achieved by doping the sheet by atom pairs with central symmetry. Figure 9 (bottom) shows the

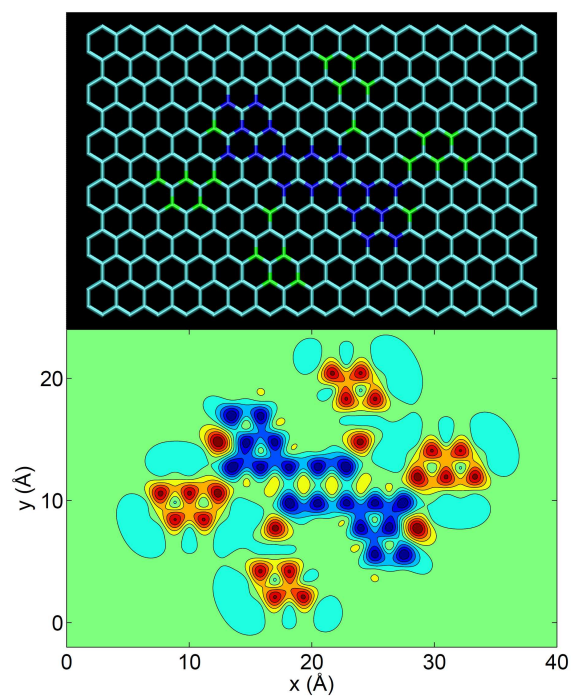


Figure 9. (left) The doping pattern of the nest designed for the (M)-HNS enantiomer docked above the sheet. (bottom) The electrostatic potential distribution formed above (or below) the doped graphene sheet (complementary to that in Figure 8 (bottom right)).

profile of the electrostatic field generated in a (x, y) plane positioned at a distance of 1 Å above (or below) the sheet. The partial positive charges of the boron dopants in the graphene match the partial negative charges of the oxygens in nitro-groups in the (M)-HNS, and the partial negative charges of the nitrogen dopants in the graphene match the partial positive charges of the electron deficient benzene rings in the (M)-HNS. The formed nest possesses a two-dimensional chirality (185).

4.3 Simulation of selective molecular docking

Next, we use molecular dynamics (MD) simulations to model nesting and sensing of the HNS on the doped graphene sheet. The simulations are realized with the NAMD package (53), based on the CHARMM27 force field (54). We use the NVT ensemble without periodic boundary conditions, where Langevin damping is used to thermalize the system and model its vibrational damping, as explained later, and the simulation time step is 1 fs. The vibrational properties are described by Lennard-Jones potentials, parametrized in the HNS as in the trinitrobenzyl molecule (186), while graphene is parametrized by CHARMM27, where $k_{bond} = 305 \text{ kcal}/\text{\AA}^2$, $K_{angle} = 40 \text{ kcal/mol rad}^2$, and $K_{dihedral} = 3.1 \text{ kcal/mol}$.

In Figure 10, we show that the (M)-HNS enantiomer can properly dock ($T = 75 \text{ K}$) in the chiral nest only from the top side of the graphene sheet. On the top, the (M)-HNS lays in the nest, while on the bottom, it stands like a “scorpio”. Therefore, by blocking the bottom side, the nest matches only the (M)-HNS enantiomer. This enantio-

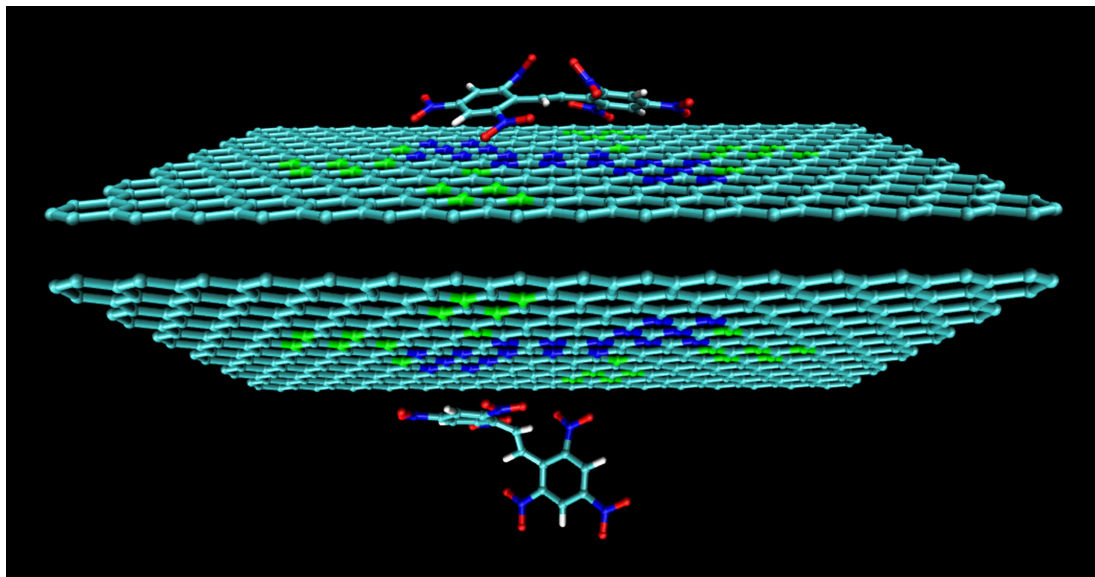


Figure 10. (top) (M)-HNS enantiomer docked in the nest on the graphene sheet designed for it. (bottom) However, (M)-HNS enantiomer does not bind to the nest at the bottom of the graphene sheet, because this nest (with vertically mirrored electric field) matches the opposite (P)-HNS enantiomer.

selectivity is caused by the fact that the bottom of the sheet creates an electric field that is a mirror image (in the z axis) of that above the sheet. Therefore, this field matches a mirror imaged molecule, i.e. the (P)-HNS enantiomer. The (M)-HNS enantiomer can still bind to it, but its nesting configuration is very different, which might be recognized by vibrational means.

We calculate the binding energy of the nested (M)-HNS, shown in Figure 10 (top). Initially, we center the molecule in the nest and allow the system to relax for $t = 25$ ps at the temperature of $T = 75$ K. At this temperature the (M)-HNS has enough

energy to quickly explore the doped graphene, but once docked it shows only very small vibrational motion. By using VMD (187), we obtain (from 225 ps long simulations) the total (electrostatic, van der Waals (vdW), and HNS configuration) binding energy of the (M)-HNS to the top of the nest of $\Delta E_{nest-t} \approx -39.1$ kcal/mol, while to the bottom of the nest it is $\Delta E_{nest-b} \approx -30.2$ kcal/mol, and its binding energy to the undoped graphene is $\Delta E_{graphene} \approx -28.2$ kcal/mol. Due to the large difference of $\Delta E = \Delta E_{nest-t} - \Delta E_{graphene} \approx -10.9$ kcal/mol, the (M)-HNS remains (Coulombically) bound to the top of the nest at $T = 300$ K.

From practical reasons, it is interesting to find out if the (M)-HNS nests on its own. When it is displaced from the nest by 20 Å in the x -axis and 5 Å in the z -axis, it diffuses back to the nest after $\tau_{nest} \approx 200$ ps ($T = 75$ K). We also test if other residual molecules can stay in the nest at room temperature. It turns out that water molecules leave it at $T = 300$ K. Similarly, we test binding to the nest of stilbene, an achiral molecule similar to HNS but with hydrogens replacing the nitro groups. The binding energy is $\Delta E_{nest} \approx -27.3$ kcal/mol, while its binding energy to the undoped graphene is $\Delta E_{graphene} \approx -18.0$ kcal/mol. Therefore, the (M)-HNS binds by $\Delta E \approx -1.6$ kcal/mol stronger to the nest than stilbene, despite the similarity of the two structures. These results show that when various molecules are captured in the nest, practically only the (M)-HNS can remain there at larger temperatures.

4.4 Simulation of molecular sensing

We start the MD simulations of molecular sensing by comparing the elastic properties of our model graphene with experiments. First, we calculate the Young's modulus of graphene defined as $E = \sigma/\epsilon$, where σ is the stress and ϵ the applied strain (188). We clamp one side of the graphene sheet and exert an in-plane stretching force on the edge opposite the clamped side. The induced stress is given by $\sigma = nF/w_g t_g$, where n is the number of atoms with force F acting on each of them, $t_g \approx 3.4 \text{ \AA}$ is the thickness (interlayer separation of graphite) and w_g is the width of the graphene ($y \approx 24 \text{ \AA}$). Likewise, the strain is $\epsilon = \Delta l/l_0$, where Δl is the change in length of the graphene, with the original length l_0 , due to the force acting on it. We find that our model graphene has the Young's modulus of $E \approx 1 \text{ TPa}$, in good agreement with the experimental value of $E \approx 1 \pm 0.1 \text{ TPa}$ (189).

Next, we determine the flexural rigidity D of our model graphene by rolling it into a cylinder and calculating the difference in configuration energies (190). The associated energy density, $W = \frac{1}{2} D \kappa^2$, can be used to obtain the flexural rigidity D from the curvature of the rolled graphene, $\kappa = R^{-1}$. Our graphene gives $D \approx 4.5 \text{ eV \AA}^2/\text{atom}$, in a reasonable agreement with *ab initio* results, giving $D \approx 3.9 \text{ eV \AA}^2/\text{atom}$ (191; 192). Therefore, the elastic parameters of our model graphene should match the real values.

We continue with modeling the (M)-HNS sensing in a nest formed on a small piece of doped graphene, shown in Figure 9 (top), and clamped at the shorter sides. In experi-

ments, the sheet can be suspended over a gap, clamped on two edges, and vibrated by an oscillatory electric field applied to an electrode located below the sheet (193; 194). The highly polarizable graphene sheet becomes periodically attracted to the electrode and mechanically oscillated. The vibration amplitude can reflect the presence of the molecule in the nest, since the effective mass and thus the frequency of selected normal vibrational modes are shifted.

We model sensing of the (M)-HNS nested on the doped graphene sheet that is driven by an oscillatory force of $F(t) = A \sin(\omega t) \theta(t)$, where $\theta(t)$ is the Heaviside step function. For simplicity, the force is applied in the z direction to each of the 6 carbon atoms in the center of the graphene sheet. The vibration of the graphene sheet may be approximately characterized by the absolute displacement of each atom in the z direction (neglecting the x and y displacements). We can model the excitation of normal modes in the clamped graphene sheet as driven and damped harmonic oscillators. The displacement in the z direction in the center of the sheet (or other selected points) can be described for each normal mode by the equation,

$$m_e \ddot{z}(t) + b \dot{z}(t) + k z(t) = F(t) , \quad (4.2)$$

where m_e is the effective mass of the oscillator (normal mode), b is its damping constant and k is its force constant. Equation 4.2 has the solution (195),

$$\begin{aligned} z(t) = & \theta(t) A e^{-\delta t} \frac{2 \delta \omega \omega_d \cos(\omega_d t) + \omega \Delta_- \sin(\omega_d t)}{(\omega_0^2 - \omega^2)^2 + 4 \delta^2 \omega^2} \\ & + \theta(t) A \frac{-2 \delta \omega \omega_d \cos(\omega t) + \omega_d \Delta_+ \sin(\omega t)}{(\omega_0^2 - \omega^2)^2 + 4 \delta^2 \omega^2}, \end{aligned} \quad (4.3)$$

where $\Delta_{\pm} = \delta^2 + \omega^2 \pm \omega_d^2$, $\omega_0 = \sqrt{k/m_e}$ is the intrinsic frequency, $\delta = b/2m_e$ is the effective damping, and $\omega_d = \sqrt{\omega_0^2 - \delta^2}$ is the resonant frequency of the damped oscillator.

The coefficient δ in Equation 4.3 represents the total damping of the chosen normal mode r in the graphene sheet suspended over a gap and clamped at the edges (196). This damping is caused by coupling of the normal mode to other internal and external (at the contacts) degrees of freedom (vibrational, electronic, etc.) (197). In our simulations, we approximate this total damping by applying to the system a Langevin damping of 0.2 (ps)^{-1} , which roughly corresponds to theoretical values obtained for graphene mechanically oscillated at the frequency of 100 GHz (196).

The steady-state component in Equation 4.3 (second term), valid for one normal mode, has a resonant character, where the position and width of the resonance could be used to detect the mass of the nested molecule. Its nesting configuration (198) might be also detected, because different normal modes have their effective masses, oscillation maxima, and nodes distributed differently on the graphene. These modes may sense the

configurations of the molecule, depending on its nesting position at the maxima and/or nodes of the modes.

The sensitivity of a given mode to the attached molecule can be obtained from the change of its frequency when the molecule is bound. Assuming, for simplicity, that the HNS molecule sits in the “center of the mode vibration”, where its mass, m_{HNS} , may simply add to the effective mass of the mode, m_e , we obtain for the ratio of the intrinsic frequencies of the two (free and with molecule) oscillators,

$$\frac{\omega_{unbound}}{\omega_{bound}} = \sqrt{1 + \frac{m_{HNS}}{m_e}}. \quad (4.4)$$

Here, we assume that the force constant of the mode, k , is the same for both the bound and unbound cases. This shows that modes with smaller effective masses m_e are more sensitive, because the HNS mass is a larger perturbation for them. By exciting the system at different driving frequencies, ω , we can detect the modified resonances of the individual modes. Since the driving may simultaneously excite many different modes of finite energy widths, we need to separate their contributions to determine which mode contributes most for specific resonant frequencies.

4.5 Results and discussions

We illustrate these ideas by detecting the (M)-HNS nested on both sides of the doped graphene. We use the “axial” and “edge” normal vibrational modes of the clamped graphene sheet, shown in the insets of Figure 11 and Figure 12, respectively. First,

we obtain the “reference frames” of these two modes by exciting the empty sheet, held on its two edges, at two frequencies that are close to their resonances. In the initial simulations, realized at $T = 5$ K, we pick frames with a maximum atom displacement and use them as the reference frames, shown in Figure 11-Figure 12. The frames are obtained after relaxing the transient component in the solution (Equation 4.3). The axial mode corresponds to the displacement of the graphene sheet, as in TA phonon modes with waves propagating along the sheet (199). The edge mode has the same type of displacement but the TA waves propagate in the orthogonal direction, where the graphene edges are free.

In the simulations of the molecular detection (realized at $T = 75$ K), we relax the transient component in Equation 4.3 and find the oscillatory contributions of these two modes to the total vibration of the graphene sheet. We approximately separate the amplitude of vibrations of the modal type r at frequency ω , $A_r(\omega)$, by projecting the actual frames on the reference frame of the chosen mode,

$$A_r(\omega) = \frac{1}{N_f} \sum_{i=1}^{N_f} \left| \sum_{j=1}^{N_a} z_j^{si}(\omega) z_j^r(\omega_r) \right|. \quad (4.5)$$

Here, N_f is the number of frames sampled from the molecular dynamics trajectory and used in the averaging, and N_a is the number of atoms in the sheet. $z_j^{si}(\omega)$ are the z -coordinates of atom j in the simulation frame i at frequency ω . Likewise, $z_j^r(\omega_r)$ are the z -coordinates of atom j in the reference frame of mode r at the modal resonant frequency

ω_r . From the $A_r(\omega)$ amplitude we can obtain the position and width of the resonance of the mode r .

In our simulations, the force F of the amplitude $A = 10.4$ pN is applied on each of the 6 C atoms, and its frequency ranges in the interval of $\omega = 1 - 900$ GHz, in stepwise increments of 3 GHz. Each frequency step is held constant for 0.5 ns comprised of 2000 frames. The first 100 frames (0.025 ns) are discarded in order to eliminate transient vibrations caused by the change in frequency (first term in Equation 4.3). The remaining 1900 frames (0.475 ns) per frequency step are analyzed, as shown in Equation 4.5.

In Figure 11, we show the results of our simulations of (M)-HNS sensing realized by the axial mode at $T = 75$ K; this low temperature is chosen to reduce the noise level of the vibrating system. We compare frequency dependent values of the projected amplitude obtained for the vibrations of the free sheet (unbound case), the sheet with the (M)-HNS bound at the top and bottom, respectively. The full width half-max (FWHM) of 52 – 55 GHz is similar in all the cases and fixed mostly by the Langevin damping. On the other hand, the resonant frequencies are shifted from the unbound value of $\omega_{unbound} \approx 220$ GHz to the values of $\omega_{bound} \approx 202$ GHz and $\omega_{bound} \approx 205$ GHz for the case when the (M)-HNS is bound above and below the graphene, respectively. Although, the last two frequencies are close, we can distinguish between the two cases. From the unbound and bound (above graphene) frequencies, and the HNS mass, $m_{HNS} \approx 450$ g/mol, we can obtain, using Equation 4.4, the effective mass of the axial mode, $m_e \approx 2,419$ g/mol.

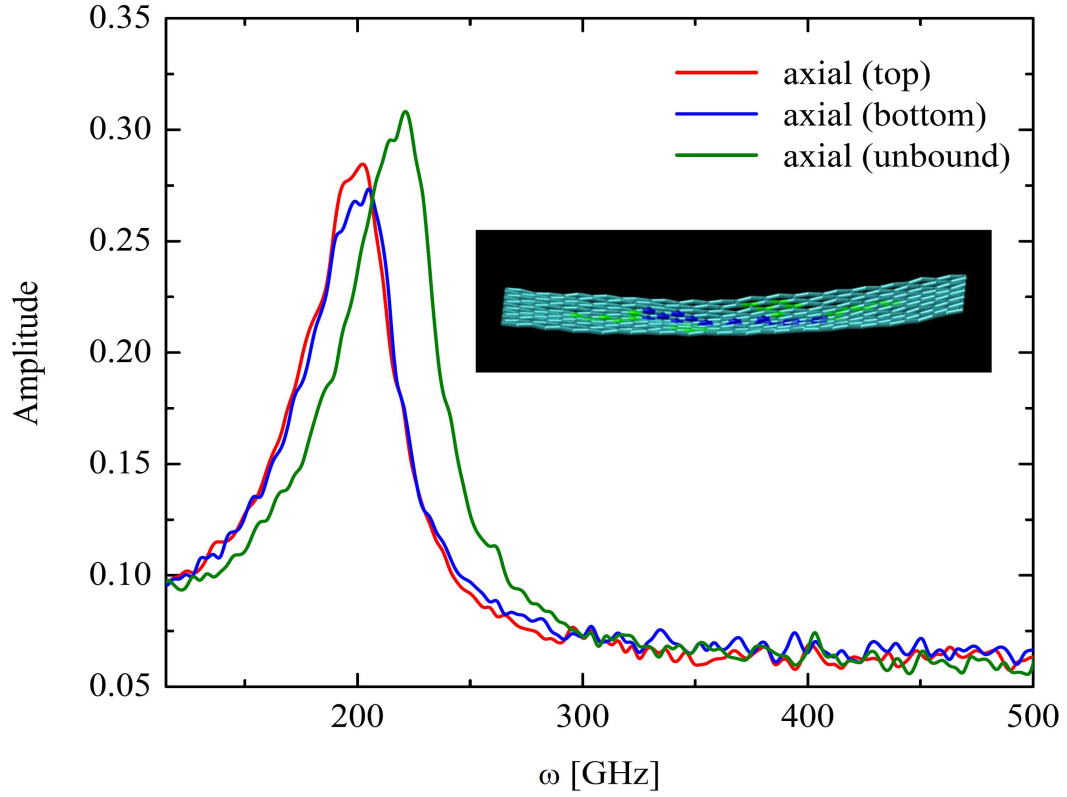


Figure 11. (left) The frequency dependent values of the projected amplitude of the axial vibration mode ($T = 75$ K). We display the vibrations of the free sheet, the sheet with the HNS bound at the top and bottom, respectively. (inset) The atom displacements in the reference frame of the axial vibration mode in the clamped graphene sheet ($T = 5$ K).

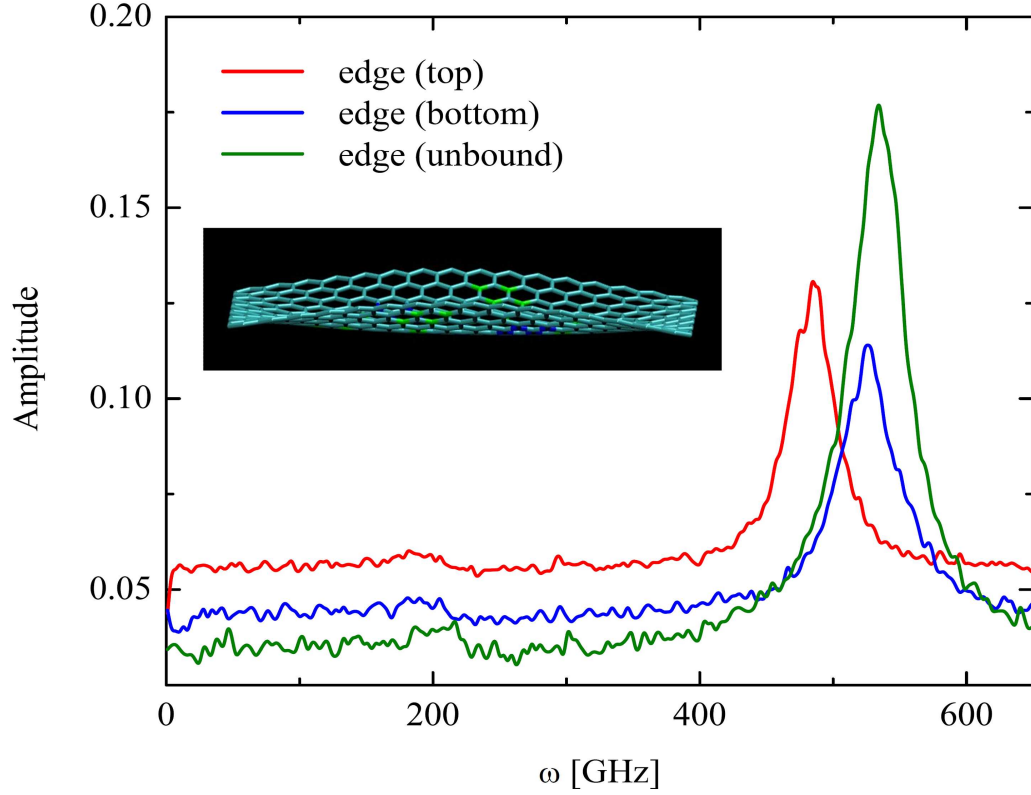


Figure 12. (left) The frequency dependent values of the projected amplitude of the edge vibration mode ($T = 75$ K). We display the vibrations of the free sheet, the sheet with the HNS bound at the top and bottom, respectively. (inset) The atom displacements in the reference frame of the edge vibration mode in the clamped graphene sheet ($T = 5$ K).

Let's now evaluate the same spectra for the edge mode, as shown in Figure 12. In this case, the resonance shifts from the unbound-case frequency of $\omega_{unbound} \approx 535$ GHz (FWHM ≈ 48.2 GHz) to $\omega_{bound} \approx 484$ GHz (FWHM ≈ 46.1 GHz) and $\omega_{bound} \approx 526$ GHz (FWHM ≈ 53.1 GHz) for the case when the HNS is bound above and below the graphene, respectively. We can also find the effective mass of the edge mode, $m_e \approx 2,027$ g/mol, using Equation 4.4. In this case, we can not only clearly detect the presence of the bound (M)-HNS, but we can also see where it is bound. Therefore, if only one side of the graphene is exposed, we could distinguish between the two HNS enantiomers.

The above results show that the edge mode is much more sensitive than the axial mode in the detection of the HNS configurations. This is because (1) the effective mass, m_e , of the edge mode is smaller than that of the axial mode and (2) the fact that the different (M)-HNS configurations influence very differently the resonance in the edge mode. In the axial mode, the configuration of the (M)-HNS molecule does not matter much, because the molecule is in both cases (above and below) close to the maximum of mode oscillations. On the other hand, in the edge mode, when the (M)-HNS is above the graphene, it is close to the maximum of oscillations, while when it sits below the graphene it is positioned very close to the nodal point of this mode. In principle, we can use this type of spectroscopy to fully recover the average orientation of the nested molecules.

4.6 Conclusions

In summary, we have shown that polar molecules may be selectively captured by electrostatic nests formed on doped graphene sheets. Their presence and docking configurations can be detected by the described configuration-sensitive spectroscopy from the shifts of resonant frequencies in selected vibrational modes of the graphene sheet. With this spectroscopy, one can detect and possibly sort the chirality of enantiomers by vibrational means, when attached to flat but chiral surfaces. The potential applications for this method might include explosives and hazardous molecule detection. However, the idea of selective nests and patterned doping on graphene sheets has potentially broader application to directed transported of adsorbates on material surfaces. Future research might be in this direction.

CHAPTER 5

NANODROPLET TRANSPORT ON VIBRATED NANOTUBES

We show by classical non-reactive molecular dynamics simulations that water nanodroplets can be transported along and around the surfaces of vibrated carbon nanotubes. In our simulations, a nanodroplet with the diameter of ≈ 4 nm is adsorbed on a (10,0) single-wall carbon nanotube, which is vibrated at one end with the frequency of 208 GHz and the amplitude of 1.2 nm. The generated linearly polarized transverse acoustic waves passes linear momentum to the nanodroplet, which becomes transported along the nanotube with the velocity of ≈ 30 nm/ns. When circularly polarized waves are passed along the nanotubes, the nanodroplets rotate around them and eventually become ejected from their surfaces when their angular velocity is ≈ 50 rad/ns.

5.1 Introduction

Carbon nanotubes (200) (CNT) can serve as nanoscale railroads for transport of materials, due to their linear structure, mechanical strength, slippery surfaces, and chemical stability (201). For example, electric currents passing through CNTs can drag atoms/molecules intercalated/adsorbed on CNTs (202; 203; 204). Polar molecules and ions adsorbed on CNT surfaces can also be dragged by ionic solutions passing through the tubes (205; 206; 207). Recently, nanoparticles (208; 209) and nanodroplets (210; 211)

have been dragged along CNTs by hot phonons in thermal gradients. Analogously, breathing (212) and torsional (213) coherent phonons can pump fluids inside CNTs.

Materials adsorbed on macroscopic solid-state surfaces can be transported by surface acoustic waves (SAW) (214). This method has many practical applications, such as conveyor belt technologies (215), ultrasonic levitation of fragile materials (216), slipping of materials on tilted surfaces (217; 218), threading of cables inside tubes (219), and droplet delivery in microfluidics (220; 221; 222; 223; 224).

In this work, we examine the possibility of using SAW at the nanoscale. We use classical molecular dynamics (MD) simulations to model transport (drag) of water nanodroplets on the surface of CNTs by coherent acoustic waves. Such coherent vibrations might be generated by piezo-electric generators (225; 226). In analogy to coherent control of molecules by light (227), specialized pulses of coherent phonons might also be used in precise manipulation of materials.

5.2 Model System

Our model systems are formed by nanodroplets consisting of a number, N_w , of water molecules adsorbed at $T = 300$ K on the (10,0) CNT, and transported along/around its surface by coupling to coherent transversal acoustic (TA) phonon waves, as shown in Figure 13. We simulate the systems with classical molecular dynamics simulations, using NAMD (53), with the CHARMM27 force field (54) with the TIP3P model for water molecules in the nanodroplet, and VMD (187) for visualization and analysis. The

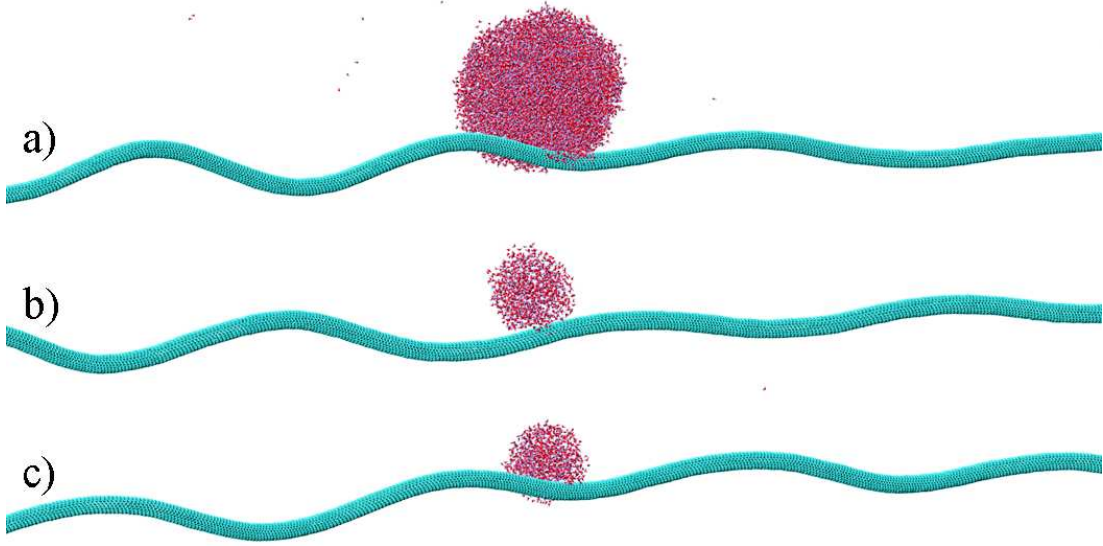


Figure 13. Nanodroplets of a) $N_w = 10,000$ and b) $N_w = 1,000$ waters adsorbed on the (10,0) CNT and dragged by the linearly polarized TA vibrational wave with the amplitude of $A = 1.2$ ($T = 300$ K). c) A nanodroplet of $N_w = 1,000$ adsorbed on the same CNT is dragged by a circularly polarized vibrational wave of $A = 0.75$ nm.

nanodroplets couple to the CNT by van der Waals (vdW) forces, described in CHARMM with the Lennard-Jones potential energy (228)

$$V_{LJ}(r_{ij}) = \epsilon_{ij} \left[\left(\frac{R_{min,ij}}{r_{ij}} \right)^{12} - 2 \left(\frac{R_{min,ij}}{r_{ij}} \right)^6 \right]. \quad (5.1)$$

Here, $\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$ is the depth of the potential well, $R_{min,ij} = \frac{1}{2}(R_{min,i} + R_{min,j})$ is the equilibrium vdW distance, and r_{ij} is the distance between a CNT atom and a water atom.

The edge atoms at one of the ends of the 450 nm long CNT are fixed. At this end the tube is also oscillated. To prevent the CNT translation, four dummy atoms are placed in its interior at both ends. Otherwise, the tube is left free. A small Langevin damping (122) of 0.01 ps^{-1} is applied to the system to continuously thermalize it, while minimizing the unphysical loss of momenta (205); the time step is 2 fs. At the two CNT ends, two regions with high damping of 10 ps^{-1} are established to absorb the vibrational waves. One region (35 nm long) is close to the generation point, and the other (180 nm long) is at the other CNT end. We model the systems in a NVT ensemble (periodic cell of $15 \times 15 \times 470 \text{ nm}^3$).

5.3 Nanodroplet transport by linearly polarized waves

The vibrational waves are generated at one CNT end by applying a periodic force (orthogonal to its axis), $F = F_0 \sin(\omega t)$, on the carbon atoms separated 35 – 40 nm from the CNT end. This generates a linearly polarized TA vibration wave, $A_y(t) = A \sin(\omega t)$, where $\omega \approx 208 \text{ GHz}$, $k = 2\pi/\lambda \approx 0.157 \text{ nm}^{-1}$, and $A \approx 0.3 - 2.1 \text{ nm}$ for $F_0 = 0.6948 - 5.558 \text{ pN/atom}$. The TA waves propagate along the nanotube with the velocity of $v_{vib} = \omega/k \approx 1,324 \text{ nm/ns}$, scatter with the nanodroplet, and become absorbed at the tube ends. In our simulations, we let the wave pass around the droplet for a while and then evaluate its average steady-state translational, v , and angular, ω_d , velocities.

In Figure 14, we show the (linear) velocities of nanodroplets with $N_w = 1,000$ and 10,000 water molecules in dependence on the vibrational amplitude, A . The data are obtained by averaging the droplet motion over trajectories of the length of $t \approx 7.2$ ns. We can see that the 10-times smaller droplet moves about 15-times faster for the same driving conditions. At small amplitudes, $A < 1.2$ nm, the velocities roughly depend quadratically on the driving amplitude. At larger amplitudes, $A > 1.2$ nm, they gain a linear dependence.

The nanodroplet is transported by absorbing momentum from the vibrational wave. Its steady-state motion is stabilized by frictional dissipation of the gained momentum with the nanotube, which carries it away through the highly damped and fixed atoms. In the first approximation, the droplet motion might be described by the Boltzmann equation. In the steady state, obtained when a wave of a constant amplitude is passed through the CNT, the momentum of the droplet averaged over a short time (50 ps) is constant. Then, the constant driving force acting on the droplet, $\dot{P}_{drive}$, is equal to the friction force, $\dot{P}_{friction}$, between the droplet and the CNT (228) (linear motion - vectors omitted),

$$\begin{aligned}\dot{P}_{drive} &= \int p F(r) \frac{\partial f}{\partial p} dr dp \\ &= \int p \left(\frac{\partial f}{\partial t} \right)_{coll} dr dp = \dot{P}_{friction} .\end{aligned}\tag{5.2}$$

Here, $f(r, p)$ is the position and momentum distribution function of the waters in the nanodroplet (normalized to N_w) and $F(r)$ is the force acting on each of the waters at r . The collision term $(\frac{\partial f}{\partial t})_{coll}$ describes scattering of waters with each other and the CNT, where the last option causes the droplet to relax its momentum (229). In the approximation of the momentum relaxation time (230), τ_p , the damping term can be described as,

$$\int p \left(\frac{\partial f}{\partial t} \right)_{coll} dr dp = \int p \frac{f - f_0}{\tau_p} dr dp \approx \frac{P_{droplet}}{\tau_p}, \quad (5.3)$$

where $P_{droplet}$ is the steady-state average momentum of the nanodroplet (205; 206).

As the acoustic wave propagates along the CNT, it carries the momentum density (231),

$$g(t, x) = \mu \omega k A^2 [1 + \cos(2 k x - 2 \omega t)] , \quad (5.4)$$

where μ is the CNT mass per unit length and the other symbols are the same as before. Assuming, for simplicity, that the momentum density of the wave is fully passed to the droplet (only approximately true, as seen in Figure 13), we obtain

$$\dot{P}_{drive} = \frac{1}{2} \mu \omega^2 A^2 = \frac{P_{droplet}}{\tau_p}. \quad (5.5)$$

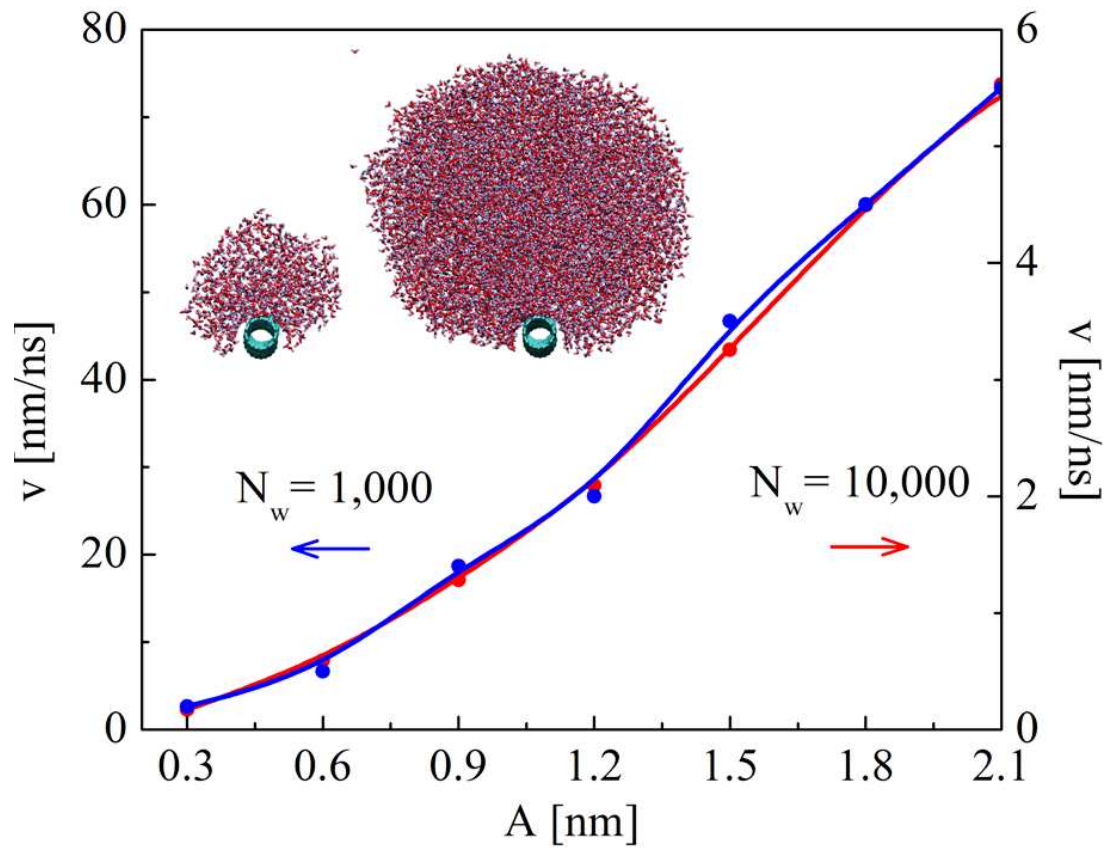


Figure 14. The drag velocity of nanodroplets with $N_w = 1,000$ and 10,000 waters in dependence on the amplitude, A , of the linearly polarized wave, with the frequency of $\omega = 208$ GHz. (inset) The adsorbed nanodroplets viewed in the CNT axis.

Equation 5.5 shows that the droplet velocity scales as

$$v_t = \frac{P_{droplet}}{m} \approx \frac{A^2 \tau_p}{m}. \quad (5.6)$$

Moreover, the momentum relaxation time, $\tau_p \approx S^{-1}$, can be assumed to scale inversely with the contact area, S , between the droplet and the CNT, due to friction. The 15 times larger velocity of the 10 times smaller droplet with a smaller contact area matches our expectations from Equation 5.6. The quadratic dependence of the droplet velocities on the driving amplitude, A , shown in Figure 14, also roughly agrees with Equation 5.6.

5.4 Nanodroplet transport by circularly polarized waves

Next, we simulate transport of nanodroplets with $N_w = 1,000$ and $2,000$ waters, adsorbed on the (10,0) CNT, by circularly polarized TA waves. Application of the force of $F(t) = (F_x, F_y) = F_0 (\sin(\omega t), \cos(\omega t))$, $F_0 = 0.4864 - 2.084$ pn/atom, on the same C atoms as before generates a circularly polarized wave, $A(t) = (A_x, A_y) = A (\sin(\omega t), \cos(\omega t))$, where $A \approx 0.21 - 0.75$ nm, $\omega \approx 208$ GHz, and $k \approx 0.157$ nm⁻¹. The circularly polarized TA waves carry both linear and angular momenta and pass them to the nanodroplets, which are transported along the CNT and rotated around it.

In Figure 15, we plot the translational, v , and the angular, ω_d , velocities of the nanodroplets in dependence on the wave amplitude, A . For $N_w = 1,000$, ω_d rapidly grows with A till $\omega_{d,max} \approx 50.5$ rad/ns, where the droplet is ejected from the CNT surface, due to large centrifugal forces. The larger droplet rotates with $\approx 30 - 40\%$ smaller angular

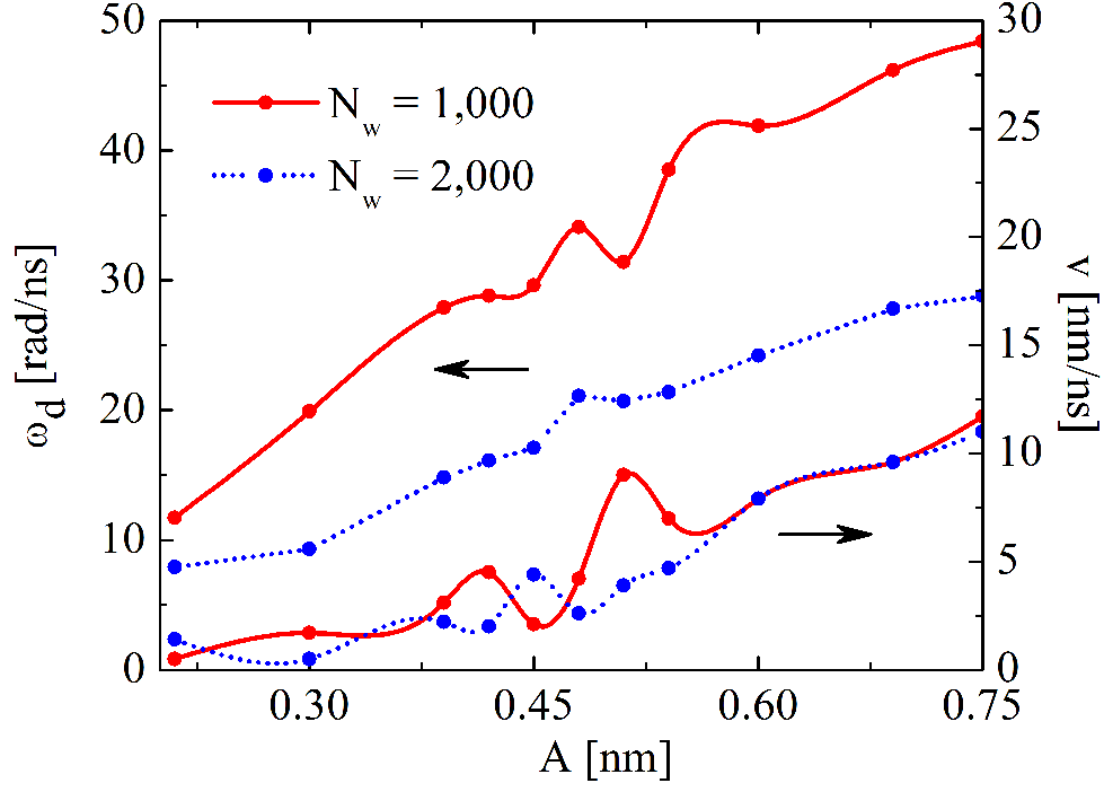


Figure 15. The average translational v and angular ω_d velocities of water nanodroplets with $N_w = 1,000$ and $2,000$, in dependence on the wave amplitude, A , when driven by circularly polarized waves.

velocity, in analogy to the situation in a linear transport. At $A = 0.4 - 0.6$ nm, both the linear and angular velocities show certain resonant features for both droplets. At these amplitudes of the circular waves the coupling to the droplets can be dramatically altered, since the wave amplitudes are similar to the droplet sizes. Interestingly, the translational velocities, v , are very similar for both droplets. This might be due to better transfer of linear momentum to the larger droplet from circularly polarized waves.

We can perform similar analysis of the angular momentum passage from the circular wave to the droplet and back to the CNT, like we did for the linear momentum in Equation 5.2-Equation 5.6. In a steady state, obtained when a circularly polarized wave of a constant amplitude is passed through the CNT, the average angular momentum of the droplet around the (equilibrium position of) CNT axis is constant. The driving momentum of force, $\dot{L}_{drive}$, acting on the droplet is equal to its friction counterpart, $\dot{L}_{friction}$, acting between the droplet and the CNT (197). Assuming that the whole angular momentum density of the wave is passed to the droplet and using the approximation of the angular momentum relaxation time, we find

$$\dot{L}_{drive} = f(\mu, \omega, A) = \frac{L_{droplet}}{\tau_L} = \frac{I\omega_d}{\tau_L} = C, \quad (5.7)$$

where $f(\mu, \omega, A)$ is the angular momentum density (size) of the circularly polarized wave, I is the droplet moment of inertia with respect to the (equilibrium) CNT axis, and τ_L is the angular momentum relaxation time. In the steady state, the average rates of driving

and damping are constant, as shown by C . The moment of inertia is $I = \sum_{i=1}^n m_w r_i^2 \propto N_w$, where m_w is the mass of a water molecule, and r_i is the distance of each water molecule from the (equilibrium) CNT axis. Using this I in Equation 5.7, we find that $\omega_d \propto N_w^{-1}$, in rough agreement with Figure 15.

We can also describe the droplet ejection. The angular motion of the droplet around the (equilibrium) CNT axis generates a radial centrifugal force, $F_c = m \omega_d^2 / h$, where m is the droplet mass and h is its distance from the (equilibrium) CNT axis. When the centrifugal force exceeds the vdW force which binds the droplet to the CNT, the droplet is ejected (232). This happens for the centrifugal force of $F_c = 150.2$ pN, obtained for $A = 0.9$ nm, $\omega_d = 50.5$ rad/ns, and $h = 19.7$ Å. We can roughly estimate the vdW binding forces for a relaxed water droplet coupled to a frozen CNT by applying a fictitious force on the droplet in the direction orthogonal to the CNT axis. This gives the force of $F_{vdW} \approx 229$ pN. In the presence of droplet rotation around the CNT, the vdW forces should be smaller, since the droplet has a smaller contact with the CNT, i.e. $F_c \approx F_{vdW}$.

In order to better understand the droplet-CNT dynamics, we present in Figure 16 the time-dependent motion of the nanodroplet with $N_w = 1,000$ transported by circularly polarized waves. The droplet and CNT form a coupled system where the CNT vibrates around its axis and the droplet rotates around it. We describe the droplet rotation around the actual position of the CNT by the angle θ of the vector pointing from the center of mass of a CNT segment local to the droplet to the actual droplet center of mass. The

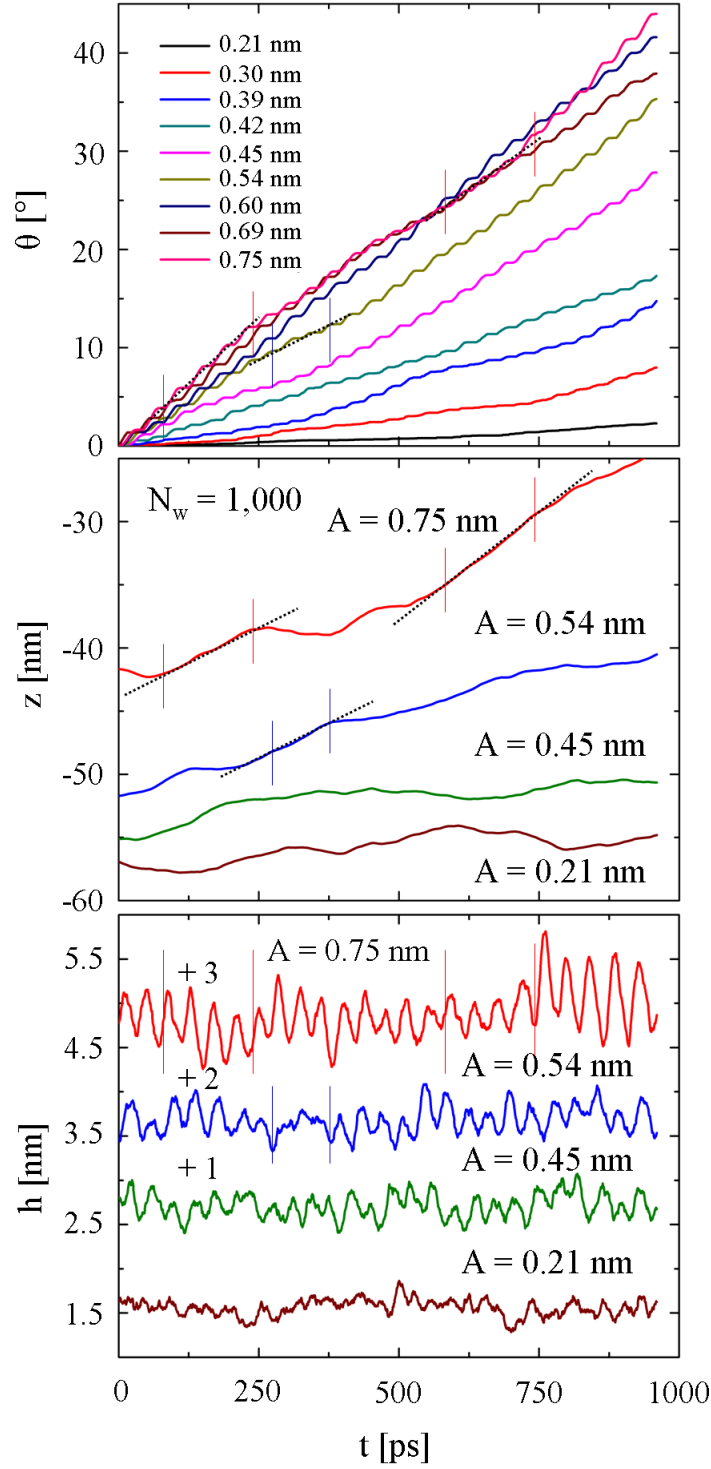


Figure 16. Time dependent angle of rotation (top), position (middle), and height (bottom) of the $N_w = 1,000$ droplet center of mass above the local CNT center of mass as the CNT is driven by circularly polarized waves of $\omega = 208$ GHz at amplitudes ranging from $A = 0.21$ nm to $A = 0.75$ nm. Tangents between vertical lines indicate regions of surfing where the nanodroplet slides down the CNT surface.

CNT segment is defined as a 2 nm section of the CNT bisected by the droplet. The time dependence of θ for different amplitudes A is in Figure 16 (top), the accompanied translation of the droplet along the CNT is in Figure 16 (middle), and the radial distance of the droplet from the CNT axis is in Figure 16 (bottom).

The droplet motion on the circularly polarized waves resembles surfing, where the droplet is sometimes grabbed better by the waves and for a while moves fast forward. At small waves, surfers cannot ride waves and neither can the droplet. This happens at $A = 0.21$ nm, where the vertical and longitudinal displacements of the droplet on the CNT are very small, as shown in Figure 16 (bottom) and (middle), respectively. Therefore, a small momentum is transferred to the water droplet which almost “bobs” in place like a “buoy”, much like a surfer waiting for a wave. At larger amplitudes, the droplet can catch some of the waves and glide on them. We can see that at $A > 0.45$ nm, the droplet sometimes ($t \approx 125$ ps and 700 ps) starts to progress forward quickly. The same is seen even better at the larger amplitudes, $A = 0.54$ nm and $A = 0.75$ nm, as denoted by the dotted tangential lines. In real surfing, the gravitational force of fixed spatial orientation accelerates the surfer on the traveling tilted wave. On the CNT, the gravitational force is replaced by the inertia forces acting on the nanodroplet surfing of the circularly polarized wave.

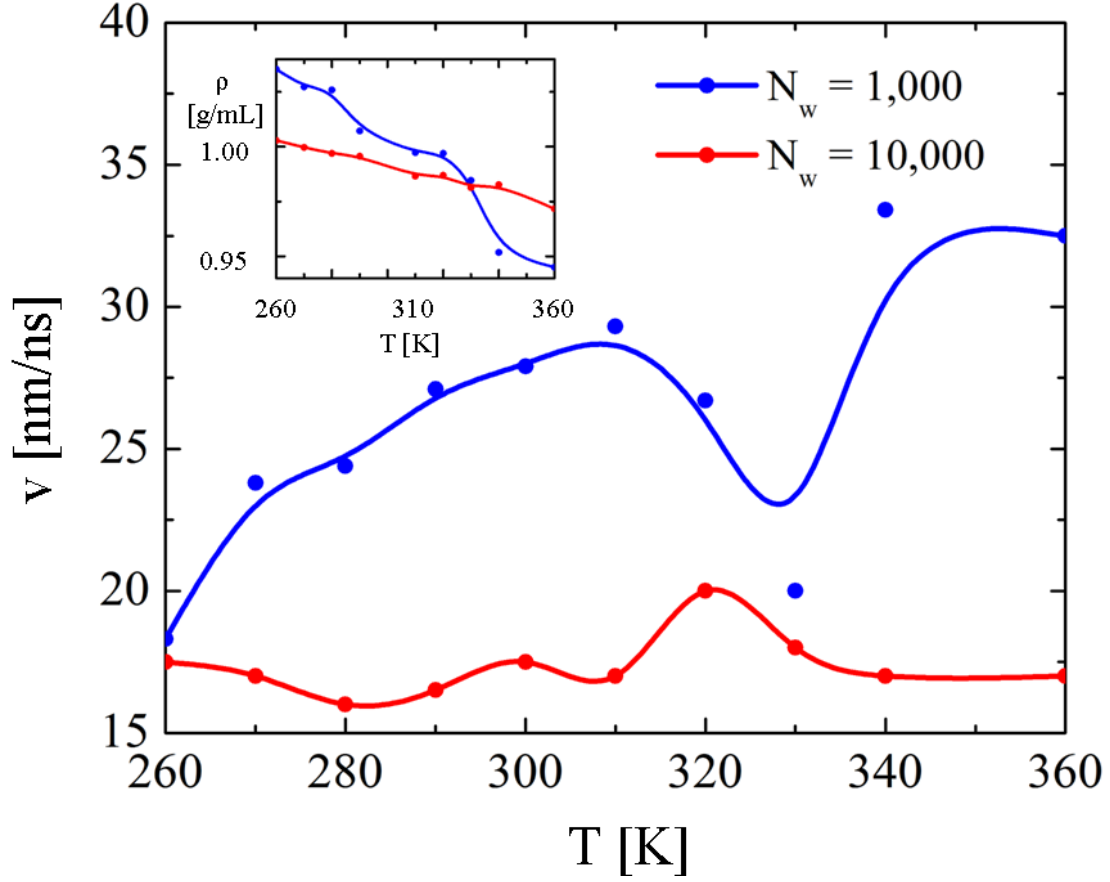


Figure 17. Temperature dependent translational velocities, v , of the $N_w = 1,000$ and 10,000 droplets dragged by linearly polarized vibrational waves of $\omega = 208$ GHz and $A = 1.2$ nm.
(inset) The temperature dependence of the effective nanodroplet density.

5.5 Temperature effects

In Figure 17 (inset), we also present the temperature dependence of the translational velocity of $N_w = 1,000$ and $10,000$ droplets, transported by linearly polarized waves of $\omega \approx 208$ GHz and $A = 1.2$ nm. We can see that v increases with temperature for the small droplet, but it stays largely constant for the large droplet. In the region of $T = 300 - 340$ K, we can observe some anomaly. The effect is much more apparent for the $N_w = 1000$ droplet, where we can see a sharp slowing down of the droplet. In contrast, the larger droplet is accelerated here. This anomaly may be potentially linked with the reduced water densities in the droplets at higher temperatures (inset). At lower densities, the momentum transfer should be different, due to changed viscoelastic properties of the droplets. Although the droplets quickly evaporate molecules, sometimes also due to driving, they operate in saturated conditions inside small boxes allowing them to maintain a relatively stable number of molecules ($5 - 10$ %).

5.6 Conclusions

We have demonstrated that TA vibrational waves on CNTs can translate/rotate nanodroplets adsorbed on their surfaces, in dependence on the wave amplitude, polarization and frequency, the droplet size, and the temperature of the system. This material transport, which complements other transport methods at the nanoscale, could be applied also on planar surfaces, such as graphene. It has potential applications in molecular delivery (233), fabrications of nanostructures (234; 235), and nanofluidics (236).

CHAPTER 6

GRAPHITIZATION BY THERMAL ANNEALING

Buckling in monolayer graphitic materials and the reduction of interlayer electronic repulsion in bilayer and multilayer graphitic materials is important to the graphitization process. Using a first principles approach, we model monolayer and bilayer graphitic systems and map the potential energy surface of buckling angles. Next we model the graphitization of diamond to rhombohedral graphite using an interpolated method. Finally we explore graphitization in diamond nanowires using a molecular dynamics approach and the AIREBO many-body potential.

6.1 Introduction

Graphite, diamond, and amorphous/glassy carbon are of great interest to the basic and applied research communities (237). Ultrahard materials often exist in one of many interesting diamond-like phases of carbon, boron-nitride, and silicon carbide (238), and high-pressure phases of carbon are an active area of research (239; 240; 241). Diamond can be graphitized thermal annealing, and hybrid diamond-graphite materials can be made by vapor deposition (242; 243; 244; 245), and extensive theoretical research investigating hybrid diamond-graphite materials has predicted junctions of diamond and graphite materials (246; 247; 248). Experiments have shown the coexistence of diamond and graphite in hybrid diamond-graphite nanowires (249) and also AA-graphite on (111)

diamond (250). Radiation has also been shown to produce hybrid materials in graphite (251) including cross-links in multi-wall nanotubes that increase strength (252). The significant interest in hybrid (253) and meta-stable materials make the diamond-graphite transition an important area of research.

This chapter is divided into four sections and discusses buckling in graphitic materials, interlayer repulsion in buckled graphene bilayers, the graphite to diamond transition, and the graphitization of diamond nanowires by thermal annealing.

6.2 Buckling in Graphene Monolayers

Using the LCBPOII potential, Los showed that graphene is intrinsically rippled (254), meaning that graphene is inherently three dimensional. Buckling of graphene is an important mechanism for breaking the plane of what would otherwise be a two-dimensional material (255; 256; 257). In these examples, the buckling is over several atoms. However, recent work has examined the possibility of large buckling angles in neighboring atoms of graphene (258) and also for other semiconductors (259).

Graphitic carbon is the stiffest material of graphitic silicon, silicon carbide, and boron-nitride for out of plane buckling, as shown in Figure 18. Here we compare the energies of buckling for a graphitic sheet of carbon (C-C), silicon (Si-Si), silicon-carbide (Si-C) and boron-nitride (B-N), while holding the unbuckled equilibrium bond length between first neighbors constant. The potential energy surface was scanned on a grid of one degree per step using the HSE hybrid functional with the 6-21G basis set and periodic

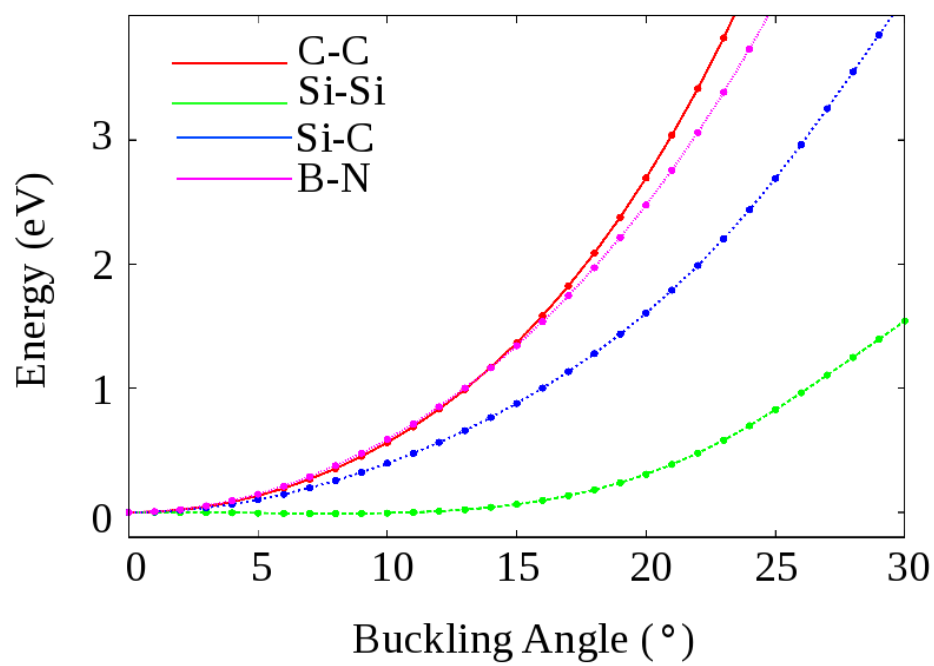


Figure 18. Graphitic carbon (C-C), silicon (Si-Si), silicon-carbide (Si-C) and boron-nitride (B-N) monolayers are bent out of plane at constant bond length.

boundary conditions with the Gaussian 09 software package, which is a method that has been shown to provide good results for graphene. (35).

Graphitic silicon has been the subject of theoretical investigation, but never experimentally observed (260; 261; 262). Yin and Cohen argued that the thermodynamic driving force is too great for graphitic silicon to be stable. Studies of graphitic silicon are still useful because they can help to parameterize empirical methods for molecular dynamics or other modeling efforts. Graphitic boron-nitride (263; 264) and silicon-carbide materials (265; 266), on the other hand, have been observed.

6.3 Interlayer Repulsion in Buckled Graphene Bilayers

Electronic repulsion between layers of graphene gives the characteristic separation of graphite (267; 268). Recent research into the growth of graphene from silicon carbide surfaces by thermal annealing demonstrates that the interfacial graphene layer is buckled with some carbons having partial sp^3 character. Buckling in graphene reduces interlayer electronic repulsion. Lennard-Jones potentials are often used to simulate interactions between graphene layers and other molecules, solvents or surfaces. The important point to recognize here is that the attractive r^6 part of the potential is dispersion. The repulsive r^{12} part of the potential rapidly rises and essentially goes to infinity in the Lennard-Jones model. The r^{12} repulsive Lennard-Jones term is used to approximate the electronic repulsion between layers of graphite in many nonreactive molecular dynamics models, but the scaling is too steep to give an accurate model of the real system.

The highest occupied crystal orbital (HOCO) of a graphene bilayer has asymmetric molecular orbitals in each layer with no overlap, as shown in Figure 19. Consequently, the squeezing of these layers by reducing the distance of separation can increase the energy. As it is the HOCO, the repulsion between layers is purely electronic in nature.

This observation can be extended to pure silicon systems. The HOCO of graphitic silicon is also antisymmetric and the interlayer repulsion is also a consequence of electronic repulsion. However, for graphitic silicon carbide, there is overlap between layers, potentially due to charge transfer from the silicon to the more electronegative carbon.

Buckling of the model graphitic layers can be achieved by imposing a puckering angle on the graphene by breaking the plane with one of the graphitic carbons at a constant bond length. This effectively breaks the symmetry of the HOCO and reduces the interlayer repulsion.

Our model is a four atom buckled graphene bilayer unit cell that interpolates between planar and buckled graphene bilayers as shown in Figure 20. The model depends parametrically on bond length B , buckling angle θ , and interlayer separation Z . We define the bond length as the distance between nearest neighbor carbon atoms. The buckling angle in the bilayer is formed when a carbon atom is displaced vertically from the graphene sheet in the direction of the opposite graphene. The vertex of the angle is an unperturbed atom in the graphene with rays pointing to a neighboring displaced

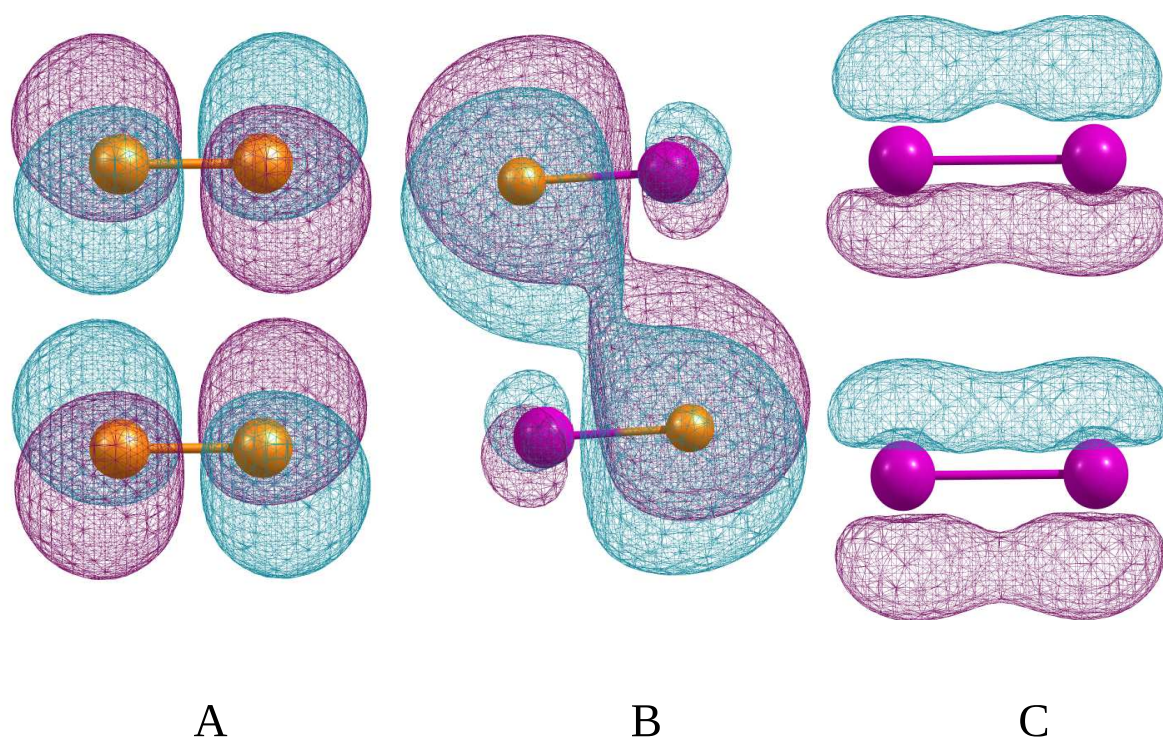


Figure 19. Electronic repulsion between layers of graphite (A) is due to the antisymmetry of the HOMO in separate layers. This is not the case for graphitic silicon carbide (B) but is true for graphitic silicon (C).

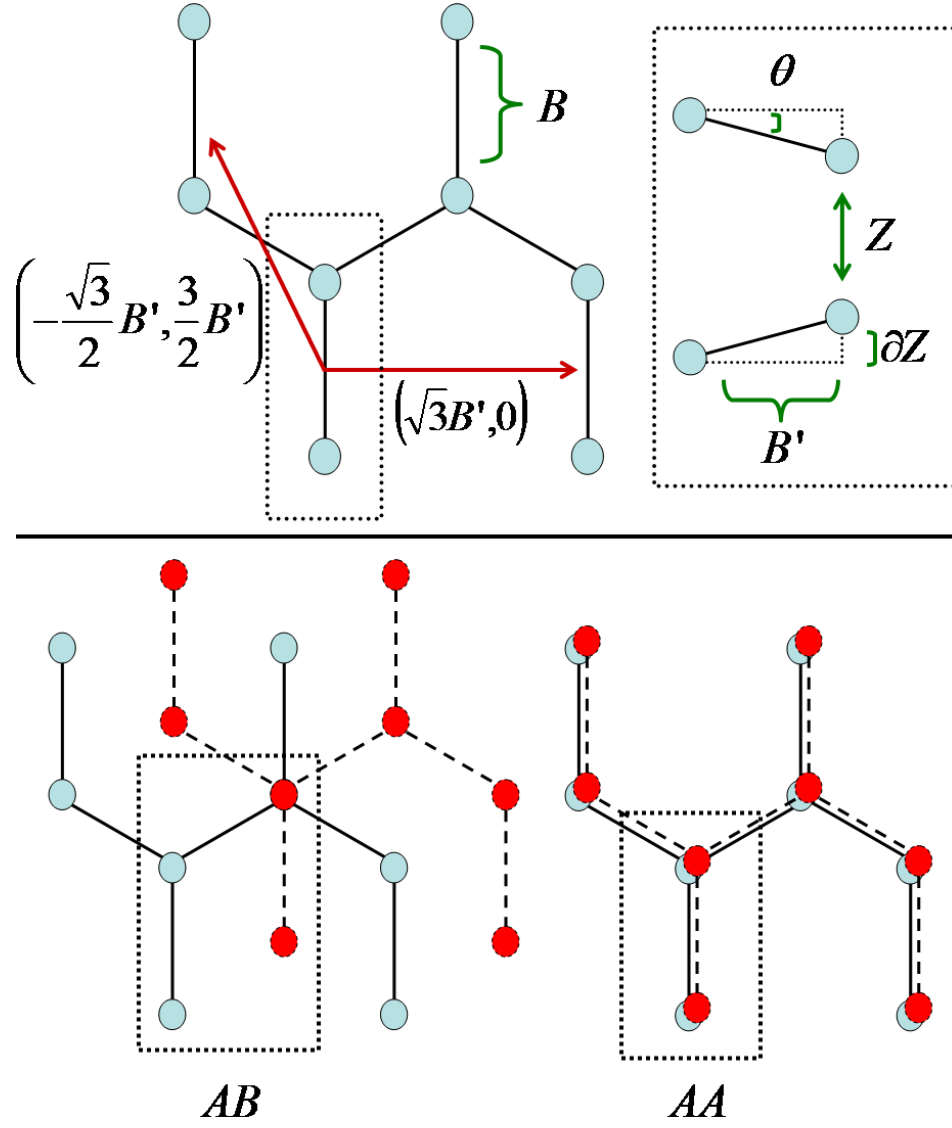


Figure 20. The buckling of a graphitic bilayer can be modeled parametrically with dependence on three variables: bond length (B), buckling angle (θ), and interlayer separation (Z). The x-y plane of a single layer of graphene is shown (left) with translation vectors, and the z plane of an AA stacked bilayer is shown (right) with interlayer separation ∂Z .

TABLE I

GRAPHENE BILAYER COORDINATES AND VECTORS							
AA Bilayer	x	y	z	AB Bilayer	x	y	z
C1	0	$\frac{1}{2}B$	dZ	C1	0	$\frac{1}{2}B$	dZ
C2	0	$-\frac{1}{2}B$	dZ	C2	0	$-\frac{1}{2}B$	dZ
C3	0	$\frac{1}{2}B$	Z-dZ	C3	$\frac{\sqrt{3}}{2}B$	B	Z-dZ
C4	0	$-\frac{1}{2}B$	Z-dZ	C4	$\frac{\sqrt{3}}{2}B$	0	Z-dZ
TV1	$-\frac{\sqrt{3}}{2}B'$	$\frac{3}{2}B'$	0	TV2	$\sqrt{3}B'$	0	0

atom and to the displaced atom's original unperturbed position. We define the interlayer separation Z as the distance between the plane of displaced atoms in each graphene.

Two translation vectors describing the buckled bilayers are fixed at a 120° angle. The magnitude of the translation vectors depend on the projection of the buckled bond on to the XY plane, given as $B' = B \cos \theta$. This means that the bond length between carbon atoms remains fixed, but the translation vectors get shorter with increasing buckling angle. The displacement away from the XY plane by the buckled carbon atoms is given as $dZ = B \sin \theta$. The initial position of the carbon atoms can also be given in terms of these parameters, as shown in Table I. We scan the potential energy surface by varying the interlayer separation variable Z to determine the energy of electronic repulsion between layers for different buckling angles, θ , with fixed bond length, B .

The difference between a buckled graphene monolayer and a buckled graphene bilayer is that the bilayer has a minima in the angle, as shown in Figure 21. The bilayers form

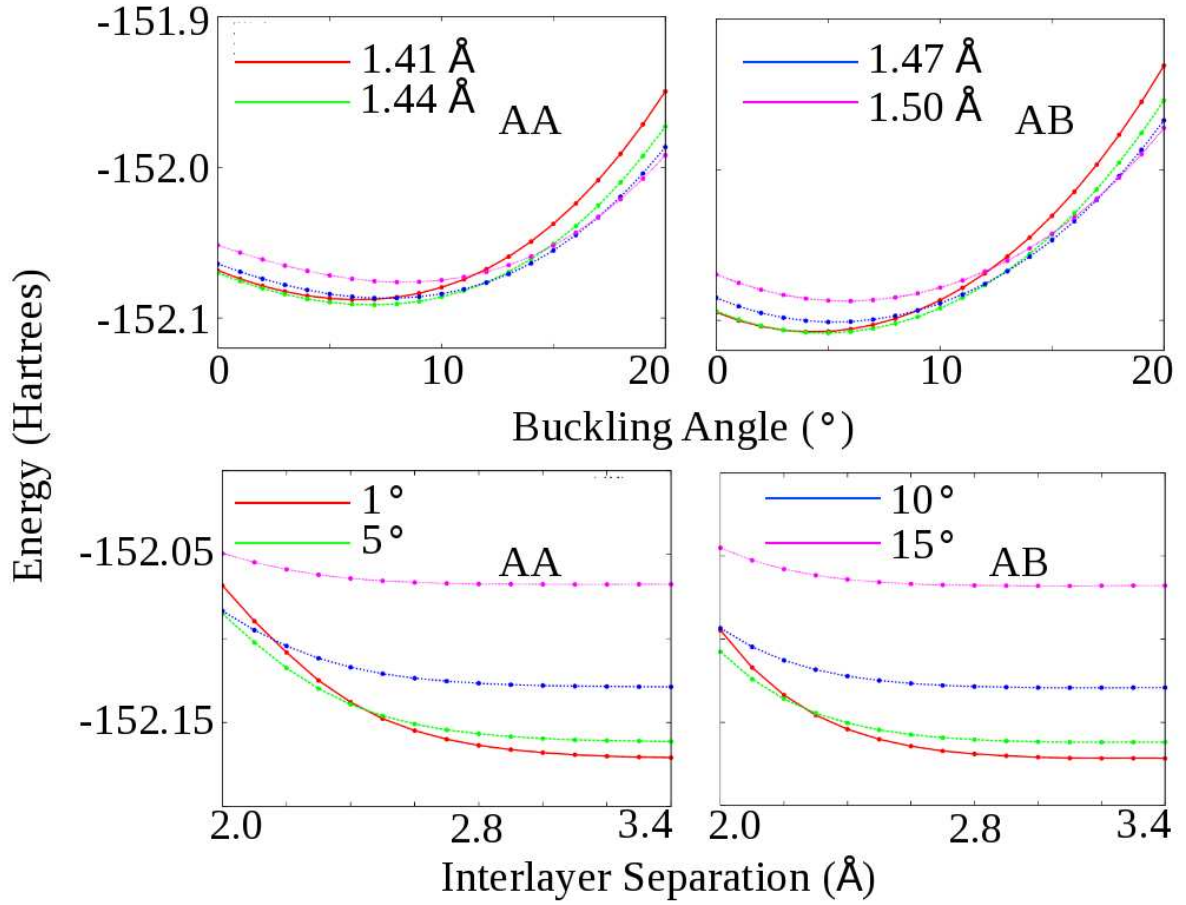


Figure 21. The total energy of a buckled graphene bilayer with respect to buckling angle at constant interlayer separation of 2 Å of an AA stacked graphene bilayer is shown in (upper left) and of an AB stacked graphene bilayer in (upper right). Likewise the total energy of a buckled graphene bilayer with respect to interlayer separation at constant optimal unbuckled graphene bond length is shown (bottom left) and (bottom right).

a bond which stabilizes in a bent configuration. However, the monolayer has no minima meaning that graphene will be very rigid, as shown in Figure 18. This may suggest that a supported graphene monolayer may be more flexible than a monolayer suspended over a gap because there may be some bent configurations where a graphene sheet might stabilize. It also means that bending the angle of planar graphene is very important for the diamond to graphite transition.

6.4 Diamond to Graphite Phase Transition

The diamond to graphite phase transition is a very important model, developed by Kertesz and Hoffmann (269) and later extended to calculate the transition state by Fahy, Louie, and Cohen (270). The diamond-graphite pathway and value of the transition state energy are still used today to benchmark the quality of empirical molecular dynamics potentials and to understand graphitization in diamond materials. In this section we will develop a method of rapidly evaluating the quality of empirical molecular dynamics potentials by scanning the diamond to graphite phase transition.

The model consists of twelve atoms and interpolates between diamond and rhombohedral graphite as shown in Figure 22. This graphitization model uses a similar scheme which depends parametrically on bond length, buckling angle, and interlayer separation. Due to three dimensional periodicity, we introduce a new description of interlayer separation where $S = Z + dZ$. The bond length ranges from 1.41 Å to 1.56 Å, and the buckling angle ranges from 19.47° to 0°, consistent with the graphite to diamond pathway. The

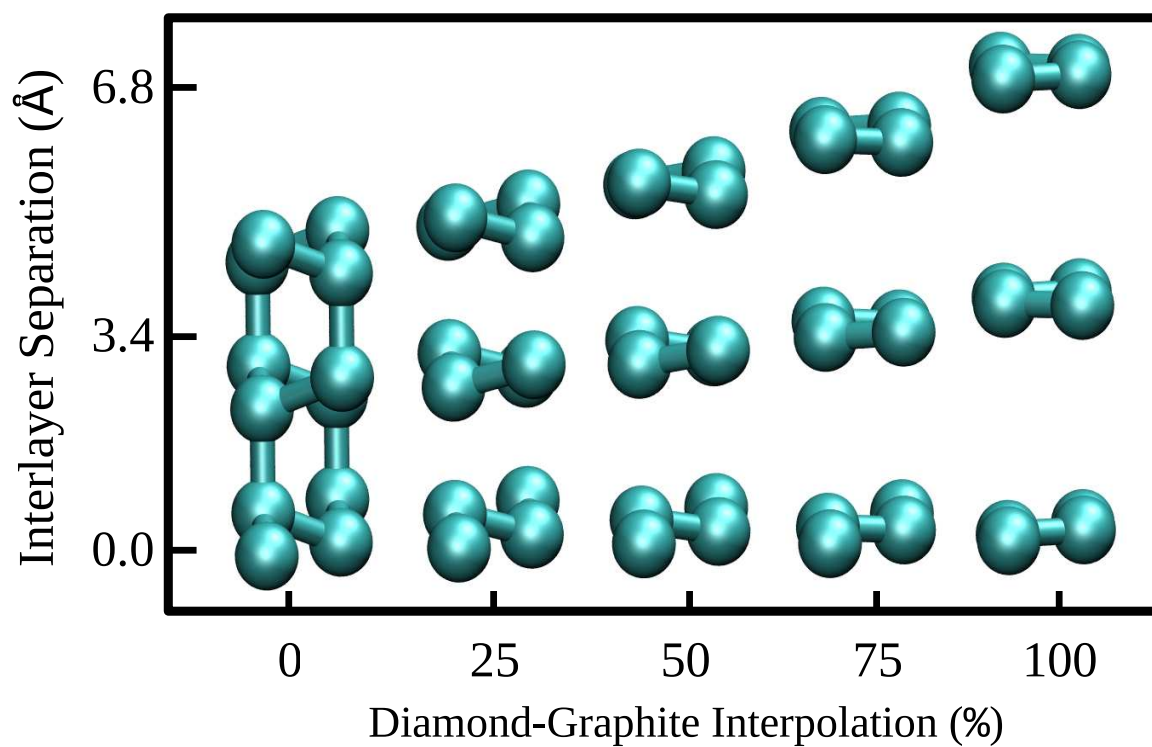


Figure 22. Graphitization of diamond can be modeled as a linear interpolation of bond length, buckling angle, and interlayer separation. Here a 12-atom unit cell of diamond (left) moves through intermediate states (center) with a final state of rhombohedral graphite (right).

TABLE II

DIAMOND TO GRAPHITE COORDINATES AND VECTORS

	x	y	z		x	y	z
C1	0	0	$-\frac{1}{2}\text{dZ}$	C7	0	$2B'$	$S+\frac{1}{2}\text{dZ}$
C2	0	B'	$\frac{1}{2}\text{dZ}$	C8	$\frac{\sqrt{3}}{2}B'$	$\frac{5}{2}B'$	$S-\frac{1}{2}\text{dZ}$
C3	$\frac{\sqrt{3}}{2}B'$	$\frac{3}{2}B'$	$-\frac{1}{2}\text{dZ}$	C9	0	0	$2S+\frac{1}{2}\text{dZ}$
C4	$\frac{\sqrt{3}}{2}B'$	$\frac{5}{2}B'$	$\frac{1}{2}\text{dZ}$	C10	$\frac{\sqrt{3}}{2}B'$	$\frac{1}{2}B'$	$2S-\frac{1}{2}\text{dZ}$
C5	$\frac{\sqrt{3}}{2}B'$	$\frac{1}{2}B'$	$S+\frac{1}{2}\text{dZ}$	C11	$\frac{\sqrt{3}}{2}B'$	$\frac{3}{2}B'$	$2S+\frac{1}{2}\text{dZ}$
C6	0	B'	$S-\frac{1}{2}\text{dZ}$	C12	0	$2B'$	$2S-\frac{1}{2}\text{dZ}$
TV1	$\sqrt{3}B'$	0	0	TV2	0	$3B'$	0
TV3	0	0	3S				

interlayer separation is given as the distance between B' layers which ranges from 2.06 Å to 3.40 Å. The translation vectors in the XY plane are again fixed at a 120° angle with magnitudes depending on the projection of the buckled bond as described before. In addition, a third translation vector orthogonal to the XY plane is included with magnitude depending on interlayer separation, S . With this model we can linearly interpolate each parametric variable V , where V is B , S , or θ . V can be interpolated from the initial condition V_I to the final condition V_F by $V(A) = A * V_I + (1 - A) * V_F$ where A indicates an intermediate fractional state of the diamond to rhombohedral graphite reaction coordinate. This unoptimized pathway can be used to quickly scan the potential energy surface.

We test several molecular dynamics potentials to see how well they match the density functional theory results. The HSE/6-21G model is the benchmark, shown in Figure 23

, and it gets the $\approx 0.33\text{ eV}$ diamond to graphite barrier correctly (270). However the molecular dynamics models all have higher transition state barriers. This may impact simulations by slowing down the kinetic rate of graphitization. On the other hand, DFTB seems to have too low a barrier, potentially leading to predictions of graphitization at a low temperature or a shorter amount of time than observed in experiment. In the next section we will use the AIREBO potential despite its high barrier because it is freely available and gets the interlayer separation correctly. A screening function was implemented for a Tersoff potential. However, the modified potential had deep potential wells which were found to unphysically bind in certain configurations.

6.5 Diamond Nanowire Graphitization

Diamond nanowires are an interesting material which can have a completely diamond core and a slightly graphitic outer layer. Very small diamond nanowires are more properly described as buckywire because the fraction of sp^2 hybridized content is so high relative to the total number of carbon atoms. Extensive structural studies of the nanowires have indicated that the wires are very stable materials which might be useful for applications requiring a relatively chemically inert, physically robust support (271; 272; 273).

The graphitization of diamond-like materials is a fundamental problem with important applications in catalytic production of synthetic fuels. Kinetically stable high density diamond materials are insulating and chemically inert. When heated, growth of graphitic layers on step sites (274) and $\langle 111 \rangle$ planes increases the overall surface area of the

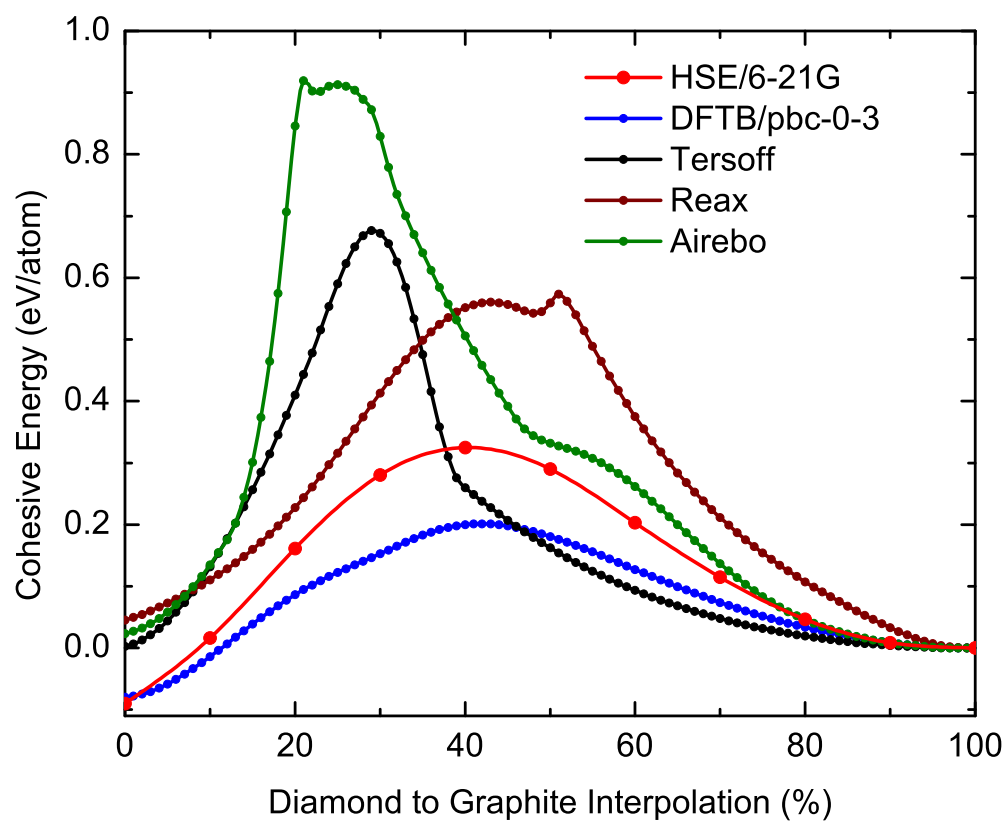


Figure 23. Graphitization of diamond can be modeled as a linear interpolation of bond length, buckling angle, and interlayer separation. A 12-atom unit cell of diamond is interpolated on a grid of one percent per step using DFT, DFTB, and MD methods.

bulk material and unlinks carbon from tetrahedral to trigonal planar geometries. The large surface area and chemical stability of graphitic materials make them promising candidates for catalytic supports. The area of greatest interest is the process by which graphitization occurs after the first layer has formed (275; 244). Experimental results of graphitized hybrid diamond nanowires shows the interlayer separation of graphitic outer layers remains at 3.4 Å while preserving a diamond inner core.

We model the graphitization of diamond nanowires using the AIREBO potential on model systems consisting of 3 basic shapes, 4 different sizes, and 4 different temperatures for a total of 48 variants. The shapes are diamond, hexagon, and cuboctahedron as shown in Figure 24 and are measured in size by counting rings from the center to the outside edge as shown in Figure 25.

Each simulation is minimized and is run at 0.5 fs/step for 2ns (4,000,000 steps) with a Langevin thermostat averaging stochastic kicks so the total momentum is zero. Simulations were run at 2100 K, 1800 K, 1500 K, 1200 K. In addition, two harmonic constraints were put on each half of the atoms to prevent the wire in the simulation from gaining rotational velocity.

The trajectories of the simulation were post-processed to determine the sp^2 fraction of each system. This was accomplished by counting the number of neighbors of each atom that was located within a radius of 1.85 Å. Diamond shaped diamond nanowires graphitize most easily because they only have $\langle 111 \rangle$ surfaces as shown in Figure 27.

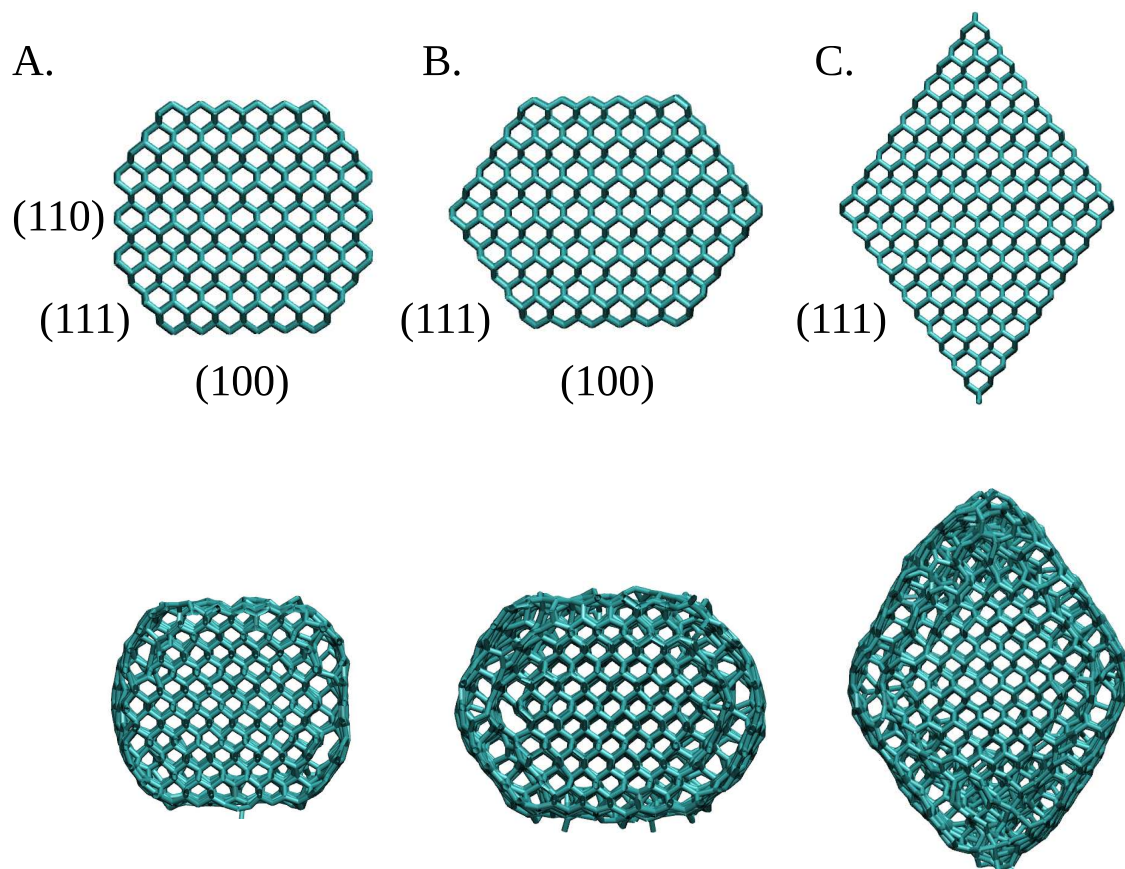


Figure 24. The top row shows pristine (A) cuboctahedron, (B) hexagon, and (C) diamond shaped nanowires. The bottom row shows the graphitized nanowires after $\approx 2ns$ of thermal annealing. The nanowires are oriented to run lengthwise along the $\langle 110 \rangle$ direction with surfaces labeled on the top row.

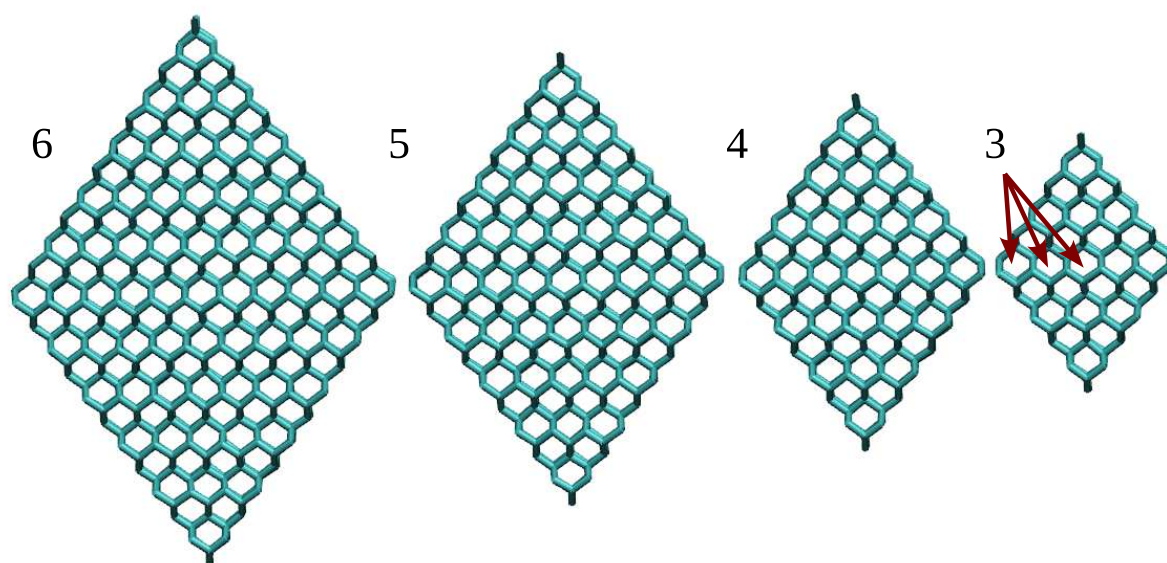


Figure 25. Diamond nanowires are shown in order of size. A method of identifying the width of the wire is shown whereby the number of rings is counted from the center to the outside edge.

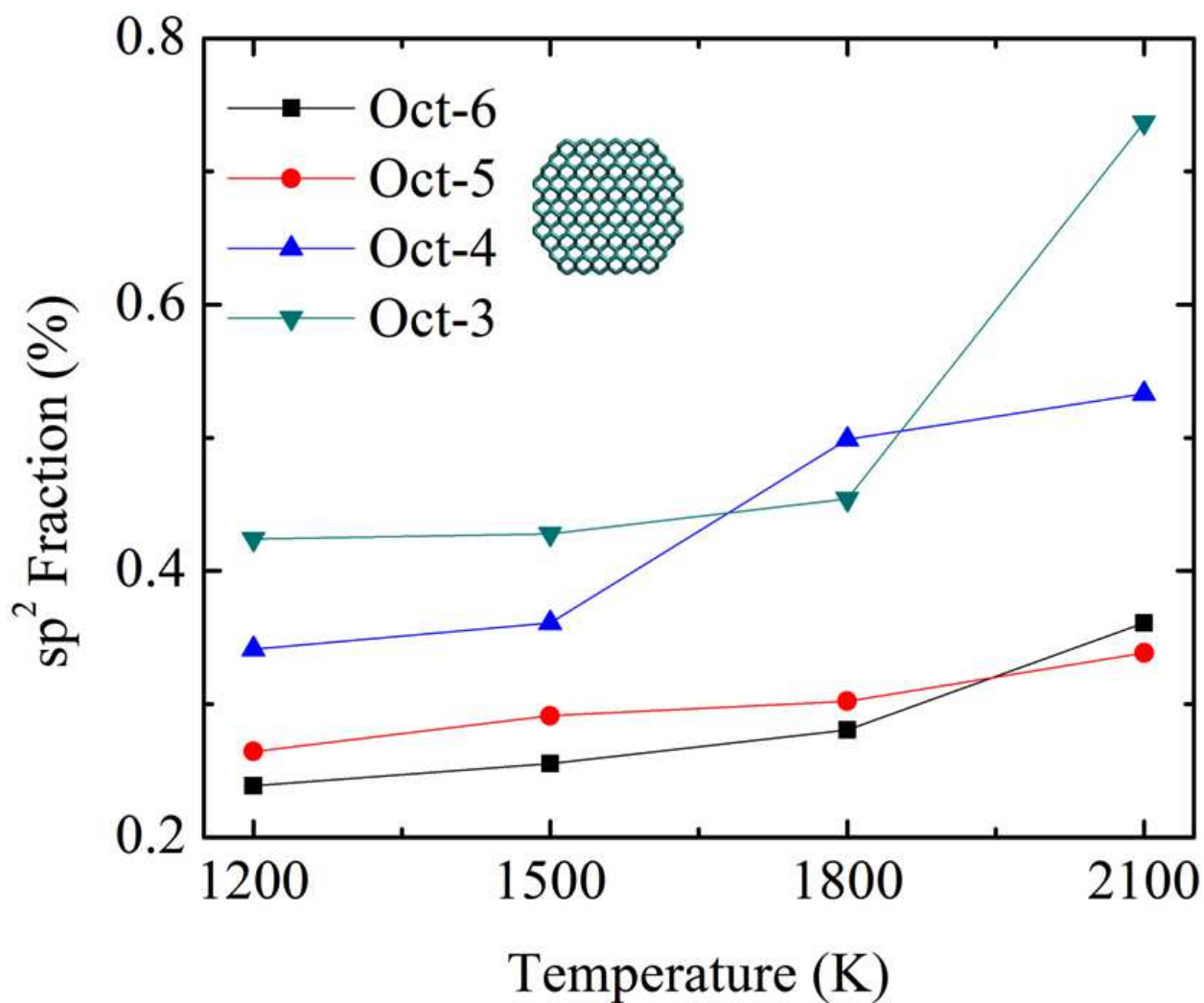


Figure 26. The sp^2 fraction of cuboctahedron shaped diamond nanowires is shown by temperature after 2ns of thermal annealing. Inset is a figure of the initial configuration. The wires have $\langle 100 \rangle$ and $\langle 110 \rangle$ surfaces that are extremely slow to graphitize. Small wires can graphitize suddenly leading to a jump in sp^2 fraction.

These wires had the most onion-like shapes compared to other simulations due to graphitization of interior planes. The slower progress of graphitization in hexagon wires is due to the $\langle 100 \rangle$ surfaces as shown in Figure 28. Unlike the $\langle 111 \rangle$ surfaces, the $\langle 100 \rangle$ surfaces cannot simply form a uniform sp^2 plane. Half the atoms in the $\langle 100 \rangle$ surfaces lie in a trough, meaning that the atoms are separated in space in the direction orthogonal to the axis of the wire. Essentially, to make a graphitic layer, some atoms must join the new graphitic surface and others must burrow deeper. The opposite direction of travel makes graphitization very slow. Lastly, the cuboctahedral nanowires are most resistant to graphitization with both additional $\langle 100 \rangle$ surfaces and $\langle 110 \rangle$ surfaces, as shown in Figure 26.

6.6 Conclusions

As monolayers, graphitic materials are extremely resistant to buckling. However, in bilayer and multilayer graphite materials, buckled layers find bonding states in adjacent layers. The interlayer repulsion in graphitic materials is due to the lack of overlap in the HOCO of the neighboring layers. By buckling the graphite, the previously sp^2 carbon atoms gain sp^3 character as dangling bonds. This change in configuration reduces interlayer repulsion allowing the diamond to graphite transition. The role of buckling and interlayer repulsion can be seen in the graphitization process of diamond nanowires where the $\langle 111 \rangle$ plane is the first to graphitize. As the heated $\langle 111 \rangle$ surface expands, the top layer flattens out gaining sp^2 character and is repelled by the layer

underneath which is also losing buckling angle. In this chapter we have shown monolayer buckling energies, and bilayer interlayer repulsion. We have shown an interpolated model of graphitization to benchmark molecular dynamics methods, and we have shown graphitization in diamond nanowires. Future work will develop more versatile empirical potentials for problems in graphitization.

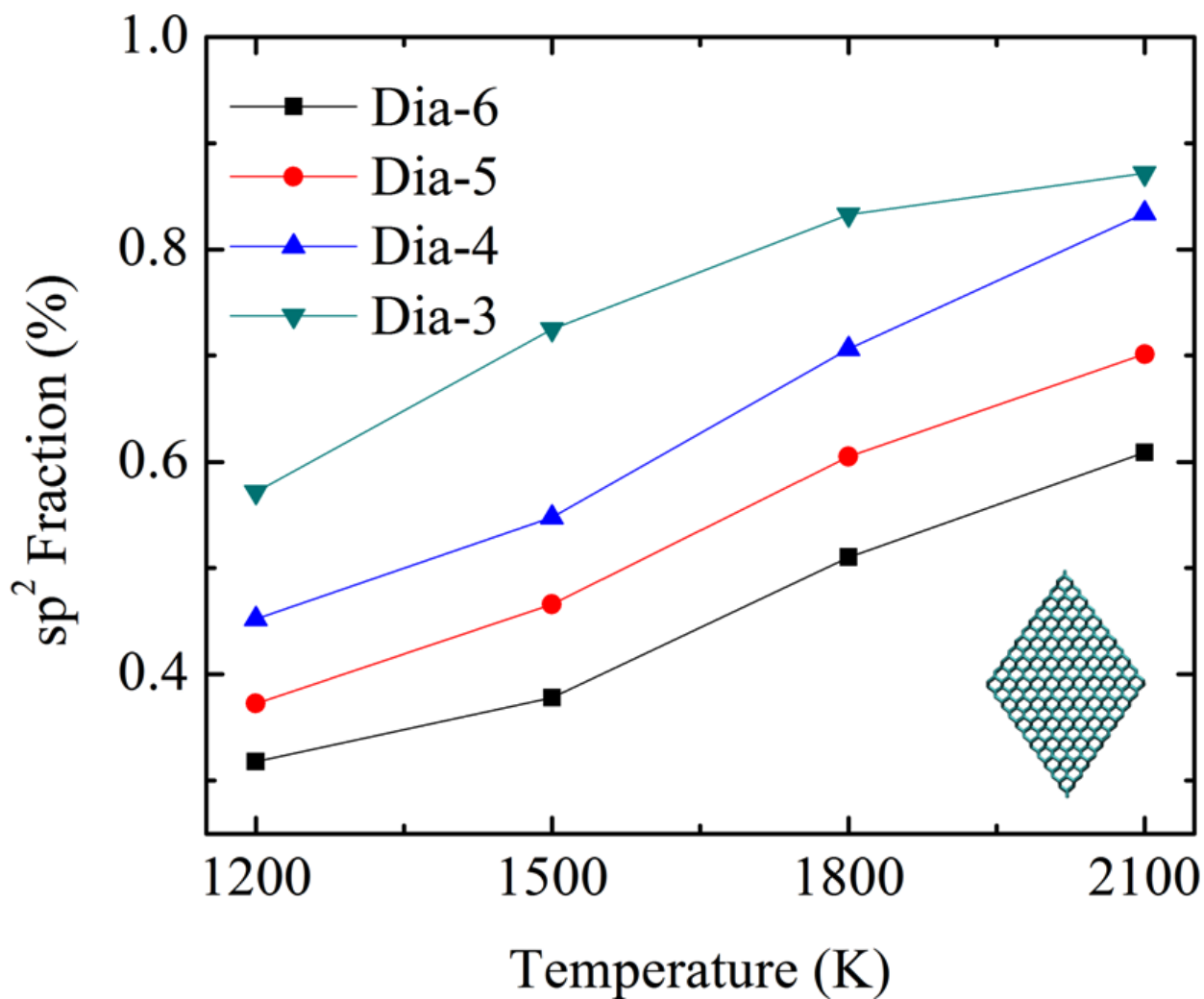


Figure 27. The sp^2 fraction of diamond shaped diamond nanowires is shown by temperature after 2ns of thermal annealing. Inset is a figure of the initial configuration. The wires consist only of $\langle 111 \rangle$ surfaces and therefore graphitize very easily. Larger wires graphitize more slowly than smaller wires.

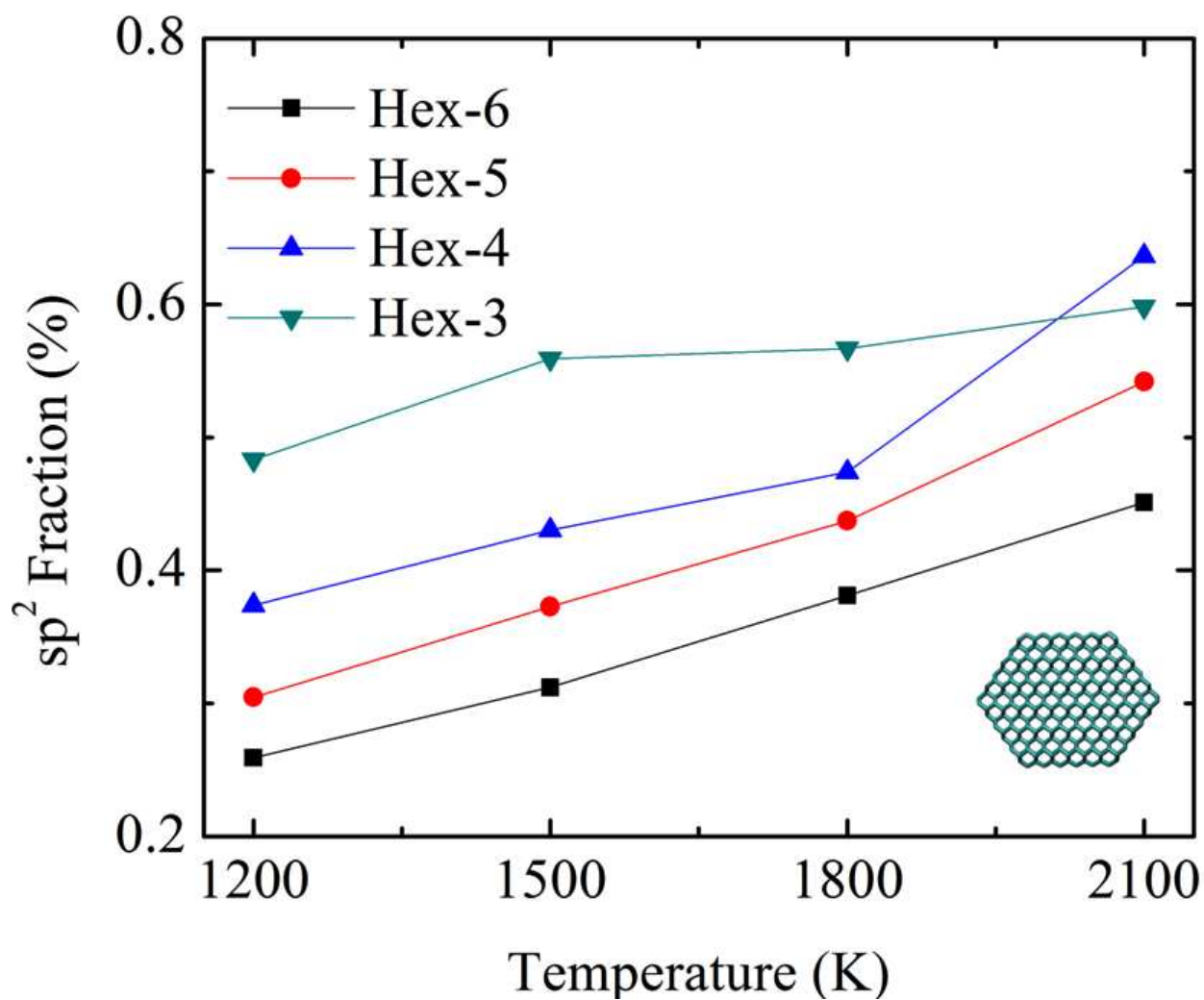


Figure 28. The sp^2 fraction of hexagon shaped diamond nanowires is shown by temperature after 2ns of thermal annealing. Inset is a figure of the initial configuration. The wires have $< 100 >$ surfaces that are extremely slow to graphitize. Small wires can graphitize suddenly leading to a jump in sp^2 fraction.

CHAPTER 7

SHIFTED-SPLINED ELECTROSTATICS METHODS

Electrostatics are a particularly difficult problem in strongly ionic systems because energy contributions decay very slowly with interatomic distance as r^{-1} meaning that they are more computationally expensive due to longer cut off requirements. However, the electrostatic forces drop off much more quickly than the electrostatic potential at r^{-2} . This leads to a problem of how to include electrostatics as a pairwise linear scaling force field with the smallest cut off radius possible. In this chapter, shifted-splined approximations to the electrostatic potential will be explored to provide reasonable results at the lowest possible computational price.

7.1 Introduction

In the early days of molecular dynamics, truncated electrostatic force fields were found to introduce artifacts (55). Because the potential was abruptly cut off at some arbitrary cut off distance r_c , a step function was introduced whereby an atom would feel no force outside the cutting radius and suddenly have a nonzero force applied. The effect was to accumulate water molecules as an artificial hydration shell just outside the cut off distance, which was clearly an unphysical result.

The most common approaches to electrostatics is to divide the potential into a short and long range component. The short range electrostatics are treated pairwise and the

long range is treated in k-space in the Ewald summation, PPPM, and PME methods. The recent and highly successful Wolf summation also divides the potential into short and long range parts but uses a damping function to rapidly converge the long range electrostatics in real space.

7.2 Spline Cutoff Functions

However, there is still a robust interest in electrostatics schemes that have finite cutoffs where the electrostatic potential goes to zero (57; 65). To this end, electrostatics have been treated as shifted potentials, shifted force, and as shifted force gradients. Only the shifted force gradient has been shown to conserve energy for strongly ionic systems (56). The roots of this effect was explained by Zhou (276) for a problem of energy conservation in thermal conductivity simulations of semiconductors using the Tersoff potential. What Zhou found out was that potentials that have non-zero force gradients at the outer cutoff of a potential tend to lose energy conservation. The cause of loss of energy conservation is that the force gradient is discontinuous at the cutoff, meaning that a particle at the cutoff will feel an infinite 'jerk' when it is instantly accelerated at the boundary. The lack of smoothness, meaning second derivative continuous in this context, in a potential causes loss of energy conservation in shifted-potential and shifted-force electrostatic methods.

The solution proposed by Zhou for the Tersoff potential was to spline the potential to zero in the smoothing region of the potential. The original Tersoff cutoff function in the smoothing region can be shown as,

$$\begin{aligned}
 f_C(r_{ij}) &= \frac{1}{2} - \frac{1}{2} \sin \left[\frac{\pi (r_{ij} - R)}{D} \right], |R - r_{ij}| \leq D \\
 f'_C(r_{ij}) &= -\frac{\pi}{4D} \cos \left[\frac{\pi (r_{ij} - R)}{D} \right], |R - r_{ij}| \leq D \\
 f''_C(r_{ij}) &= \frac{\pi^2}{8D^2} \sin \left[\frac{\pi (r_{ij} - R)}{D} \right], |R - r_{ij}| \leq D
 \end{aligned} \tag{7.1}$$

here all parameters are the same as in Equation 2.28 and it is clear that $f''_C \neq 0$ at the outer cutoff where $r_{ij} = R + D$. In the cubic spline method, the smoothing region is divided into three segments with the first segment lying between r_s and r_1 , the second segment lying between r_1 and r_2 , and the third segment lying between r_2 and r_c . The inner cutoff is then $r_s = R - D$, the outer cutoff is $r_c = R + D$ and the inner points are

$r_1 = R - \frac{D}{3}$ and $r_2 = R + \frac{D}{3}$ respectively. The cubic spline cutoff function can be shown as,

$$f_C(r) = \begin{cases} F(r_{ij}), & r_{ij} \leq r_s \\ \sum_{n=0}^2 \frac{F^{(n)}(r_{ij})}{n!} (r_{ij} - r_s)^n + a_3 (r_{ij} - r_s)^3, & r_s < r_{ij} < r_1 \\ \sum_{n=0}^3 b_n (r_{ij} - r_2)^n, & r_1 \leq r_{ij} \leq r_2 \\ c_3 (r_{ij} - r_c)^3, & r_2 < r_{ij} < r_c \\ 0, & r_c < r_{ij} \end{cases} \quad (7.2)$$

where $F(r_{ij})$ is the underlying function that the cut off function modifies, a_3, b_0, b_1, b_2, b_3 , and c_3 are spline coefficients. These coefficients are obtained by setting the cutoff function, first and second derivatives to zero at the cutoff and requiring continuity, including first and second derivatives, at r_s, r_1 , and r_2 . This is very tedious and requires solving these linear equations as a matrix using a Gauss-Jordan or Cramer's Rule method. The analytical functional form of the spline will depend in part on the underlying function, $F(r_{ij})$. In terms of implementation in a molecular dynamics package, two approaches can be made. The first is to calculate the spline coefficients numerically at the beginning of the simulation for every pair of atom types. The second option is to create a table of energies and forces for each atom type pair and interpolate by lookup, linear, or cubic

spline between the fixed known values. The advantage to the numerical approach over a table is numerical stability particularly if the system is not thermostatted.

7.3 Splined Electrostatics

In the context of electrostatics, the cubic spline cutoff is not new. Ding examined optimal spline cutoff conditions for use in a study of dendrimers with the CHARMM and AMBER force fields (277). What they found was that introducing a cubic spline in electrostatics created a “bump” in the force profile as shown in the inset in Figure 29. This error could be reduced by using an extended smoothing range, in effect flattening the force profile. Nevertheless, the real problem is that the force is no longer monotonically decreasing with radius when the electrostatic potential is splined.

The reason why there is a bump is because the potential must drop so quickly to zero. For example (assuming all constants are 1), the electrostatic potential is essentially $\frac{1}{r}$ at $r = 1 \text{ \AA}$ and the force is $\frac{1}{r^2}$. In order for the potential to monotonically decrease in the smoothing region, the force can be no greater than $\frac{1}{r_s^2}$ so the potential must be shifted by a constant so that $V(r_s) = V'(r_s)$ at smoothing region r_s .

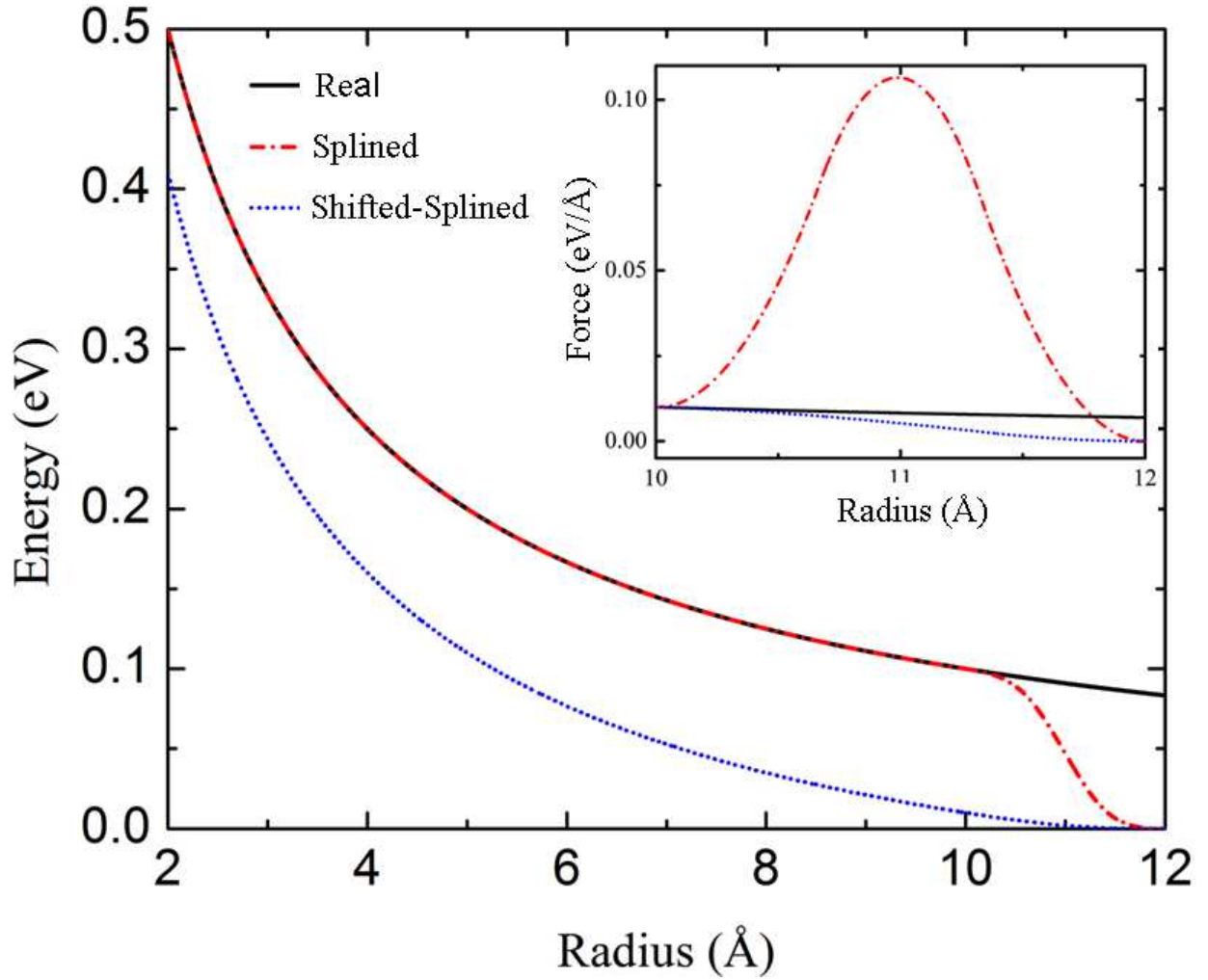


Figure 29. The electrostatic potential between two arbitrary particles is shown for the real, shifted, and shifted-splined variants. Inset is the electrostatic force in the splined region. Splines introduce large bumps in forces unless the potential is also shifted. All constants are set to 1 and the splined region is between 10 – 12 Å. The shifted potential is modified by a constant such that $V_{shift} = V_{coul}(10) - V'_{coul}(10)$.

The clear solution is to introduce a shift to the electrostatic potential so that the potential and the force have the same value at the beginning of the smoothing region.

This can be shown as,

$$V_{coul}(r_{ij}) = \begin{cases} V_{coul}(r_{ij}) - V_{shift}, & r_{ij} \leq r_s \\ \sum_{n=0}^2 \frac{\partial^n}{\partial r_{ij}^n} \left(\frac{V_{coul}(r_{ij}) - V_{shift}}{n!} \right) (r_{ij} - r_s)^n + a_3(r_{ij} - r_s)^3, & r_s < r_{ij} < r_1 \\ \sum_{n=0}^3 b_n(r_{ij} - r_2)^n, & r_1 \leq r_{ij} \leq r_2 \\ c_3(r_{ij} - r_c)^3, & r_2 < r_{ij} < r_c \\ 0, & r_c < r_{ij} \end{cases} \quad (7.3)$$

where V_{coul} is the electrostatic potential, the shift is defined $V_{shift} = V_{coul}(r_s) - V'_{coul}(r_s)$, and the junctions are defined $r_1 = \frac{2}{3}(r_c - r_s)$ and $r_2 = \frac{4}{3}(r_c - r_s)$. The other parameters are as described previously. The result of this shift is to make the potential energy and forces decrease monotonically with radius as can be seen in Figure 29. The disadvantage of this approach is to introduce an error into the potential. However, the forces are $\frac{1}{r^2}$ which decays very quickly. Molecular dynamics relies on forces so the error introduced by a shift in potential is less of a concern.

7.4 Applications to UO_2

Heat dissipation is an important factor in safely using and storing nuclear fuels. Uranium oxide has a low thermal conductivity which can allow temperatures to rise quickly. Uranium and uranium oxide spent fuels are initially stored in water to safely maintain temperatures well below the melting point. Power disruptions from a tsunami interrupted cooling of fuel rods at the Fukushima daiichi power plant resulting in a meltdown (278; 279). Increasing thermal conductivity of fuels will result in a faster cooling rate which could improve safety.

We investigate by molecular dynamics the phonon thermal conductivity of uranium dioxide. The systems were modeled using the LAMMPS molecular dynamics package (280). The fluorite structure of UO_2 (281) is aligned in the (110) direction with lattice constant of 5.46 Å, which increased to 5.52 Å at 1200K. We used a 24.8 nm long block as shown in Figure 30 where the model had a cross section of 2.3 nm x 4.4 nm. The atom count of the UO_2 block is 18144.

We use the partially ionic model (PIM) of the Born-Mayer-Huggins (BMH) potential to model the UO_2 material (282; 283). The PIM features a reduced ionicity with less than full ionic charge on U and O atoms, and it matches the UO_2 lattice constant at

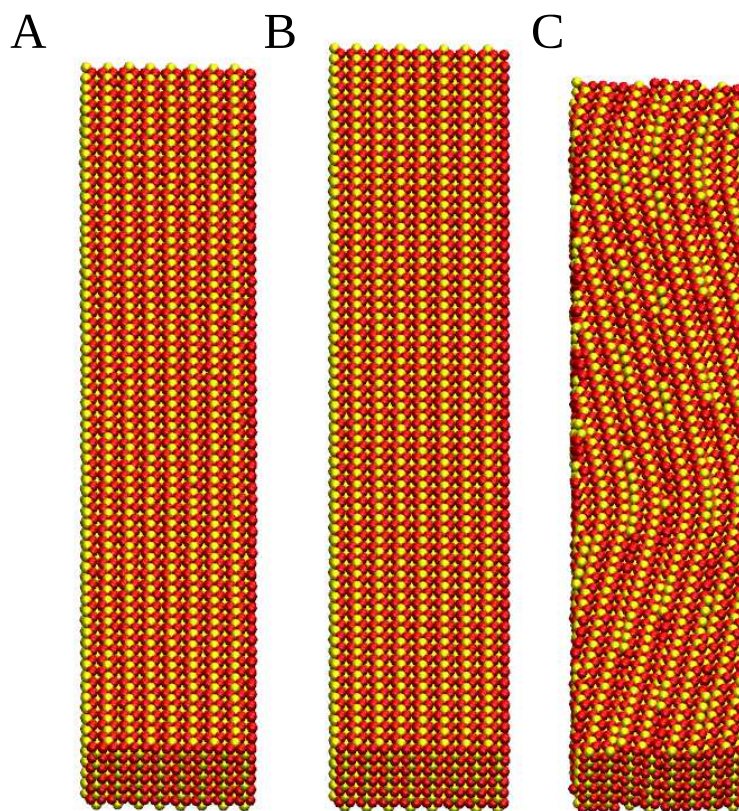


Figure 30. Configuration of 25 nm fluorite UO_2 blocks modeled by (A) PPPM electrostatics method, (B) shifted-splined method with 12 Å and 15 Å inner and outer cutoffs, and (C) shifted-splined method with 10 Å and 12 Å inner and outer cutoffs. The (C) method has too short a cut off and gives incorrect results.

temperatures over 1000K, which a full ionic model gets wrong. This potential is given as,

$$U(r_{ij}) = \frac{z_i z_j e^2}{r_{ij}} + f_0(b_i + b_j) * \exp\left(\frac{a_i + a_j - r_{ij}}{b_i + b_j}\right) - \frac{c_i c_j}{r_{ij}^6} \quad , \quad (7.4)$$

where r_{ij} is the distance between atoms i and j , z_i is the ionic charge of atom i , f_0 is the adjustable parameter (0.434 eV/Å), and c_i is a van der Waals parameter. The parameters are based on thermal expansion and compressibility experimental data (284) and are shown in Table III.

TABLE III

POTENTIAL PARAMETERS				
BMH	z_i	a_i (Å)	b_i (Å)	c_i ($\sqrt{\text{eV}}\text{Å}^3$)
U	2.70	1.318	0.0360	0.0
O	-1.35	1.847	0.1660	4.166

To test the validity of our shifted-spline model, we equilibrated the UO_2 model system using the NPT ensemble for 500 ps (1,000,000 steps). The 12 Å and 15 Å inner and outer cutoffs did a reasonable job of matching the radial distribution function of the

PPPM method as shown in Figure 31. However, the 10 Å and 12 Å inner and outer cutoffs were too short and too inaccurate as shown in Figure 30.

7.5 Thermal Conductivity

To establish a basis of comparison, we performed thermal conductivity calculations with the PPPM method. The shifted-spline method was implemented as a spline-interpolation table and therefore numerical stability for long trajectory calculations in NVE ensemble was insufficient for good comparison when applied to the thermal conductivity problem. Future work will implement the shifted-spline method as an analytic function as an electrostatics pair potential in the LAMMPS package. Here, we show the results for the PPPM thermal conductivity calculation.

We use the Muller-Plathe method (285) of nonequilibrium molecular dynamics to calculate the thermal conductivity of the pure oxide. The simulation cell is divided into slabs in the direction of heat flux. We used 80 slabs for 24.8 nm blocks. The highest velocities of the atoms in the slab at the boundaries are swapped with the lowest velocities of atoms with the same mass in the center slab at a rate of 1 swap per 250 steps for each atom type. This generates a thermal gradient while conserving energy and momentum. The thermal conductivity can be calculated as

$$\lambda = -\frac{\sum_{transfers} \frac{m}{2}(v_h^2 - v_c^2)}{2tA_{xy} < \partial T / \partial z >} \quad , \quad (7.5)$$

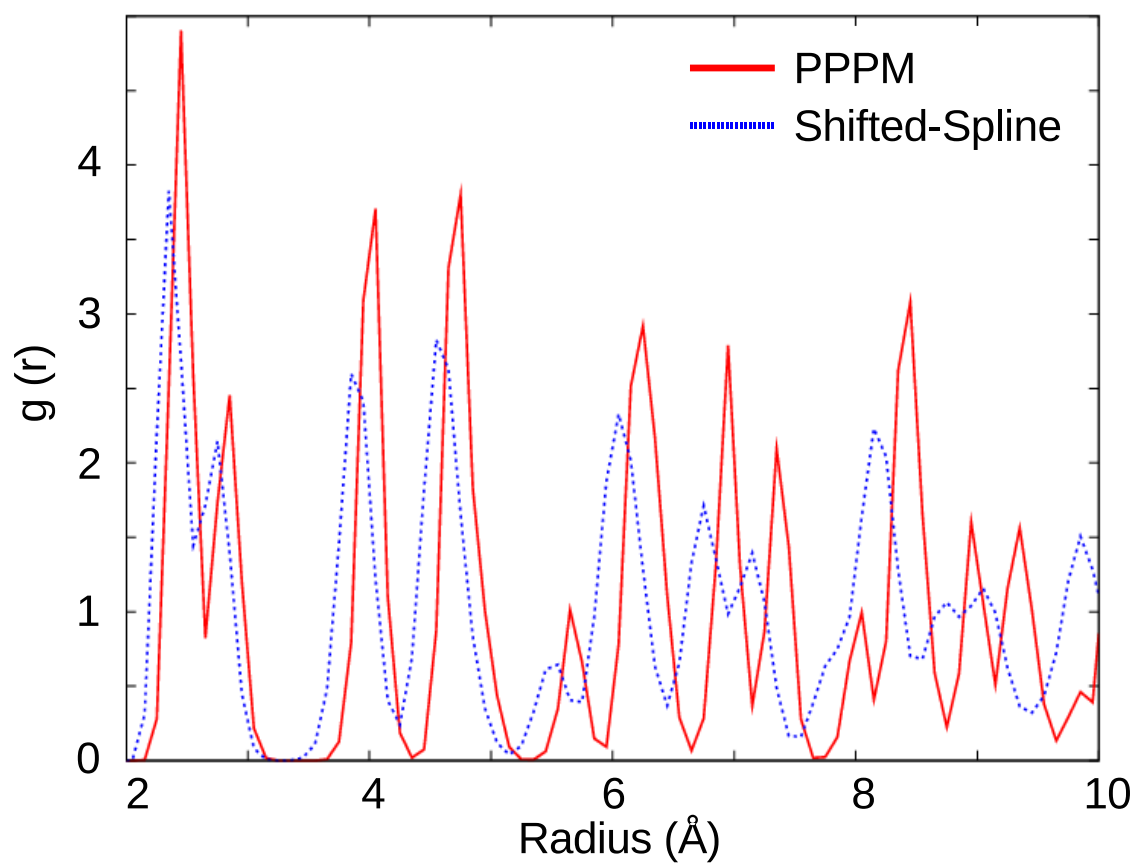


Figure 31. Radial distribution function of fluorite UO_2 model with PPPM and shifted-spline model using 12 $\text{\AA}$ and 15 $\text{\AA}$ inner and outer cutoffs.

where λ is the thermal conductivity, m is the exchanged atomic mass, v_h and v_c are the hot and cold velocities, t is the cumulative time of the simulation during which exchanges occur, A is the cross sectional area from which atoms are exchanged, and $\langle \partial T / \partial z \rangle$ is the average change in temperature per slab length.

The simulations were run with a time step of 0.5 fs. The systems were thermalized for 500 ps with a NPT ensemble using a Nose-Hoover thermostat at 1000K temperature. When thermalization completed, the ensemble was changed to NVE and the simulation continued with the Muller-Plathe reverse nonequilibrium dynamics for 1.0 ns. The CNT simulations were thermalized for 1.0 ns in a NPT ensemble and then continued with nonequilibrium dynamics for 5.0 ns.

TABLE IV

THERMAL CONDUCTIVITY			
Components	Length (nm)	Cross Section (nm ²)	Therm. Cond. K (W/mK)
UO ₂	24.5	10.3	3.99
UO ₂	49.1	10.3	4.47
Components	α	K_∞ (W/mK)	
UO ₂	13.252	5.1	

The thermal conductivity of an infinitely long block of UO_2 can be estimated by graphical methods. Our models are of finite length and we can plot the thermal conductivity as a function of inverse length. This can be shown as,

$$\frac{1}{K} = \frac{1}{K_\infty} + \frac{\alpha}{L} \quad (7.6)$$

where α is a parameter, K is the thermal conductivity at a finite length L , and K_∞ is the thermal conductivity at an infinite length. In this method, the thermal conductivity at infinite length is the y-intercept of the plot.

The thermal conductivity of UO_2 bulk has been calculated using Kubo-Green methods to be approximately 4.5 W/mK and shown experimentally to be approximately 4.5 W/mK at 1000K (282; 283). Our results give 5.1 W/mK, as shown in Table IV, using the PPPM method of electrostatics. It is clear that the model will have to be run for much longer averaging and future work will attempt to use a shifted-spline method for the thermal conductivity problem.

7.6 Conclusions

In this chapter, a shifted-spline approach to electrostatics was developed and then applied to UO_2 , a strongly ionic system. The result was that a shifted-spline potential with inner and outer cutoffs of 12 and 15 angstroms gave approximately 30% faster calculation than a PPPM calculation with 1.0×10^{-4} forces convergence for the same

number of steps. Future work will implement the shifted-spline method as an analytic function as an electrostatics pair potential in the LAMMPS package.

CHAPTER 8

CONCLUDING REMARKS

The future of graphitic carbon as a support material at the nanoscale is very bright. In the the first project, first principles were used to model the C-H bond breaking of methane on supported Pt and Pd catalysts. In the second project, molecular dynamics models showed the transport of water droplet on carbon nanotubes by coherent vibrations. The third project discussed the selective binding of molecules to electrostatic nests on doped graphene and configuration-sensitive sensing by vibration. In the fourth project, problems in buckled graphitic materials were explored including the graphitization of diamond wires by thermal annealing. Finally, in the last project, computationally inexpensive techniques for modeling electrostatics were developed for strongly ionic materials.

The problem facing nanotechnology is a problem of scale. Nanomachines are very promising with the potential to manipulate assemblies of several thousand atoms or capture molecules on functionalized surfaces. However the ability to manipulate a few molecules with a high degree of precision does not translate into an ability to manipulate large quantities of atoms at a high degree of precision. Likewise subnanometer metal clusters are extremely successful catalysts. A significant concern might be how to stabilize these clusters against degradation and still retain the catalytic properties.

Nevertheless, devices at the nanoscale have enormous potential to perform tasks that at larger scale would require greater energy inputs, size requirements, and with less sensitivity. The success of diamond nanoparticles as substrates for chemotherapy is a huge advance that allows doctors to give patients less drug with fewer side effects that works better than traditional approaches (5). Nanotechnology, like drug discovery, is moving past trial- and-error approaches that waste valuable time and resources. As computer power rapidly increases and theoretical models are able to take advantage of it, computational modeling the design of materials and devices will be able to provide increasingly accurate predictions to guide experimental efforts. The future of computational chemistry looks very bright indeed!

CITED LITERATURE

1. Krauss, A., Auciello, O., Gruen, D., Jayatissa, A., Sumant, A., Tucek, J., Mancini, D., Moldovan, N., Erdemir, A., Ersoy, D., Busmann, M. G. H., Meyerg, E., and Dingh, M.: Ultrananocrystallinediamond thin films for MEMS and moving mechanical assembly devices. Diamond Relat. Mater., 10:1952–1961, 2001.
2. Los, J. H., Pineau, N., Chevrot, G., Vignoles, G., and Leyssale, J.-M.: Formation of multiwall fullerenes from nanodiamonds studied by atomistic simulations. Phys. Rev. B, 80:155420, 2009.
3. Pol, V. G., Motiei, M., Gedanken, A., Calderon-Moreno, J., and Yoshimura, M.: Carbon spherules: synthesis, properties and mechanistic elucidation. Carbon, 42:111–116, 2004.
4. Pastewka, L., Moser, S., Gumbsch, P., and Moseler, M.: Anisotropic mechanical amorphization drives wear in diamond. Nat. Mater., 10:34–38, 2011.
5. Chow, E. K., Zhang, X.-Q., Chen, M., Lam, R., Robinson, E., Huang, H., Schaffer, D., Osawa, E., Goga, A., and Ho, D.: Nanodiamond therapeutic delivery agents mediate enhanced chemoresistant tumor treatment. Sci. Transl. Med., 3:73ra21, 2011.
6. Iijima, S.: Direct observation of the tetrahedral bonding in graphitized carbon black by high resolution electron microscopy. J. Crys. Growth, 50:675–680, 1980.
7. Guo, T., Nikolaev, P., Rinzler, A. G., Tomanek, D., Colbert, D. T., and Smalley, R. E.: Self-assembly of tubular fullerenes. J. Phys. Chem., 99:10694–10697, 1995.
8. Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D., Zhang, Y., Dubonos, S. V., Grigorieva, I. V., and Firsov, A. A.: Electric field effect in atomically thin carbon films. Science, 22:666–669, 2004.
9. Zhu, Y., Murali, S., Stoller, M. D., Ganesh, K. J., Cai, W., Ferreira, P. J., Pirkle, A., Wallace, R. M., Cyhosh, K. A., Thommes, M., Su, D., Stach, E. A.,

- and Ruoff, R. S.: Carbon-based supercapacitors produced by activation of graphene. Science, 332:1537–1541, 2011.
10. Hewitt, C. A., Kaiser, A. B., Roth, S., Craps, M., Czerw, R., and Carroll, D. L.: Multilayered carbon nanotube/polymer composite based thermoelectric fabrics. Nano Lett., 12:1307–1310, 2012.
 11. Hartree, D. R.: The wave mechanics of an atom with a non-coulomb central field. Part I. Theory and Methods. Proc. Cambridge Phil. Soc., 24:89–110, 1928.
 12. Levine, I. N.: Quantum Chemistry. Upper Saddle River, NJ, Prentice Hall, 6 edition, 2008.
 13. Blinder, S. M.: Basic concepts of self-consistent-field theory. Am. J. Phys., 33:431–443, 1965.
 14. Simons, J.: Equations of motion methods for computing electron affinities and ionization potentials. In Theory and Applications of Computational Chemistry: The First Forty Years, eds. C. E. Dykstra, G. Scuseria, G. Frenking, and K. S. Kim, pages 443–461. Amsterdam, Elsevier Science, 2005.
 15. Curtiss, L. A., Redfern, P. C., Raghavachari, K., and Pople, J. A.: Gaussian-3 theory: a variation based on third-order perturbation theory and an assessment of the contribution of core-related correlation. Chem. Phys. Lett., 313:600–607, 1999.
 16. Raghavachari, K. and Anderson, J. B.: Electron correlation effects in molecules. J. Phys. Chem., 100:12960–12973, 1996.
 17. Koch, W. and Holthausen, M. C.: A Chemists Guide to Density Functional Theory. Morlenbach, WILEY-VCH Verlag GmbH, 2001.
 18. Lowdin, P.-O.: Quantum theory of many-particle systems. III. Extension of the Hartree-Fock scheme to include degenerate systems and correlation effects. Phys. Rev., 97:1509–1520, 1955.
 19. Cramer, C. J. and Truhlar, D. G.: Density functional theory for transition metals and transition metal chemistry. Phys. Chem. Chem. Phys., 11:10757–10816, 2009.

20. Becke, A. D.: A new mixing of hartree-fock and local density-functional theories. J. Chem. Phys., 98:1372–1377, 1993.
21. Lee, C., Yang, W., and Parr, R. G.: Development of the colle-salvetti correlation-energy formula into a functional of the electron density. Phys. Rev. B, 37:785–789, 1988.
22. Perdew, J. P. and Schmidt, K.: Jacob’s ladder of density functional approximations for the exchange-correlation energy. AIP Conf. Proc., 577:1–20, 2001.
23. Heyd, J., Scuseria, G. E., and Ernzerhof, M.: Hybrid functionals based on a screened coulomb potential. J. Chem. Phys., 118:8207–8215, 2003.
24. Hohenberg, P. and Kohn, W.: Inhomogeneous electron gas. Phys. Rev., 136:B864–B871, 1964.
25. Kohn, W. and Sham, L. J.: Self-consistent equations including exchange and correlation effects. Phys. Rev., 140:A1133–A1138, 1965.
26. Pople, J. A., Gill, P. M. W., and Johnson, B. G.: Kohn-Sham density-functional theory within a finite basis set. Chem. Phys. Lett., 199:557–560, 1996.
27. Perdew, J. P., Burke, K., and Ernzerhof, M.: Generalized gradient approximation made simple. Phys. Rev. Lett., 77:3865–3868, 1996.
28. Perdew, J. P. and Wang, Y.: Accurate and simple analytic representation of the electron-gas correlation energy. Phys. Rev. B, 45:13244–13249, 1992.
29. van de Walle, A. and Ceder, G.: Correcting overbinding in local-density-approximation calculations. Phys. Rev. B, 59:14992–15001, 1999.
30. Perdew, J. P., Ruzsinszky, A., Constantin, L. A., Sun, J., and Csonka, G. I.: Some fundamental issues in ground-state density functional theory: A guide for the perplexed. J. Chem. Theory Comput., 5:902–908, 2009.
31. Stephens, P. J., Devlin, F. J., Chabalowski, C. F., and Frisch, M. J.: Ab initio calculation of vibrational absorption and circular dichroism spectra using density functional force fields. J. Phys. Chem., 98:11623–11627, 1994.

32. Becke, A. D.: Density-functional exchange-energy approximation with correct asymptotic behavior. Phys. Rev. A, 38:3098–3100, 1988.
33. Curtiss, L., Raghavachari, K., Trucks, G. W., and Pople, J. A.: Gaussian-2 theory for molecular energies of first- and second-row compounds. J. Chem. Phys., 94:7221–7230, 1991.
34. Kudin, K. N.: Linear Scaling Density Functional Theory with Gaussian Orbitals and Periodic Boundary Conditions. Ph.d. thesis, Rice University, Houston, TX, 2000.
35. Avramov, P. V., Sakai, S., Entani, S., Matsumoto, Y., and Naramoto, H.: Abinitio lc-dft study of graphene, multilayergraphenes and graphite. Chem. Phys. Lett., 508:86–89, 2011.
36. Yousaf, K. E. and Brothers, E. N.: Applications of screened hybrid density functionals with empirical dispersion corrections to rare gas dimers and solids. J. Chem. Theory Comput., 6:864–872, 2010.
37. Perdew, J. P., Ernzerhof, M., and Burke, K.: Rationale for mixing exact exchange with density functional approximations. J. Chem. Phys., 105:9982–9984, 1996.
38. Dear, M. J. S. and Thiel, W.: Ground states of molecules. 38. The MNDO Method. Approximations and parameters. J. Am. Chem. Soc., 99:4899–4907, 1977.
39. Dewar, M. J. S., Zoebisch, E. G., Healy, E. F., and Stewart, J. J. P.: Development and use of quantum mechanical molecular models. 76. AM1: a new general purpose quantum mechanical molecular model. J. Am. Chem. Soc., 107:3902–3909, 1985.
40. Stewart, J. J. P.: Optimization of parameters for semiempirical methods v: Modification of NDDO approximations and application to 70 elements. J. Molec. Model., 11:1173–1213, 2007.
41. Pople, J. and Beveridge, D. L.: Approximate Molecular Orbital Theory. USA, McGraw-Hill, 1970.

42. Slater, J. C. and Koster, G. F.: Simplified lcao method for the periodic potential problem. Phys. Rev., 94:1498–1524, 1954.
43. Paxton, A. T.: An introduction to the tight binding approximation implementation by diagonalisation. In Multiscale Simulation Methods in Molecular Sciences, eds. J. Grotendorst, N. Attig, S. Blugel, and D. Marx, pages 145–176. Julich, Julich Supercomputing Centre, 2009.
44. Foulkes, W. M. C. and Haydock, R.: Tight-binding models and density-functional theory. Phys. Rev. B, 39:12520–12536, 1989.
45. Porezag, D., Frauenheim, T., Kohler, T., Seifert, G., and Kaschner, R.: Construction of tight-binding-like potentials on the basis of density-functional theory: Application to carbon. Phys. Rev. B, 51:12947–12957, 1995.
46. Sternberg, M., Galli, G., and Frauenheim, T.: NOON - a non-orthogonal localised orbital order-n method. Comp. Phys. Comm., 118:200–212, 1999.
47. Elstner, M.: SCC-DFTB: what is the proper degree of self-consistency? J. Phys. Chem. A, 111:5614–5621, 2007.
48. Seifert, G.: Tight-binding density functional theory: An approximate Kohn-Sham DFT scheme. J. Phys. Chem. A, 111:5609–5613, 2007.
49. Aradi, B., Hourahine, B., and Frauenheim, T.: DFTB+, a sparse matrix-based implementation of the DFTB method. J. Phys. Chem. A, 111:5678–5684, 2007.
50. Koskinen, P. and Makinen, V.: Density-functional tight-binding for beginners. Comp. Mat. Sci., 47:237–253, 2009.
51. Rahman, A.: Correlations in the motion of atoms in liquid argon. Phys. Rev., 136:A405–A411, 1964.
52. Alder, B. J. and Wainwright, T. E.: Studies in molecular dynamics. I. General methods. J. Chem. Phys., 31:459–466, 1959.

53. Phillips, J. C., Braun, R., Wang, W., Gumbart, J., Tajkhorshid, E., Villa, E., Chipot, C., Skeel, R. D., Kale, L., and Schulten, K. J.: Scalable molecular dynamics with NAMD. J. Comput. Chem., 26:1781–1802, 2005.
54. MacKerell, J. A., Bashford, D., Bellott, M., Dunbrack, J. R. L., Evanseck, J. D., Field, M. J., Fischer, S., Gao, J., Guo, H., Ha, S., Joseph-McCarthy, D., Kuchnir, L., Kuczera, K., Lau, F. T. K., Mattos, C., Michnick, S., Ngo, T., Nguyen, D. T., Prodhom, B., Reiher, III, W. E., Roux, B., Schlenkrich, M., Smith, J. C., Stote, R., Straub, J., Watanabe, M., Wirkiewicz-Kuczera, J., Yin, D., and Karplus, M.: All-atom empirical potential for molecular modeling and dynamics studies of proteins. J. Phys. Chem. B, 105:3586–3617, 1998.
55. Loncharich, R. J. and Brooks, B. R.: The effects of truncating long-range forces on protein dynamics. Proteins:Proteins Struct. Funct. Bioinf., 6:32–45, 1989.
56. Kale, S. and Herzfeld, J.: Pairwise long-range compensation for strongly ionic systems. J. Chem. Theory Comput., 7:3620–3624, 2011.
57. Hansen, J. S., Schroder, T. B., and Dyre, J.: Simplistic Coulomb forces in molecular dynamics: Comparing the Wolf and shifted-force approximation. J. Phys. Chem. B, 116:5738–5743, 2012.
58. Ewald, P. P.: Die berechnung optischer und elektrostatischer gitterpotentiale. Ann. Phys., 369:253–287, 1921.
59. Hockney, R. W., Goel, S. P., and Eastwood, J. W.: A 10000 particle molecular dynamics model with long range forces. Chem. Phys. Lett., 21:589–591, 1973.
60. Eastwood, J. W.: Optimal particle-mesh algorithms. J. Comput. Phys., 18:1–20, 1975.
61. Darden, T., York, D., and Pedersen, L.: Particle mesh Ewald: An $N \cdot \log(N)$ method for Ewald sums. J. Chem. Phys., 98:10089–10092, 1993.
62. Wolf, D., Keblinski, P., Philpot, S. R., and Eggebrecht, J.: Exact method for the simulation of Coulombic systems by spherically truncated, pairwise r^{-1} summation. J. Chem. Phys., 110:8254–8283, 1999.

63. Fennell, C. J. and Gezelter, J. D.: Is the Ewald summation still necessary? Pairwise alternatives to the accepted standard for long-range electrostatics. J. Chem. Phys., 124:234104, 2006.
64. Fukuda, I., Yonezawa, Y., and Nakamura, H.: Molecular dynamics scheme for precise estimation of electrostatic interaction via zero- dipole summation principle. J. Chem. Phys., 134:164107, 2011.
65. Toxvaerd, S. and Dyre, J. C.: Communication: Shifted forces in molecular dynamics. J. Chem. Phys., 134:081102, 2011.
66. Mao, Z., Garg, A., and Sinnott, S. B.: Molecular dynamics simulations of the filling and decorating of carbon nanotubes. Nanotechnology, 10:273–277, 1999.
67. Grimme, S.: Accurate description of van der Waals complexes by density functional theory including empirical corrections. J. Comput. Chem., 25:1463–1473, 2004.
68. Grimme, S.: Semiempirical GGA-type density functional constructed with a long-range dispersion correction. J. Comput. Chem., 27:1787–1798, 2006.
69. Grimme, S., Antony, J., Ehrlich, S., and Krieg, H.: A consistent and accurate ab initio parameterization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. J. Chem. Phys., 132:154104, 2010.
70. London, F.: The general theory of molecular forces. Trans. Faraday Soc., 33:8b–26, 1937.
71. Daw, M. S. and Baskes, M. I.: Semiempirical, quantum mechanical calculation of hydrogen embrittlement in metals. Phys. Rev. Lett., 50:1285–1288, 1983.
72. Daw, M. S. and Baskes, M. I.: Embedded-atom method: Derivation and application to impurities, surfaces, and other defects in metals. Phys. Rev. B, 29:6443–6453, 1984.
73. Finnis, M. W. and Sinclair, J. E.: A simple empirical N-body potential for transition metals. Phil. Mag. A, 50:45–55, 1984.

- 74. Sutton, A. P. and Chen, J.: Long-range Finnis–Sinclair potentials. Phil. Mag. Lett., 61:139–146, 1990.
- 75. Gupta, R. P.: Lattice relaxation at a metal surface. Phys. Rev. B, 23:6265–6270, 1981.
- 76. Tersoff, J.: New empirical model for the structural properties of silicon. Phys. Rev. Lett., 56:632–635, 1986.
- 77. Stillinger, F. H. and Weber, T. A.: Computer simulation of local order in condensed phases of silicon. Phys. Rev. B, 31:5262–5271, 1985.
- 78. Abell, G. C.: Empirical chemical pseudopotential theory of molecular and metallic bonding. Phys. Rev. B, 31:6184–6196, 1985.
- 79. Ferrante, J., Smith, J. R., and Rose, J. H.: Diatomic molecules and metallic adhesion, cohesion, and chemisorption: A single binding-energy relation. Phys. Rev. Lett., 50:1385–1386, 1983.
- 80. Rose, J. H., Smith, J. R., and Ferrante, J.: Universal features of bonding in metals. Phys. Rev. B, 28:1835–1845, 1983.
- 81. Ferrante, J., Smith, J. R., and Rose, J. H.: Universal binding energy relations in metallic adhesion. Proceedings of the 34th International Meeting of the Socit de Chimie Physique, 7:19–30, 1982.
- 82. Brenner, D. W.: The art and science of an analytic potential. Phys. Stat. Sol. (b), 217:23–40, 2000.
- 83. Tersoff, J.: New empirical approach for the structure and energy of covalent systems. Phys. Rev. B, 37:6991–7000, 1988.
- 84. Tersoff, J.: Modeling solid-state chemistry: Interatomic potentials for multicomponent systems. Phys. Rev. B, 39:5566–5568, 1989.
- 85. Erhart, P. and Albe, K.: Analytical potential for atomistic simulations of silicon, carbon, and silicon carbide. Phys. Rev. B, 71:035211, 2005.

86. Albe, K., Nordlund, K., and Averback, R. S.: Modeling the metal-semiconductor interaction: Analytical bond-order potential for platinum-carbon. Phys. Rev. B, 65:195124, 2001.
87. Brenner, D. W.: Empirical potential for hydrocarbons for use in simulating the chemical vapor deposition of diamond films. Phys. Rev. B, 42:9458–9471, 1990.
88. Brenner, D. W.: Relationship between the embedded-atom method and tersoff potentials. Phys. Rev. Lett., 63:1022, 1989.
89. Baskes, M. I.: Modified embedded-atom potentials for cubic materials and impurities. Phys. Rev. B, 46:2727–2742, 1992.
90. Lee, B.-J., Baskes, M. I., Kim, H., and Cho, Y. K.: Second nearest-neighbor modified embedded atom method potentials for bcc transition metals. Phys. Rev. B, 64:184102, 2001.
91. Lee, B.-J. and Lee, J. W.: A modified embedded atom method interatomic potential for carbon. Calphad, 29:7–16, 2005.
92. Zhou, X. W. and Doty, F. P.: Embedded-ion method: An analytical energy-conserving charge-transfer interatomic potential and its application to the la-br system. Phys. Rev. B, 78:224307, 2008.
93. Stuart, S., Tutein, A. B., and Harrison, J. A.: A reactive potential for hydrocarbons with intermolecular interactions. J. Chem. Phys., 112:6472–6486, 2000.
94. Brenner, D. W., Shenderova, O. A., Harrison, J. A., Stuart, S. J., Ni, B., and Sinnott, S. B.: A second-generation reactive empirical bond order (REBO) potential energy expression for hydrocarbons. J. Phys. Condens. Matter, 14:783–802, 2002.
95. Dyson, A. J. and Smith, P. V.: Extension of the brenner empirical interatomic potential to C-Si-H systems. Surf. Sci., 355:140–150, 1996.
96. Sbraccia, C., Silvestrelli, P. L., and Ancilotto, F.: Modified XB potential for simulating interactions of organic molecules with Si surfaces. Surf. Sci., 516:147–158, 2002.

97. Yasukawa, A.: Using an extended tersoff interatomic potential to analyze the static-fatigue strength of SiO_2 under atmospheric influence. JSME Int. J., Ser. A, 39:313–320, 1996.
98. Yu, J. and Philpott, S. B. S. S. R.: Charge optimized many-body potential for the Si/SiO_2 system. Phys. Rev. B, 75:085311, 2007.
99. Mikulski, P. T., Knippenberg, M. T., and Harrison, J. A.: Merging bond-order potentials with charge equilibration. J. Chem. Phys., 131:241105, 2009.
100. Bazant, M. Z. and Kaxiras, E.: Environment-dependent interatomic potential for bulk silicon. Phys. Rev. B, 56:8542–8552, 1997.
101. Marks, N. A.: Generalizing the environment-dependent interaction potential for carbon. Phys. Rev. B, 63:035401, 2000.
102. Lucas, G., Bertolus, M., and Pizzagalli, L.: An environment-dependent interatomic potential for silicon carbide: calculation of bulk properties, high-pressure phases, point and extended defects, and amorphous structures. J. Phys.: Condens. Matter, 22:035802, 2010.
103. Los, J. H. and Fasolino, A.: Intrinsic long-range bond-order potential for carbon: Performance in Monte Carlo simulations of graphitization. Phys. Rev. B, 68:024107, 2003.
104. Los, J. H., Ghiringhelli, L. M., Meijer, E. J., and Fasolino, A.: Improved long-range reactive bond-order potential for carbon. I. Construction. Phys. Rev. B, 72:214102, 2005.
105. van Duin, A. C. T., Dasgupta, S., Lorant, F., and III, W. A. G.: Reaxff: a reactive force field for hydrocarbons. J. Phys. Chem. A, 105:9396–9409, 2001.
106. Chenoweth, K., van Duin, A. C. T., and III, W. A. G.: Reaxff reactive force field for molecular dynamics simulations of hydrocarbon oxidation. J. Phys. Chem. A, 112:1040–1053, 2008.
107. Zybin, S. V., III, W. A. G., Xu, P., Budzien, J., and Thompson, A.: Reactive molecular dynamics of shock- and shear-induced chemistry in energetic ma-

- terials for future force insensitive munitions. HPCMP-UGC, pages 230–236, 2009.
108. Rappe, A. K. and III, W. A. G.: Charge equilibration for molecular dynamics simulations. J. Phys. Chem., 95:3358–3363, 1991.
 109. Pettifor, D. G. and Oleinik, I. I.: Bounded analytic bond-order potentials for σ and π bonds. Phys. Rev. Lett., 84:4124–4127, 2000.
 110. Pettifor, D. G., Oleinik, I. I., Nguyen-Manh, D., and Vitek, V.: Bond-order potentials: bridging the electronic to atomistic modelling hierarchies. Comp. Mat. Sci., 23:33–37, 2002.
 111. Mrovec, M., Moseler, M., Elsasser, C., and Gumbsch, P.: Atomistic modeling of hydrocarbon systems using analytic bond-order potentials. Prog. Mater. Sci., 52:230–254, 2007.
 112. Ward, D. K., Zhou, X. W., Wong, B. M., Doty, F. P., and Zimmerman, J. A.: Analytical bond-order potential for the cadmium telluride binary system. Phys. Rev. B, 85:115206, 2012.
 113. Pettifor, D. G. and Oleinik, I. I.: Interatomic bond-order potentials and structural prediction. Prog. Mat. Sci., 49:285–312, 2004.
 114. Nguyen-Manh, D., Pettifor, D. G., and Vitek, V.: Analytic environment-dependent tight-binding bond integrals: Application to mosi_2 . Phys. Rev. Lett., 85:4136–4139, 2000.
 115. Tang, M. S., Wang, C. Z., Chan, C. T., and Ho, K. M.: Environment-dependent tight-binding potential model. Phys. Rev. B, 53:979–982, 1996.
 116. Baskes, M. I., Angelo, J. E., and Bisson, C. L.: Atomistic calculations of composite interfaces. Modell. Simul. Mater. Sci. Eng., 2:505–518, 1994.
 117. Kumagai, T., Hara, S., Choi, J., Izumi, S., and Kato, T.: Development of empirical bond-order-type interatomic potential for amorphous carbon structures. J. Appl. Phys., 105:064310, 2009.

- 118. Pastewka, L., Pou, P., Perez, R., Gumbsch, P., and Moseler, M.: Describing bond-breaking processes by reactive potentials: Importance of an environment-dependent interaction range. Phys. Rev. B, 78:161402, 2008.
- 119. Perriot, R., Lin, Y., Zhakhovsky, V. V., Pineau, N., Los, J. H., Maillet, J. B., Soulard, L., White, C. T., and Oleynik, I. I.: Shock compression of diamond: Molecular dynamics simulations using different interatomic potentials. AIP Conf. Proc., 1426:1175–1178, 2012.
- 120. Verlet, L.: Computer “experiments” on classical fluids I. Thermodynamical properties of Lennard-Jones molecules. Phys. Rev., 159:98–103, 1967.
- 121. Smith, W. and Forester, T. R.: Dlpoly 2.0: A general-purpose parallel molecular dynamics simulation package. J. Molec. Graphics, 14:136–141, 1996.
- 122. Schneider, T. and Stoll, E.: Molecular-dynamics study of three-dimensions one-component model for distortive phase transitions. Phys. Rev. B, 17:1302–1322, 1978.
- 123. Hoover, W. G.: Canonical dynamics: Equilibrium phase-space distributions. Phys. Rev. A, 31:1695–1697, 1985.
- 124. Nose, S.: A unified formulation of the constant temperature molecular dynamics methods. J. Chem. Phys., 81:511–519, 1984.
- 125. Berendsen, H. J. C., Postma, J. P. M., van Gunsteren, W. F., di Nola, A., and Haak, J. R.: Molecular dynamics with coupling to an external bath. J. Chem. Phys., 81:3684–3690, 1984.
- 126. Smith, W.: Calculating the pressure. CCP5 Newsletter, 39:1–7, 1993.
- 127. Tsai, D. H.: The virial theorem and stress calculation in molecular dynamics. J. Chem. Phys., 70:1375–1382, 1979.
- 128. Thompson, A. P., Plimpton, S. J., and Mattson, W.: General formulation of pressure and stress tensor for arbitrary many-body interaction potentials under periodic boundary conditions. J. Chem. Phys., 131:154107, 2009.

129. Labinger, J. and Bercaw, J.: Understanding and exploiting ch bond activation. Nature, 417:507–514, 2002.
130. Vajda, S., Pellin, M., Greeley, J., Marshall, C., Curtiss, L., Ballentine, G., Elam, J., Catillon-Mucherie, S., Redfern, P., Mehmood, F., , and Zapol, P.: Sub-nanometer platinum clusters as highly active and selective catalysts for the oxidative dehydrogenation of propane. Nat. Mater., 8:213–216, 2009.
131. Titov, A., Zapol, P., Král, P., Liu, D.-J., Iddir, H., Baishya, K., , and Curtiss, L.: Catalytic Fe-xN sites in carbon nanotubes. J. Phys. Chem. C, 113:21629–21634, 2009.
132. Cuong, N., Fujiwara, A., Mitani, T., and Chi, D.: Effects of carbon supports on Pt nano-cluster catalyst. Comput. Mater. Sci., 44:163–166, 2008.
133. Kim, S., Jung, Y., and Park, S.-J.: Preparation and electrochemical behaviors of platinum nanocluster catalysts deposited on plasma-treated carbon nanotube supports. Colloids Surf., A, 313-314:189–192, 2008.
134. Prasomsri, T., Shi, D., and Resasco, D. E.: Anchoring Pd nanoclusters onto pristine and functionalized single-wall carbon nanotubes: A combined dft and experimental study. Chem. Phys. Lett., 497:103–107, 2010.
135. Cuong, N., Sugiyama, A., Fujiwara, A., Mitani, T., and Chi, D. H.: Density functional study of Pt₄ clusters adsorbed on a carbon nanotube support. Phys. Rev. B, 79:235417, 2009.
136. T. W. Odom, J. H. Hafner, C. M. L.: Scanning probe microscopy studies of carbon nanotubes. Topics Appl. Phys., 80:173–211, 2001.
137. Green, A. A. and Hersam, M. C.: Nearly single-chirality single-walled carbon nanotubes produced via orthogonal iterative density gradient ultracentrifugation. Adv. Mater., 23:2185–2190, 2011.
138. Hersam, M. C.: Progress towards monodisperse single-walled carbon nanotubes. Nat. Nanotechnol., 3:387–394, 2008.
139. Becke, A. D.: Density-functional thermochemistry. III. The role of exact exchange. J. Chem. Phys., 98:5648–5652, 1993.

140. Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G. A., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H. P., Izmaylov, A. F., Bloino, J., Zheng, G., Sonnenberg, J. L., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Montgomery, J. A., Jr., Peralta, J. E., Ogliaro, F., Bearpark, M., Heyd, J. J., Brothers, E., Kudin, K. N., Staroverov, V. N., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant, J. C., Iyengar, S. S., Tomasi, J., Cossi, M., Rega, N., Millam, J. M., Klene, M., Knox, J. E., Cross, J. B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R. E., Yazyev, O., Austin, A. J., Cammi, R., Pomelli, C., Ochterski, J. W., Martin, R. L., Morokuma, K., Zakrzewski, V. G., Voth, G. A., Salvador, P., Dannenberg, J. J., Dapprich, S., Daniels, A. D., Farkas, ., Foresman, J. B., Ortiz, J. V., Cioslowski, J., , and Fox, D. J.: Gaussian 09, Revision A.1. Wallingford, CT, Gaussian, Inc, 2009.
141. Cox, B. J. and Hill, J. M.: Exact and approximate geometric parameters for carbon nanotubes incorporating curvature. Carbon, 45:1453–1462, 2007.
142. Schlegel, B.: Optimization of equilibrium geometries and transition structures. J. Comput. Chem., 3:214–218, 1982.
143. Park, S., Srivastava, D., , and Cho, K.: Generalized chemical reactivity of curved surfaces: Carbon nanotubes. Nano Lett., 3:1273–1277, 2003.
144. Horner, D., Redfern, P., Sternberg, M., Zapol, P., and Curtiss, L.: Increased reactivity of single wall carbon nanotubes at carbon ad-dimer defect sites. Chem. Phys. Lett., 450:71–75, 2007.
145. Lu, X. and Chen, Z.: Curved pi-conjugation, aromaticity, and the related chemistry of small fullerenes ($< C_{60}$) and single-walled carbon nanotubes. Chem. Rev., 105:3643–3696, 2005.
146. Liu, Z.-P. and Hu, P.: General rules for predicting where a catalytic reaction should occur on metal surfaces: A density functional theory study of C-H and C-O Bond breaking/making on flat, stepped, and kinked metal surfaces. J. Am. Chem. Soc., 125:1958–1967, 2003.
147. Michaelides, A. and Hu, P.: insight into microscopic reaction pathways in heterogeneous catalysis. J. Am. Chem. Soc., 122:9866–9867, 2000.

148. Kunz, R. R., Gregory, K. C., Hardy, D., Oyler, J., Ostazeski, S. A., and Fountain, A. W. I.: Measurement of trace explosive residues in a surrogate operational environment: implications for tactical use of chemical sensing in C-IED operations. Anal. Bioanal. Chem., 395:357–369, 2009.
149. Ni, M., Stetter, J., and Buttner, W.: Orthogonal gas sensor arrays with intelligent algorithms for early warning of electrical fires. Sens. Actuators B, 130:889–899, 2008.
150. Li, R., Wang, P., and Hu, W. L.: A novel method for wine analysis based on sensor fusion technique. Sens. Actuators, B, 66:246–250, 2000.
151. Willis, C., Church, S., Guest, C., Cook, W., McCarthy, N., Bransbury, A., Church, M., and Church, J.: Olfactory detection of human bladder cancer by dogs: proof of principle study. BMJ, 329:1–6, 2004.
152. Modi, A., Koratkar, N., Lass, E., Wei, B., and Ajayan, P.: Miniaturized gas ionization sensors using carbon nanotubes. Nature, 424:171–174, 2003.
153. Zhong, Z., Wang, D., Cui, Y., Bockrath, M., and Lieber, C.: Nanowire crossbar arrays as address decoders for integrated nanosystems. Science, 302:1377–1379, 2003.
154. Kong, J., Franklin, N., Zhou, C., Chapline, M., Peng, S., Cho, K., and Dai, H.: Nanotube molecular wires as chemical sensors. Science, 287:622–624, 2000.
155. Hu, J., Odom, T., and Lieber, C.: Chemistry and physics in one dimension: Synthesis and properties of nanowires and nanotubes. Acc. Chem. Res., 32:435–445, 1999.
156. Freitag, M., Johnson, A., Kalinin, S., and Bonnell, D.: Role of single defects in electronic transport through carbon nanotube field-effect transistors. Phys. Rev. Lett., 89:216801, 2002.
157. Staii, C. and Johnson, A.: Dna-decorated carbon nanotubes for chemical sensing. Nano Lett., 5:1774–1778, 2005.

158. Chen, R., Bangsaruntip, S., Drouvalakis, K., Kam, N., Shim, M., Li, Y., Kim, W., Utz, P., and Dai, H.: Noncovalent functionalization of carbon nanotubes for highly specific electronic biosensors. PNAS, 100:4984–4989, 2003.
159. Snow, E., Perkins, F., Houser, E., and Reinecke, T.: Chemical detection with a single-walled carbon nanotube capacitor. Science, 307:1942–1945, 2005.
160. Qi, P., Vermesh, O., Grecu, M., Javey, A., Wang, Q., and Dai, H.: Toward large arrays of multiplex functionalized carbon nanotube sensors for highly sensitive and selective molecular detection. Nano Lett., 3:347–351, 2003.
161. Williams, K., Veenhuizen, P., Torre, B., R., E., and Dekker, C.: Carbon nanotubes with dna recognition. Nature, 420:761, 2002.
162. Wang, F., Gu, H., and Swager, T.: Carbon nanotube/polythiophene chemiresistive sensors for chemical warfare agents. J. Am. Chem. Soc., 130:5392–5393, 2008.
163. Zhang, T., Nix, M., Yoo, B., Deshusses, M., and Myung, N.: Electrochemically functionalized single-walled carbon nanotube gas sensor. Electroanal., 18:1153–1158, 2006.
164. Dan, Y., Lu, Y., Kybert, N., Luo, Z., and Johnson, A.: Intrinsic response of graphene vapor sensors. Nano Lett., 9:1472–1475, 2009.
165. Ilic, B., Krylov, S., Kondratovich, M., and Craighead, H.: Optically actuated nanoelectromechanical oscillators. IEEE J. Quantum Electron., 13:392–399, 2007.
166. Garcia-Sanchez, D., Paulo, A., Esplandiu, M., Perez-Murano, F., Forro, L., Aguasca, A., and Bachtold, A.: Mechanical detection of carbon nanotube resonator vibrations. Phys. Rev. Lett., 99:088501, 2007.
167. Li, C. and Chou, T.: Mass detection using carbon nanotube-based nanomechanical resonators. Appl. Phys. Lett., 84:5246–5248, 2004.
168. Jorio, A., Dresselhaus, G., Dresselhaus, M., Souza, M., Dantas, M., Pimenta, M., Rao, A., Saito, R., Liu, C., and Cheng, H.: Polarized raman study of

- single-wall semiconducting carbon nanotubes. Phys. Rev. Lett., 85:2617–2620, 2000.
169. Casiraghi, C., Hartschuh, A., Qian, H., Piscanec, S., Georgi, C., Fasoli, A., Novoselov, K., Basko, D., and Ferrari, A.: Raman sepctroscopy of graphene edges. Nano lett., 9:1433–1441, 2009.
 170. Schedin, F., Geim, A., Morozov, S., Hill, E., Blake, P., Katsnelson, M., and Novoselov, K.: Detection of individual gas molecules adsorbed on graphene. Nature Materials, 6:652–655, 2007.
 171. Bunch, J. S., Zande, A., Verbridge, S., Frank, I., Tanenbaum, D., Parpia, J., Craighead, H., and McEuen, P.: Electromechanical resonators from graphene sheets. Science, 315:490–493, 2007.
 172. Wang, B. and Král, P.: Optimal atomistic modifications of material surfaces: Design of selective nesting sites for biomolecules. Small, 3:580–584, 2007.
 173. Katano, S., Kim, Y., Hori, M., Trenary, M., and Kawai, M.: Reversible control of hydrogenation of a single molecule. Science, 316:1883–1886, 2007.
 174. Richard Balog, R. and Liv Hornekaer, L.: Bandgap opening in graphene induced by patterned hydrogen adsorption. Nat. Mater., 9:315–319, 2010.
 175. Li, J., Kudin, K., McAllister, M., Prudhomme, R., Aksay, I., and Car, R.: Oxygen-driven unzipping of graphitic materials. Phys. Rev. Lett., 96:176101, 2006.
 176. Xu, Z. and Xue, K.: Engineering graphene by oxidation: a first-principles study. Nanotechnology, 21:045704, 2010.
 177. Liu, Z., Robinson, J., Sun, X., and Dai, H.: Pegylated nanographene oxide for delivery of water-insoluble cancer drugs. J. Am. Chem. Soc., 130:10876–10877, 2008.
 178. Stankovich, S. and Ruoff, R.: Graphene-based composite materials. Nature, 442:282–286, 2006.
 179. Wang, X. and Dai, H.: N-doping of graphene through electrothermal reactions with ammonia. Science, 324:768–771, 2009.

180. Wang, H. and Dai, H.: Chemical self-assembly of graphene sheets. Nano Res, 2:336–342, 2009.
181. Li, C. and Qian, Y.: Synthesis and characterization of nitrogen-rich graphitic carbon nitride. Mater. Chem. Phys., 103:427–432, 2007.
182. Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Montgomery, J. A., Jr., Vreven, T., Kudin, K. N., Burant, J. C., Millam, J. M., Iyengar, S. S., Tomasi, J., Barone, V., Mennucci, B., Cossi, M., Scalmani, G., Rega, N., Petersson, G. A., Nakatsuji, H., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Klene, M., Li, X., Knox, J. E., Hratchian, H. P., Cross, J. B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R. E., Yazyev, O., Austin, A. J., Cammi, R., Pomelli, C., Ochterski, J. W., Ayala, P. Y., Morokuma, K., Voth, G. A., Salvador, P., Dannenberg, J. J., Zakrzewski, V. G., Dapprich, S., Daniels, A. D., Strain, M. C., Farkas, O., Malick, D. K., Rabuck, A. D., Raghavachari, K., Foresman, J. B., Ortiz, J. V., Cui, Q., Baboul, A. G., Clifford, S., Cioslowski, J., Stefanov, B. B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Martin, R. L., Fox, D. J., Keith, T., Al-Laham, M. A., Peng, C. Y., Nanayakkara, A., Challacombe, M., Gill, P. M. W., Johnson, B., Chen, W., Wong, M. W., Gonzalez, C., and Pople, J. A.: Gaussian 03, Revision C.02. Wallingford, CT, Gaussian, Inc, 2004.
183. Wang, B. and Král, P.: Chemically tunable nanoscale propellers of liquids. Phys. Rev. Lett., 98:266102, 2007.
184. Xu, W., Jin, L., Lu, Y., Lan, B., and Zou, Z.: C₃-symmetric molecules with axial chirality and handed arrangement of dipole fields. Chem. Res. Chinese U., 23:628–930, 2007.
185. Ernst, K. H.: Supramolecular surface chirality. Top. Curr. Chem., 265:209–252, 2006.
186. Michael, D. and Benjamin, I.: Molecular dynamics simulation of the waternitrobenzene interface. J. Electroanal. Chem., 450:335–345, 1998.
187. W. Humphrey, A. Dalke, K. S.: VMD: visual molecular dynamics. J. Mol. Graph., 14:33–38, 1996.

188. Chou, P. and Pagano, N.: Elasticity: Tensor, Dyadic, and Engineering Approaches. Princeton, Van Nostrand, 1967.
189. Lee, C., Wei, X., Kysar, J., and Home, J.: Intrinsic strength of monolayer graphene. Science, 321:385–387, 2008.
190. Lu, Q., Arroyo, M., and Huang, R.: Elastic bending modulus of monolayer graphene. J. Phys. D: Appl. Phys., 42:102002, 2009.
191. Arroyo, M. and Belytschko, T.: Finite crystal elasticity of carbon nanotubes based on the exponential cauchy-born rule. Phys. Rev. B, 69:115415, 2004.
192. Kudin, K. and Scuseria, G.: C₂F, BN, and C nanoshell elasticity from ab initio computations. Phys. Rev. B, 64:235406, 2001.
193. Chen, C., Rosenblatt, S., Bolotin, K., Kalb, W., Kim, P., Kyminsis, I., Stormer, H., Heinz, T., and Hone, J.: Performance of monolayer graphene nanomechanical resonators with electrical readout. Nat. Nanotechnol., 4:861–867, 2009.
194. Naik, A., Hanay, M., Hiebert, W., Feng, X., and Roukes, M.: Towards single-molecule nanomechanical mass spectrometry. Nat. Nanotechnol., 4:445–450, 2009.
195. Morse, P. and Ingard, K.: Theoretical Acoustics. Princeton, Princeton University Press, 1986.
196. Geller, M. and Varley, J.: Friction in nanoelectromechanical systems: Clamping loss in the ghz regime. arXiv [Online] <http://arxiv.org/abs/cond-mat/0512710v1>, pages 1–5, 2005 (accessed Jan 23, 2010).
197. Seoanez, C., Guinea, F., and Neto, A.: Dissipation in graphene and nanotube resonators. Phys. Rev. B, 76:125427, 2007.
198. Wang, B., Král, P., and Thanopoulos, I.: Docking of chiral molecules on twisted and helical nanotubes: Nanomechanical control of catalysis. Nano Lett., 6:1918–1921, 2006.

199. Garcia-Sanchez, D., van der Zande, A., San Paulo, A., Lassagne, B., McEuen, P., and Bachtold, A.: Imaging mechanical vibrations in suspended graphene sheets. Nano Lett., 8:1399–1403, 2008.
200. Iijima, S.: Helical microtubules of graphitic carbon. Nature, 354:56–58, 1991.
201. Saito, R., Dresselhaus, G., and Dresselhaus, M.: Physical Properties Of Carbon Nanotubes. London, World Scientific Publishing Company, 1998.
202. Král, P. and Tománek, D.: Laser-driven atomic pump. Phys. Rev. Lett., 83:5373–5376, 1999.
203. Regan, B. C., Aloni, S., Ritchie, R. O., Dahmen, U., and Zettl, A.: Carbon nanotubes as nanoscale mass conveyors. Nature, 428:924–927, 2004.
204. Svensson, K., Olin, H., and Olsson, E.: Nanopipettes for metal transport. Phys. Rev. Lett., 145901, 2004.
205. Wang, B. and Král, P.: Coulombic dragging of molecules on surfaces induced by separately flowing liquids. J. Am. Chem. Soc., 128:15984–15985, 2006.
206. Wang, B. and Král, P.: Dragging of polarizable nanodroplets by distantly solvated ions. Phys. Rev. Lett., 101:046103, 2008.
207. Zhao, Y. C., Song, L., Deng, K., Liu, Z., Zhang, Z. X., Yang, Y. L., Wang, C., Yang, H. F., Jin, A. Z., Luo, Q., Gu, C. Z., Xie, S. S., and Sun, L. F.: Individual water-filled single-walled carbon nanotubes as hydroelectric power converters. Adv. Mater., 20:1772–1776, 2008.
208. Schoen, P. A. E., Walther, J. H., Arcidiacono, S., Poulikakos, D., and Koumoutsakos, P.: Nanoparticle traffic on helical tracks: Thermophoretic mass transport through carbon nanotubes. Nano Lett., 6:1910–1917, 2006.
209. Barreiro, A., Rurali, R., Hernandez, E. R., Moser, J., Pichler, T., Forro, L., and Bachtold, A.: Subnanometer motion of cargoes driven by thermal gradients along carbon nanotubes. Science, 320:775–778, 2008.

210. Zambrano, H. A., Walther, J. H., Koumoutsakos, P., and Sbalzarini, I. F.: Thermophoretic motion of water nanodroplets confined inside carbon nanotubes. Nano Lett., 9:66–71, 2009.
211. Shiomi, J. and Maruyama, S.: Water Transport Inside a Single-walled Carbon Nanotube Driven by a Temperature Gradient. Nanotechnology, 20:055708, 2009.
212. Insepov, Z., Wolf, D., and Hassanein, A.: Nanopumping using carbon nanotubes. Nano Lett., 6:1893–1895, 2006.
213. Wang, Q.: Atomic transportation via carbon nanotubes. Nano Lett., 9:245–249, 2009.
214. Wang, Z. and Zhe, J.: Recent advances in particle and droplet manipulation for lab-on-a-chip devices based on surface acoustic waves. Lab Chip, 11:1280–1285, 2011.
215. Hashimoto, H., Koike, Y., and Ueha, S.: Transporting objects without contact using flexural travelling waves. J. Acoust. Soc. Am., 103:3230–3233, 1998.
216. Kim, G. H., Park, J. W., and Jeong, S. H.: Analysis of dynamic characteristics for vibration of flexural beam in ultrasonic transport system. J. Mech. Sci. Technol., 23:1428–1434, 2009.
217. Miranda, E. C. and Thomsen, J. J.: Vibration induced sliding: Theory and experiment for a beam with a spring-loaded mass. Nonlinear Dyn., 19:167–186, 1998.
218. Vielsack, P. and Spiess, H.: Sliding of a mass on an inclined driven plane with randomly varying coefficient of friction. J. App. Mech., 67:112–116, 2000.
219. Long, Y. G., Nagaya, K., and Niwa, H.: Vibration conveyance in spatial-curved tubes. J. Vib. Acoust., 116:38–46, 1994.
220. Biwersi, S., Manceau, J.-F., and Bastien, F.: Displacement of droplets and deformation of thin liquid layers using flexural vibrations of structures. influence of acoustic radiation pressure. J. Acoust. Soc. Am., 107:661–664, 2000.

221. Wixforth, A., Strobl, C., Gauer, C., Toegl, A., Scriba, J., and Guttenberg, Z. v.: Acoustic manipulation of small droplets. Anal. Bioanal. Chem., 379:982–991, 2004.
222. Alzuaga, S., Manceau, J.-F., and Bastien, F.: Motion of droplets on solid surface using acoustic radiation pressure. J. Sound Vib., 282:151–162, 2005.
223. Bennes, J., Alzuaga, S., Chabe, P., Morain, G., Cheroux, F., Manceau, J.-F., and Bastien, F.: Action of low frequency vibration on liquid droplets and particles. Ultrasonics, 44:497–502, 2006.
224. Jiao, Z. J., Y., H. X., and Nguyen, N.-T.: Scattering and attenuation of surface acoustic waves in droplet actuation. J. Phys. A: Math. Theor., 41:355502, 2008.
225. Mele, E. J. and Král, P.: Electric polarization of heteropolar nanotubes as a geometric phase. Phys. Rev. Lett., 88:056803, 2002.
226. Michalski, P. J., Sai, N. A., and Mele, E. J.: Continuum theory for nanotube piezoelectricity. Phys. Rev. Lett., 95:116803, 2005.
227. Král, P., Thanopoulos, I., and Shapiro, M.: Coherently controlled adiabatic passage. Rev. Mod. Phys., 79:53–77, 2007.
228. Vukovic, L. and Král, P.: Coulombically driven rolling of nanorods on water. Phys. Rev. Lett., 103:246103, 2009.
229. Matsumoto, M., Kunisawa, T., and Xiao, P.: Relaxation of phonons in classical md simulation. J. Therm. Sci. Technol., 3:159–166, 2008.
230. Král, P.: Linearized quantum transport equations: Ac conductance of a quantum wire with an electron-phonon interaction. Phys. Rev. B, 53:11034–11050, 1996.
231. Benumof, R.: Momentum propagation by traveling waves on a string. Am. J. Phys., 50:20–25, 1982.

232. Bennes, J., Alzuaga, S., Ballandras, S., Cherioux, F., and Manceau, J.-F.: Droplet ejector using surface acoustic waves. IEEE Ultrasonics Symposium, pages 823–826, 2005.
233. Craighead, H. G.: Future lab-on-a-chip technologies for interrogating individual molecules. Nature, 442:387–393, 2006.
234. Baughman, R. H., Cui, C. X., Zakhidov, A. A., Iqbal, Z., Barisci, J. N., Spinks, G. M., Wallace, G. G., Mazzoldi, A., De Rossi, D., Rinzler, A. G., Jaschinski, O., Roth, S., and Kertesz, M.: Carbon nanotube actuators. Science, 284:1340–1344, 1999.
235. Spinks, G. M., Wallace, G. G., Fifield, L. S., Dalton, L. R., Mazzoldi, A., De Rossi, D., Khayrullin, I. I., and Baughman, R. H.: Pneumatic carbon nanotube actuators. Adv. Mater., 14:1728–1732, 2002.
236. Schoch, R. B., Han, J. Y., and Renaud, P.: Transport phenomena in nanofluidics. Rev. Mod. Phys., 80:839–883, 2008.
237. Xu, L., Li, S., Wu, Z., Li, H., Yan, D., Zhang, C., Zhang, P., Yan, P., and Li, X.: Growth and field emission properties of nanotip arrays of amorphous carbon with embedded hexagonal diamond nanoparticles. Appl. Phys. A, 103:59–65, 2011.
238. Ciezak-Jenkins, J. A.: Observation of an ultrahard phase of graphite quenched from high-pressure. Army Research Laboratory, ARL-TR-5466:1–13, 2011.
239. Zhu, C. and Guo, W.: C-directional compression of nano-graphite: a comparison between effects of uniform and non-uniform pressure. Physica B, 406:2763–2766, 2011.
240. Scandolo, S., Bernasconi, M., Chiarotti, G. L., Focher, P., and Tosatti, E.: Pressure-induced transformation path of graphite to diamond. Phys. Rev. Lett., 74:4015–4018, 1995.
241. Tateyama, Y., Ogitsu, T., Kusakabe, K., and Tsuneyuki, S.: Constant-pressure first-principles studies on the transition states of the graphite-diamond transformation. Phys. Rev. B, 54:14994–15001, 1996.

242. Kuznetsov, V. L. and Butenko, Y. V.: Nanodiamond graphitization and properties of onion-like carbon. In Synthesis, Properties and Applications of Ultrananocrystalline Diamond, ed. D. M. Gruen, pages 199–216. Netherlands, Springer, 2005.
243. Rakha, S. A., Guojun, Y., Xingtai, Z., Ahmed, I., Zhu, D., and Gong, J.: Diamond nanorods from nanocrystalline diamond films. J. Cryst. Growth, 311:3332–3336, 2009.
244. Gruen, D., Redfern, P., Horner, D., Zapol, P., and Curtiss, L. A.: Theoretical studies on nanocrystalline diamond: Nucleation by dicarbon and electronic structure of planar defects. J. Phys. Chem. B, 103:5459–5467, 1999.
245. Adiga, S. P., Curtiss, L. A., and Gruen, D. M.: Molecular dynamics simulations of nanodiamond graphitization. In Nanodiamonds: Applications in Biology and Nanoscale Medicine, ed. D. Ho. New York, Springer, 2010.
246. Shenderova, O. A., Areshkin, D., and Brenner, D. W.: Bonding and stability of hybrid diamond/nanotube structures. Mol. Simul., 29:259–268, 2003.
247. Shenderova, O., Zhirnov, V. V., and Brenner, D. W.: Carbon nanostructures. Crit. Rev. Solid State Mater. Sci., 27:227–356, 2002.
248. Okada, S.: Formation of graphene nanostructures on diamond nanowire surfaces. Chem. Phys. Lett., 483:128–132, 2009.
249. Vlasov, I. I., Lebedev, O. I., Ralchenko, V. G., Goovaerts, E., Bertoni, G., van Tendeloo, G., and Konov, V. I.: Hybrid diamond-graphite nanowires produced by microwave plasma chemical vapor deposition. Adv. Mater., 19:4058–4062, 2007.
250. Lee, J.-K., Lee, S.-C., Ahn, J.-P., Kim, S.-C., Wilson, J. I. B., and John, P.: The growth of aa graphite on (111) diamond. J. Chem. Phys., 129:23409, 2008.
251. Gupta, S. and Farmer, J.: Multiwalled carbon nanotubes and dispersed nanodiamond novel hybrids: Microscopic structure evolution, physical properties, and radiation resilience. J. App. Phys., 109:014314, 2011.

252. Peng, B., Locascio, M., Zapol, P., Li, S., Mielke, S. L., Schatz, G. C., and Espinosa, H. D.: Measurements of near-ultimate strength for multiwalled carbon nanotubes and irradiation-induced crosslinking improvements. Nat. Nanotechnol., 3:626–631, 2008.
253. Ribeiro, F. J., Tangney, P., Louie, S. G., and Cohen, M. L.: Structural and electronic properties of carbon in hybrid diamond-graphite structures. Phys. Rev. B, 72:214109, 2005.
254. Fasolino, A., Los, J. H., and Katsnelson, M. I.: Intrinsic ripples in graphene. Nat. Mater., 6:858–861, 2007.
255. Schwarzbart, M., Steindl, A., and Troger, H.: Molecular statical calculations of graphene sheet buckling. Proc. Appl. Math. Mech., 8:10343–10344, 2008.
256. Pradhan, S. C. and Murmu, T.: Small scale effect on the buckling of single-layered graphene sheets under biaxial compression via nonlocal continuum mechanics. Comp. Mat. Sci., 47:268–274, 2009.
257. Mao, Y., Wang, W. L., Wei, D., Kaxiras, E., and Sodroaski, J. G.: Graphene structures at an extreme degree of buckling. ACS Nano, 5:1395–1400, 2011.
258. Khan, M. A., Mukaddam, M. A., and Schwingenschlogl, U.: Buckled graphene: A model study based on density functional theory. Chem. Phys. Lett., 498:157–161, 2010.
259. Garcia, J. C., de Lima, D. B., Assali, L. V. C., and Justo, J. F.: Group iv graphene- and graphene-like nanosheets. J. Phys. Chem. C, 115:13242–13246, 2011.
260. Yin, M. T. and Cohen, M. L.: Structural theory of graphitic and graphitic silicon. Phys. Rev. B, 29:6996–6998, 1984.
261. Wang, Y., Scheerschmidt, K., and Gosele, U.: Theoretical investigations of bond properties in graphite and graphitic silicon. Phys. Rev. B, 61:12864–12870, 2000.
262. Houssa, M., Pourtois, G., Afanas'ev, V. V., and Stesmans, A.: Can silicon behave like graphene? a first-principles study. App. Phys. Lett., 97:112106, 2010.

- 263. Redfern, P. C., Gruen, D., and Curtiss, L. A.: Effect of boron substitution on the electronic structure of nanographene and its relevance to the thermoelectric transport properties in nanocarbon ensembles. Chem. Phys. Lett., 471:264–268, 2009.
- 264. Topsakal, M., Akturk, E., and Circaci, S.: First-principles study of two- and one-dimensional honeycomb structures of boron nitride. Phys. Rev. B, 79:115442, 2009.
- 265. Huda, M. N., Yan, Y., and Al-Jassim, M. M.: On the existence of si-c double bonded graphene-like layers. Chem. Phys. Lett., 479:255–258, 2009.
- 266. Yu, M., Jayanthi, C. S., and Wu, S. Y.: Geometric and electronic structures of graphitic-like and tubular silicon carbides: Ab-initio studies. Phys. Rev. B, 82:075407, 2010.
- 267. Hasegawa, M., Nishidate, K., and Iyetomi, H.: Energetics of interlayer binding in graphite: The semiempirical approach revisited. Phys. Rev. B, 76:115424, 2007.
- 268. Berashevich, J. and Chakraborty, T.: On the nature of interlayer interactions in a system of two graphene fragments. J. Phys. Chem. C, 115:24666–24673, 2011.
- 269. Kertesz, M. and Hoffmann, R.: The graphite-to-diamond transformation. J. Solid State Chem., 54:313–319, 1984.
- 270. Fahy, S., Louie, S. G., and Cohen, M. L.: Pseudopotential total-energy study of the transition from rhombohedral graphite to diamond. Phys. Rev. B, 34:1191–1199, 1986.
- 271. Barnard, A. S., Russo, S. P., and Snook, I. K.: Surface structure of cubic diamond nanowires. Surf. Sci., 538:204–210, 2003.
- 272. Barnard, A. S., Russo, S. P., and Snook, I. K.: Bucky-wires and the instability of diamond (111) surfaces in one-dimension. J. Nanosci. Nanotech., 4:151–156, 2004.

273. Barnard, A. S.: Structural properties of diamond nanowires: theoretical predictions and experimental progress. Rev. Adv. Mater. Sci., 6:94–119, 2004.
274. Norimatsu, W. and M., K.: . Physica E, 42:691–694, 2010.
275. Tang, C., Meng, L., Xiao, H., and Zhong: Growth of graphene structure on 6H-SiC(0001): Molecular dynamics simulation. J. Appl. Phys., 103:063505, 2008.
276. Zhou, X. W. and Jones, R. E.: Effects of cutoff functions of tersoff potentials on molecular dynamics simulations of thermal transport. Modelling Simul. Mater. Sci. Eng., 19:025004, 2011.
277. Ding, H.-Q., Karasawa, N., and III, W. A. G.: Optimal spline cutoffs for coulomb and van der waal interactions. Chem. Phys. Lett., 193:197–201, 1992.
278. Cyranoski, D. and Brumfiel, G.: Fukushima impact is still hazy. Nature, 477:139–140, 2011.
279. Medalia, J.: The japanese nuclear incident: Technical aspects. Congressional Research Service, R41728:1–18, 2011.
280. Plimpton, S.: Fast parallel algorithms for short-range molecular dynamics. J. Comp. Phys., 117:1–19, 1995.
281. Skomurski, F. N., Ewinig, R. C., Rohl, A. L., Gale, J. D., and Beciker, U.: Quantum mechanical vs. empirical potential modeling of uranium dioxide (UO₂) surfaces: (111), (110), and (100). Am. Mineral., 91:1761–1772, 2006.
282. Arima, T., Yamasaki, S., Inagaki, Y., and Idemitsu, K.: Evaluation of thermal properties of UO₂ and PuO₂ by equilibrium molecular dynamics simulations from 300 to 2000K. J. Alloys Compd., 400:43–50, 2005.
283. Arima, T., Yamasaki, S., Idemitsu, K., and Inagaki, Y.: Equilibrium and nonequilibrium molecular dynamics simulations of heat conduction in uranium oxide and mixed uranium-plutonium oxide. J. Nucl. Mater., 376:139–145, 2008.

- 284. Arima, T., Idemitsu, K., Inagaki, Y., Tsujita, Y., Kinoshita, M., and Yakub, E.: Evaluation of melting point of UO_2 by molecular dynamics simulation. J. Nucl. Mater., 389:149–154, 2009.
- 285. Muller-Plathe, F.: A simple nonequilibrium molecular dynamics method for calculating the thermal conductivity. J. Chem. Phys., 106:6082–6085, 1997.
- 286. Harris, J.: Simplified method for calculating the energy of weakly interacting fragments. Phys. Rev. B, 31:1770–1779, 1985.
- 287. Aktulga, H. M., Fogarty, J. C., Pandit, S. A., and Grama, A. Y.: Parallel reactive molecular dynamics: Numerical methods and algorithmic techniques. Parallel Comput., 38:245–259, 2011.
- 288. Alaghemandi, M., Algaer, E., Bohm, M., and Muller-Plathe, F.: The thermal conductivity and thermal rectification of carbon nanotubes studied using reverse non-equilibrium molecular dynamics simulations. Nanotechnology, 20:1–8, 2009.