12-2015

Bombardment Simulations and Intercalation Studies of Carbon Materials

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Bombardment Simulations and Intercalation Studies of Carbon Materials

A Dissertation
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Chemistry

by
Charles Nolan Lowe
December 2015

Accepted by:
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Abstract

Molecular bombardment experiments have led to the possibility of altering materials with properties not normally associated with those materials. Molecular bombardment leads to defect formation in the material, potentially creating a pore, depending on the material and bombarding molecule. Carbon allotropes, specifically graphite and graphene, make excellent candidates for molecular bombardment experimentation. Depending on the bombarding molecule and the kinetic energy associated with that molecule, the defects induced will be sufficient to create a pore in the graphene. The AIREBO potential is used to simulate a graphene bilayer being bombarded with a single Ar atom, or a C\textsubscript{60} molecule, to induce the formation of a pore. The system is then annealed to simulate bond restructuring. Analysis of the pore formation is performed using a model that incorporates ring formation in the graphene bilayer as an indicator of completeness, along with the area of the pore.

Graphite has become a popular medium for intercalating lithium atoms, making it useful as an anode in Li-ion batteries. However, graphite has a relatively low specific capacity, compared to pure lithium. In search of a higher specific capacity, a novel carbon material, graphyne, which is a theoretically proposed material that consist of two-dimensional networks of carbon with both \textit{sp} and \textit{sp}\textsuperscript{2} hybridized bonds, has been proposed as a superior adsorbent. Previous theoretical studies have shown that graphyne has the ability to intercalate more lithium atoms per carbon atom than
all other known carbon allotropes. Experimental studies have found that introducing other metals such as calcium can increase the amount of Li intercalated into materials like graphite. DFT calculations implemented in VASP are used to calculate how the binding energy of lithium is affected by the intercalation of calcium into graphite and graphyne in an attempt to further increase lithium concentrations. Lithium intercalation is found to improve in both materials with the addition of the calcium cointercalant.
Dedication

For Dad.
# Table of Contents

Title Page ......................................................... i
Abstract ......................................................... ii
Dedication ....................................................... iv
Dedication ....................................................... iv
List of Tables .................................................. vii
List of Figures ................................................ viii

1 Introduction ............................................... 1
   1.1 Molecular Dynamics .................................... 2
   1.2 Density Functional Theory ............................ 5
   1.3 Carbon Nanomaterials ................................. 7
   1.4 Project Overview ...................................... 9

2 Ar Bombardment of a Graphene Bilayer ................. 10
   2.1 Introduction .......................................... 10
   2.2 Methods ................................................ 12
   2.3 Results and Discussion ............................... 19
   2.4 Conclusions ........................................... 28

3 C\textsubscript{60} Molecular Bombardment of a Graphene Bilayer ................. 29
   3.1 Introduction .......................................... 29
   3.2 Methods ................................................ 30
   3.3 Results and Discussion ............................... 34
   3.4 Conclusions ........................................... 40

4 Intercalation of Li and Ca in Graphite .................. 44
   4.1 Introduction .......................................... 44
   4.2 Methods ................................................ 45
   4.3 Results and Discussion ............................... 49
## List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>Calculated total energies for various materials necessary for adsorption</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>energy calculations.</td>
<td></td>
</tr>
<tr>
<td>4.2</td>
<td>Average adsorption energies for different lithium concentrations, Li\textsubscript{y}C\textsubscript{6},</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td>in AA-stacked graphite and AB-stacked graphite.</td>
<td></td>
</tr>
<tr>
<td>4.3</td>
<td>Average adsorption energies for different lithium concentrations and</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>different calcium concentrations, Ca\textsubscript{x}Li\textsubscript{y}C\textsubscript{6}, in AB-stacked graphite</td>
<td></td>
</tr>
<tr>
<td>4.4</td>
<td>Increase in interlayer distance change, $\tau$, for different lithium</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td>concentrations and different calcium concentrations, Ca\textsubscript{x}Li\textsubscript{y}C\textsubscript{6}, in AB-stacked graphite</td>
<td></td>
</tr>
<tr>
<td>5.1</td>
<td>Calculated total energies for various materials necessary for adsorption</td>
<td>66</td>
</tr>
<tr>
<td></td>
<td>energy calculations.</td>
<td></td>
</tr>
<tr>
<td>5.2</td>
<td>Average adsorption energies for different lithium concentrations, Li\textsubscript{y}C\textsubscript{6},</td>
<td>66</td>
</tr>
<tr>
<td></td>
<td>in graphyne.</td>
<td></td>
</tr>
<tr>
<td>5.3</td>
<td>Increase in interlayer distance change, $\tau$, for different lithium</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td>concentrations in graphyne.</td>
<td></td>
</tr>
<tr>
<td>5.4</td>
<td>Average adsorption energies for different lithium concentrations and</td>
<td>71</td>
</tr>
<tr>
<td></td>
<td>different calcium concentrations, Ca\textsubscript{x}Li\textsubscript{y}C\textsubscript{6}, in graphyne.</td>
<td></td>
</tr>
</tbody>
</table>
List of Figures

1.1 Visualization of the carbon nanomaterial graphyne. .................... 9

2.1 Schematic illustration of graphene with (a) no defects, (b) one vacancy, (c) two adjacent vacancies, and (d) four vacancies. Each carbon atom (small black circle) is surrounded with a shaded circle of radius \( r_{CC} \). The pore cross-sectional area, \( A \), is the area of the unshaded region. 14

2.2 A illustration of an ideal pore consisting of 12 heptagons, highlighted in red. .................................................. 16

2.3 Reflection, penetration, and trapping fractions of Ar expressed as a function of impact energy for varying angles. ......................... 20

2.4 Average pore area expressed as a function of impact energy for varying angles, given in \( A^2 \). Some error bars are omitted for clarity. 21

2.5 Example of distribution of average ring sizes for 20 separate impact simulations for a specific impact energy and specific angle. Inset figure shows distribution of ring sizes for a single impact simulation for a specific impact energy and specific angle. 23

2.6 Pore completeness expressed as a function of impact energy for varying angles. The scatter plots represent raw data points for 15 and 45 degree angles. 24

2.7 The maximum completeness value obtained from the fit in the previous figure, expressed as a function of angle. 25

2.8 Pore disorder expressed as a function of impact energy for varying angles. 26

2.9 Pore quality expressed as a function of impact energy for varying angles. Pore quality is the ratio of pore completeness and pore disorder. 27

3.1 Representative image of a pore formed from the collision of a \( C_{60} \) molecule into a graphene bilayer. ............................. 32

3.2 Average pore area expressed as a function of impact energy for 45° and 90° impact angles, for both 5 ns NVE and 1.2 ns NVT post-collision dynamics. Error bars show standard error. 36

3.3 Example of distribution of ring sizes for 20 separate impact simulations for a 10 keV impact energy and 90° angle under NVE post-collision dynamics. 37
3.4 Example of distribution of ring sizes for 20 separate impact simulations for a 10 keV impact energy and 90° angle under NVT post-collision dynamics

3.5 Pore completeness expressed as a function of impact energy for varying angles for both NVE and NVT post-collision dynamics

3.6 Pore disorder expressed as a function of impact energy for varying angles for both NVE and NVT post-collision dynamics

3.7 Pore quality expressed as a function of impact energy for varying angles for both NVE and NVT post-collision dynamics. Pore quality is the ratio of pore completeness and pore disorder

4.1 Image of AA-stacked graphite(left) and AB-stacked graphite(right). Materials are shown slightly off normal to show multiple layers

4.2 Lithium adsorption energy values as a function of intercalated lithium concentration in graphite. The lithium cohesive energy is also plotted

4.3 The adsorption energy values as a function of intercalated lithium concentration in graphite for different concentrations of calcium. The lithium cohesive energy is also plotted

4.4 The maximum lithium concentration that is achievable as a function of the intercalated calcium concentration for Ca_xLi_yC_6

4.5 The interlayer distance for each maximum lithium concentration obtained using a least squares linear fit of Table 4.4

4.6 Lithium adsorption energy values as a function of intercalated lithium concentration in graphite calculated using Equation 4.6. The lithium cohesive energy is also plotted

5.1 Image of graphyne supercell. Material is shown slightly off normal to show multiple layers

5.2 Lithium adsorption energy values as a function of intercalated lithium concentration, y, for structure Li_yC_6 in graphyne (blue curve). The lithium cohesive energy is also plotted (red line)

5.3 Visualization of a LiC_6 graphyne system where the lithium atoms are represented by purple spheres and carbon atoms by gray spheres

5.4 Visualization of a Li_2C_6 graphyne system where the lithium atoms are represented by purple spheres and carbon atoms by gray spheres

5.5 Visualization of a Li_3C_6 graphyne system where the lithium atoms are represented by purple spheres and carbon atoms by gray spheres

5.6 Lithium adsorption energy values as a function of intercalated lithium concentration in graphyne for different concentrations of calcium. The lithium cohesive energy is also plotted

5.7 Visualization of a Ca_0.125Li_2C_6 graphyne system where the lithium atoms are represented by purple spheres, the calcium atoms by green spheres, and carbon atoms by gray spheres
5.8 Visualization of a Ca$_{0.5}$Li$_2$C$_6$ graphyne system where the lithium atoms are represented by purple spheres, the calcium atoms by green spheres, and carbon atoms by gray spheres. ................................................................. 75

5.9 Visualization of a Ca$_{0.125}$Li$_4$C$_6$ graphyne system where the lithium atoms are represented by purple spheres, the calcium atoms by green spheres, and carbon atoms by gray spheres. A red dotted line indicates the broken bond inside of the highlighted red square. ................................. 76

5.10 Visualization of a Ca$_{0.5}$Li$_{3.5}$C$_6$ graphyne system where the lithium atoms are represented by purple spheres, the calcium atoms by green spheres, and carbon atoms by gray spheres. ................................. 77
Chapter 1

Introduction

The use of computational chemistry has become a necessary part of most modern scientific inquiries. The field of computational chemistry utilizes computers to calculate both properties and structures of molecules and materials. Problems that are small in size (< 1000 atoms) can rely on methods based around quantum mechanics called \textit{ab initio} methods. One method of interest is density functional theory (DFT) where functionals are used to determine properties of a many-electron system. Chemical problems that are large in size (> 1000 atoms) commonly use empirical methods such as molecular dynamics (MD) which are based on solving Newton’s equation of motion.

This work focuses on both MD simulations and DFT calculations to explore the physical and chemical properties of carbon nanostructures. We begin with an overview of MD and also discuss other necessary concepts. Then, an overview of DFT is given, along with details specific to the calculations performed here. Finally, we introduce the carbon nanostructures studied in this work.
1.1 Molecular Dynamics

We begin our overview of molecular dynamics by stating Newton’s second law of motion, which is given by the equation,

$$\vec{F}_i = m_i a_i. \quad (1.1)$$

In this equation, $F_i$ represents the force acting on the particle $i$, $m_i$ is the mass of the particle $i$, and $a_i$ denotes the acceleration of particle $i$. We can also write this equation in terms of the gradient of the potential energy, $\nabla_i V$,

$$\vec{F}_i = -\nabla_i V \quad (1.2)$$

By noting that acceleration is the second derivative of position with respect to time, we can combine these two equations to obtain Newton’s equation of motion,

$$-\frac{dV}{dr_i} = m_i \frac{d^2 r_i}{dt^2}. \quad (1.3)$$

We need to describe the motion of atoms based on their positions and how they change as time progresses. To do this, we assume that acceleration is constant and integrate the definition of acceleration, $a_i = \frac{dv_i}{dt}$, to get

$$v_i = a_i t + v_0. \quad (1.4)$$

Similarly, we integrate the definition of velocity, $v_i = \frac{dr_i}{dt}$, to get

$$r_i = v_i t + r_0. \quad (1.5)$$
where \( r_0 \) is the initial position and \( v_0 \) is the initial velocity. Because acceleration is constant, velocity changes uniformly from the initial value to the final value, so the average velocity is

\[
\bar{v}_i = \frac{v + v_0}{2}.
\] (1.6)

We can substitute Equation 1.4 into Equation 1.6 to get

\[
\bar{v}_i = v_0 + \frac{1}{2} a_i t.
\] (1.7)

Finally, we can substitute Equation 1.7 into Equation 1.5 to get an expression based on \( r_0 \), \( v_0 \), and \( a \):

\[
r = \frac{1}{2} a t^2 + v_0 t + r_0
\] (1.8)

where

\[
a = -\frac{1}{m} \frac{dV}{dr}
\] (1.9)

With these expressions, along with a constant acceleration and known \( r_0 \) and \( v_0 \), we can now simulate a particle’s full trajectory through space for some time \( t \) based on sequential time steps, \( \Delta t \). These time steps are kept small enough that constant acceleration can be assumed.

It is up to the user what time step to select in MD simulations. A time step that is too large will lead to failed energy conservation because the constant acceleration assumption is only valid in the limit of infinitely small time steps. Whereas a time step that is too small will not allow for a usefully long simulation time within a reasonable amount of CPU hours.

A variable time-step\(^1\) algorithm can be used to determine the time step for the integrator. This allows for longer time steps when the molecule(s) are at constant acceleration. Conversely, it allows for shorter time steps when undergoing a reaction
where acceleration values are rapidly changing.

Energy conservation is also dependent on the ensemble used. This work makes use of both the microcanonical ensemble (\(NVE\)) where the number of moles, \(N\), volume of the system, \(V\), and total energy, \(E\), are constant and the canonical ensemble (\(NVT\)) where temperature, \(T\), is held constant rather than the total energy. The microcanonical ensemble has the benefit of conserving total energy due to being an isolated system where no energy is exchanged with the surroundings. On the other hand, the canonical ensemble does not necessarily conserve total energy.

This ensemble is generally used under two conditions. One is when a temperature spike occurs, where the temperature quickly increases by a large amount. The thermostat acts as a heat sink to remove the excess energy produced from the collision(s) or reactions that caused the spike.

Another condition where the canonical ensemble is useful is for simulating the temperature of a material after a collision. It can take longer to reach the correct temperature than can be reasonably simulated with MD. By using a thermostat, we can quickly reach this temperature, allowing the correct dynamics to occur.

There are several thermostats that are commonly used in MD simulations. The one used in this work is known as the Langevin thermostat.\(^2\) The Langevin thermostat modifies Equation 1.2 to add both a frictional force, \(\gamma m_i v_i\), and random force, \(L(t)\),

\[
F_i = -\nabla_i V - \gamma m_i v_i + L(t)
\]  

(1.10)

The added forces are chosen in such a way as to maintain the desired system temperature. Although molecular dynamics can be used for any molecule or material, density functional theory can be used for small systems.
\subsection{1.2 Density Functional Theory}

We begin our overview of DFT by stating the time-independent Schrödinger equation,

\[ \hat{H} \Psi = E \Psi. \]  

Here, $\hat{H}$ is the Hamiltonian, $E$ is the total energy, and $\Psi$ is the wavefunction. The total energy can be separated into three parts after assuming the Born-Oppenheimer approximation: a kinetic energy term, $\hat{T}$, a nucleus-electron potential energy term, $\hat{V}$, and an electron-electron potential energy term, $\hat{U}$ written as

\[ E \Psi = [\hat{T} + \hat{V} + \hat{U}] \Psi \]  

Ideally, we could separate this equation into single-particle equations, but this turns out to be impossible due to the electron-electron interaction term. There are several ways to solve the Schrödinger equation using Slater determinants such as the Hartree-Fock method, coupled cluster, and configuration interaction. Hartree-Fock neglects the electron-electron correlation energy and the other methods are only useful for smaller molecules of approximately forty atoms or fewer. Another method exists that evaluates the Schrödinger equation using electron density rather than multi-electron wavefunctions. We can write this electron density as a functional of the wavefunction

\[ \rho(\vec{r}) = N \int d^3 r_2 \ldots \int d^3 r_N \Psi^*(\vec{r}, \vec{r}_2, \ldots, \vec{r}_N) \Psi(\vec{r}, \vec{r}_2, \ldots, \vec{r}_N) \]  

This method is referred to as density functional theory (DFT). DFT has the benefit of being more accurate than Hartree-Fock, while also being as easy to implement.\textsuperscript{[3]}

Using DFT, Equation 1.12 is rewritten in terms of the density

\[ E[\rho] = \hat{T}[\rho] + \hat{U}[\rho] + \int V(\vec{r})\rho(\vec{r})d^3r \]  

(1.14)

The kinetic energy and the electron-electron potential energy terms are universal operators, whereas the electron-nucleus potential energy term depends on the system to which it is applied. The electron-nucleus potential energy functional can be expressed as a sum of a Coulomb repulsion functional and an exchange-correlation functional,

\[ \hat{V} = \hat{V}_{\text{Coulomb}} + \hat{V}_{\text{exchange\text{-}correlation}}. \]

(1.15)

The exact Coulomb repulsion functional is known, however the exchange-correlation functional is only known for a free-electron gas. There are multiple ways of approximating this exchange-correlation functional. For materials such as those studied in this work, the generalized gradient approximation (GGA) is often used with good accuracy. The GGA considers the gradient of the electron density at the specific coordinate where the functional is evaluated, while also considering the spin of the electrons. This can be written as

\[ E[\rho^\uparrow, \rho^\downarrow] = \int \epsilon(\rho^\uparrow, \rho^\downarrow, \vec{\nabla}\rho^\uparrow, \vec{\nabla}\rho^\downarrow)\rho(\vec{r})d^3r \]

(1.16)

where \( \rho^\uparrow \) and \( \rho^\downarrow \) represent the up and down spins of the electron density and \( \epsilon \) is a function of both spin densities and the gradients of those spin densities. This functional has the benefit of estimating binding energies better than more simple functionals that only consider the local electron density, which will be important for the materials studied in Chapters 4 and 5.

In infinite, periodic solids with delocalized electrons like graphite, the electrons...
behave similarly to a free electron gas. This allows for the use of plane wave basis sets over traditional atom-centric basis sets, requires less computational time overall. A plane-wave basis set can be written as a density expressed as a linear combination of plane waves,

$$\rho(i) = \sum_{\vec{k}} c_i e^{-i\vec{k}\cdot\vec{r}} \quad (1.17)$$

where $\vec{k}$ is a wave vector and $\vec{r}$ is a position vector. The exact basis set is only obtained using an infinite number of plane waves. We can approximate the exact basis set by choosing a cutoff for the number of wave vectors used. This cutoff is usually expressed in terms of kinetic energy. The cutoff is chosen to minimize the number of necessary wave vectors, while still correctly approximating the electron density.

### 1.3 Carbon Nanomaterials

Carbon nanomaterials have been researched extensively in the last few decades.\cite{9-19} Previously, before the discovery of synthetic allotropes such as carbon nanotubes (CNTs), a one-dimensional cylindrical arrangement of $sp^2$ carbon, and fullerenes, a zero-dimensional arrangement of $sp^2$ carbon, studies were restricted to naturally occurring allotropes, such as diamond, composed of $sp^3$ carbon, and graphite, composed of $sp^2$ carbon. Studies related to synthetic allotropes have led to new discoveries for batteries, hydrogen storage, optics, and many other applications.\cite{20-22} For example, carbon nanotubes have the ability to adsorb hydrogen gas inside of the nanotube via capillarity, as a potential fuel storage source.\cite{9} Another example uses fullerene molecules as part of a drug delivery system, based on the fullerene’s ability to migrate into a cell.\cite{10}
A carbon nanomaterial of particular interest, graphene, consists of a single layer of $sp^2$ carbons which form an infinite hexagonally bonded network, which is isolated from graphite. Graphene has recently been extensively studied, based on its exceptional combination of properties, including structural, electronic, and mechanical properties.\textsuperscript{[17–19]} Graphene was the focus of the work that lead to the 2010 Nobel prize in physics “for groundbreaking experiments regarding the two-dimensional material graphene”.\textsuperscript{[11]} Graphene was first isolated through the technique of exfoliation, where a layer of graphene is mechanically removed from a sample of graphite through the use of adhesive tape.\textsuperscript{[23]} Later on, graphene was synthesized through chemical vapor deposition,\textsuperscript{[24]} and other experimental techniques, allowing for control of how many graphene sheets were deposited on a substrate. This has led to the use of graphene as an energy storage material.\textsuperscript{[12]} In this work, the simulation of bombarding graphene with high-energy particles will be studied.

Another carbon nanomaterial of theoretical interest is graphyne ($gpy$). Graphyne consists of $sp^2$ hexagonal carbon rings that are connected via $sp$ acetylenic linkages ($-C\equiv C-$), which produces a planar material as seen in Figure 1.1. Graphyne was first predicted to have a high chance of synthesis in 1987 by Baughman et al.\textsuperscript{[25]}, having binding energy of 7.95 eV/atom, compared to graphite’s 8.87 eV/atom, suggesting its stability. So far, attempts to synthesize graphyne have failed, causing it to remain only a theoretical material. An attempt has been made to use hexaethylbenzene as a starting material, which incorporates allyl functional groups on the exterior of a phenyl ring.\textsuperscript{[26]} Unfortunately, hexaethylbenzene is very sensitive to heat and oxygen, allowing for synthesis of only a small GPY substructure, tris[12]dehydrobenzoannulene.\textsuperscript{[26]} In this work, DFT calculations of the intercalation of lithium and calcium into graphyne, as well as graphene, will be studied.
1.4 Project Overview

This project’s goal is to study the potential of carbon nanomaterials for possible energy storage. Chapter 2 presents simulations of the bombardment of a graphene bilayer by an argon atom and the tools used to analyze these simulations. Chapter 3 presents simulations of the bombardment of a graphene bilayer by a C_{60} molecule and analysis of these simulations through the tools discussed in Chapter 2. The use of a program to visualize chemical and mathematical properties of these simulations is also presented. Chapter 4 presents calculations of the intercalation of lithium and calcium atoms in bulk graphite. Finally, Chapter 5 presents calculations of the intercalation of lithium and calcium atoms into bulk graphyne.
Chapter 2

Ar Bombardment of a Graphene Bilayer

2.1 Introduction

Ion surface collisions of graphitic materials have been heavily researched over the past few decades, through both experimentation and theoretical calculations.[27–30] Of these graphitic materials, graphene has become a major target of study, due to its exemplary electronic and mechanical properties.[17–19] The importance of the discovery and analysis of this material is made apparent by the recently awarded Nobel Prize in chemistry “for groundbreaking experiments regarding the two-dimensional material graphene”. [11] Graphene was first isolated through mechanical exfoliation[23], then later synthesized through chemical vapour deposition[24], reduction of graphene oxide[31], and other methods.

Ion collisions on graphene have previously been performed by pulsed laser deposition[32] and the resulting defects have been studied using scanning tunneling microscopy.[33] The defects created through ion irradiation of graphene also lead to
changes in the band gap of the material. These defects cause metallic graphene, normally a metal, to become an insulator through the transition from all $sp^2$-hybridized carbon atoms to include some $sp^3$-hybridized carbon atoms. Defects of this type are likely to be present in synthesized graphene.\textsuperscript{[31]} The inclusion of $sp^3$-hybridized atoms leads to topological changes to the graphene sheet, creating non-hexagonal polygons in defective graphene. The non-hexagonal polygons induce either negative or positive curvature in the once planar material, which hasn’t been observed in other materials.\textsuperscript{[35]} Defects in graphene lead to higher reactivity localized around the defects and increases the adsorption of other atoms onto graphene.\textsuperscript{[35]} The increase in adsorption of other atoms has suggested the use of defective graphene in fuel cells.\textsuperscript{[36]}

If the ion collisions onto graphene are of sufficient energy, the bombarding particle(s) will deform the graphene layer to the point that there exists a vacancy of one or more carbon atoms. Similar bombardment of a graphene bilayer, where the ion has high enough energy to alter both layers, will produce carbon atom vacancies where the two sheets will begin to interconnect. The connections that occur between layers will include polygons of different size, altering the curvature of the two sheets. If the amount of curvature induced by the different-sized polygons is sufficient, then the interconnections will form a “pore”, which is essentially a tunnel running from one side of the graphene bilayer to the other. In this paper, we study the impact of an energized Ar atom on a graphene bilayer. The results of these impacts are then analyzed using novel methods that quantify the polygons formed from the rearrangement of the carbon atoms and the formation of a “pore” after impact and during annealing.
2.2 Methods

Impacts were performed by modeling collisions between an argon atom projectile and a stationary graphene bilayer. The system was modeled with rectangular periodic boundary conditions in the two dimensions parallel to the graphene sheets, with side lengths of 66.45 Å along the [100] direction and 63.95 Å along the [120] direction. Each graphene sheet contained 1620 carbon atoms. The argon atom kinetic energies varied between 20 eV and 5 keV, at 20 eV intervals up to 100 eV, and 100 eV intervals up to 5 keV. The angle of impact was also varied from 15° to 90°, measured as the angle between the argon velocity vector and the surface plane (e.g. 90° corresponds to normal impact). Twenty separate impacts were performed for each combination of energy and angle, so that statistical analysis of the impacts could be performed. During the impact, each system was integrated with unconstrained (microcanonical) dynamics for 10 ps. Because of the relatively large variation in timesteps required during the energetic collision phase (∼ 0.05 fs) and subsequent energy dissipation phase (∼ 0.25 fs), a variable-timestep integrator\cite{1} was used to integrate the dynamics.

After the initial 10 ps of impact dynamics, the system was equilibrated in the canonical ensemble at a temperature of 2000 K for 100 ps using a Langevin thermostat\cite{2} with a time constant of 100 fs. This annealing period allowed for some slower bond rearrangement dynamics that are important in restructuring the pore geometry. All interatomic interactions were modeled with the AIREBO potential\cite{37}.

Many of the impacts generate pores in the bilayer graphene surface, and the cross-sectional area of the pore is perhaps the most important characteristic in assessing the suitability of the pore for practical applications.

We define the pore cross-sectional area, $A$, to be the geometrical area of the
largest contiguous region in the surface plane that is at least one carbon–carbon bond length \( r_{CC} = 1.42 \, \text{Å} \) from all carbon atoms, when they are projected into this surface plane. This is illustrated in Figure 2.1 for several pore sizes. An undamaged graphene sheet (Fig. 2.1(a)) contains no pores under this definition, and even a(n unreconstructed) vacancy in graphene (Fig. 2.1(b)) would have no pore area, because all points are still less a bond length or less away from some carbon atom. Two adjacent vacancies (Figs. 2.1(c)) are required before a non-zero pore area is obtained, and at least four carbon atoms must be removed (Fig. 2.1(d)) or displaced before the pore area exceeds \( 4 \, \text{Å}^2 \), potentially able to allow transport of the smallest substrates.

In our analysis, the value of \( A \) is determined numerically, by integrating the cross sectional area with a rectangular grid with spacing 0.033 Å.

Note that by projecting all atoms into the surface plane, this definition implicitly assumes that the pore is perpendicular to the surface plane. It would consequently be unreasonable for angled or sinuous pores in thick substrates, but is a reasonable approximation for bilayer graphene.

The pores generated by impact and subsequent thermal annealing will not be simple vacancies, as in Figure 2.1. Some of the dangling bonds, broken during the initial impact, will be reformed, either by crosslinking the graphene layers or reconstructing within the layer. These reconstructions are crucial to forming the pore wall, and in producing functional nanoporous materials. Thus, another important characteristic of the pores generated by impacts is the degree to which the graphitic structure has been maintained in the pore. Several measures of this graphitic structure are obtained from the distribution of ring sizes (e.g. hexagons, heptagons, etc.) that compose the pore wall and surrounding graphene layers. Only minimal rings are included in this distribution (excluding, for example, the 10-membered rings formed by two adjoining hexagons). Identifying minimal rings is not unambiguous, however,
Figure 2.1: Schematic illustration of graphene with (a) no defects, (b) one vacancy, (c) two adjacent vacancies, and (d) four vacancies. Each carbon atom (small black circle) is surrounded with a shaded circle of radius $r_{CC}$. The pore cross-sectional area, $A$, is the area of the unshaded region.

(a) No vacancies. $A = 0$.

(b) One vacancy. $A = 0$.

(c) Two vacancies. $A = \left(\frac{3\sqrt{3}}{2} - \frac{2\pi}{3}\right) r_{CC}^2 \approx 1\ \text{Å}^2$.

(d) Four vacancies. $A = \left(3\sqrt{3} - \pi\right) r_{CC}^2 \approx 4\ \text{Å}^2$. 
and depends on the criterion used to define them. We use the “shortest-path” criterion defined by Franzblau\cite{38} and originally proposed by Marians and Hobbs\cite{39}, which excludes any ring if at least half of its atoms are contained in some smaller ring.

As a measure of how fully formed a given pore is, we define a measure

$$\mu = \frac{1}{12} \sum_{i=3}^{9} n_i(i - 6), \quad \text{(2.1)}$$

where $n_i$ is the number of $i$-membered rings, or $i$-gons, in the system.\footnote{Unless you prefer Greek indices, in which case let $i$-gons be $\pi$-gons.} This measure can be understood intuitively in the following manner. The summation

$$\sum_{i=3}^{9} n_i(i - 6) \equiv \Delta b \quad \text{(2.2)}$$

that appears in Eq. 2.1 can be interpreted as a count of the number of excess bonds in the system: each hexagon ($i = 6$) in purely graphitic material contributes nothing to $\Delta b$, while each heptagon ($i = 7$), for example, contributes exactly one excess bond to $\Delta b$. An ideal pore, as illustrated in Figure 2.2, requires 12 heptagons—six at each mouth—to induce the negative curvature required by this surface. Equation 2.1 thus gives a value of $\mu = 0$ for undamaged graphene layers, and $\mu = 1$ for an ideal pore with exactly 12 heptagons. Values of $\mu > 1$ indicate more than 12 excess bonds in the structure; more than would be needed to generate a single, ideal pore.

Alternatively, we can derive Equation 2.1 as a topological description of a porous graphene bilayer treated as a polyhedral surface. (This explains why the ring count is capped at $i = 9$ in Equation 2.1 and in the equations below: doing so excludes all pore-girdling rings that would lead to a non-manifold structure.) Euler's
Figure 2.2: A illustration of an ideal pore consisting of 12 heptagons, highlighted in red.
characteristic function,
\[ \chi = V - E + F = 2(1 - g) - B, \]  
(2.3)
describes the relationship between the number of vertices \((V)\), edges \((E)\), and faces \((F)\) of a polyhedron with genus \(g\) and \(B\) boundaries. A graphene bilayer with a single pore, topologically equivalent to the one shown in Figure 2.2, has \(g = 1\) and \(B = 2\), so an Euler characteristic of \(\chi = -2\). Written in terms of the ring counts, the number of faces in the polyhedron is
\[ F = \sum_{i=3}^{9} n_i \]  
(2.4)
(i.e. the number of \(i = 3\) triangles plus the number of \(i = 4\) squares, etc.). Each of the \(i\)-gonal faces has \(i\) edges, and each edge is counted by two adjacent faces (if there are no non-manifold junctions), so the total number of edges can be expressed as
\[ E = \frac{1}{2} \sum_{i=3}^{9} in_i. \]  
(2.5)
Each edge terminates on two ends, so the total number of edge-ends is \(2E\). Under conditions where defects and dangling bonds have been annealed away and all carbon atoms have recovered \(sp^2\) hybridization, each vertex is formed from three such edge-ends, and
\[ V = \frac{2E}{3} = \frac{1}{3} \sum_{i=3}^{9} in_i. \]  
(2.6)
Since the Euler characteristic for such a pore is \(-2\), we define a measure of pore
completeness as

$$\mu = \frac{\chi}{2} = -\frac{1}{2} (V - E + F)$$

(2.7)

$$= -\frac{1}{2} \left( \frac{1}{3} \sum_{i=3}^{9} i n_i - \frac{1}{2} \sum_{i=3}^{9} i n_i + \sum_{i=3}^{9} n_i \right)$$

(2.8)

$$= \frac{1}{12} \sum_{i=3}^{9} n_i (i - 6),$$

(2.9)

as in Equation 2.1. Thus, a value of $\mu = 1$ characterizes a single pore with no non-$sp^2$ defects, and $\mu = 0$ corresponds to an undamaged graphene bilayer. Intermediate values indicate pores with walls that are incompletely formed, or that have non-$sp^2$ bonding defects. Values larger than 1 are also possible, for structures with more than one pore, or (more commonly) many non-$sp^2$ defects, or non-manifold structural defects.

This measure of completeness is not sufficient for identifying whether a pore is ideal, in the sense of being formed with as few large rings as possible. For example, the pore opening could be formed with 10 heptagons and 1 octagon, rather than 12 heptagons, and still have $\mu = 1$. Consequently, we define an additional measure of pore ideality. Ignoring the normalization coefficient in Eq. 2.1, $\mu$ can be viewed as an average deviation from, or first moment about, the 6-member rings of a purely hexagonal graphene structure. We analogously define a second moment,

$$\sigma^2 = \frac{1}{12} \sum_{i=3}^{9} n_i (i - 6)^2.$$  

(2.10)

The coefficient 1/12 is chosen so that $\sigma^2 = 1$ for an ideal pore with 12 heptagons. While $\mu$ corresponds to the mean excess ring size, $\sigma^2$ corresponds to the variance of the ring size distribution about six, and will be minimized in an ideal pore. At a given
value of $\mu$ (pore completeness), lower values of $\sigma^2$ indicate less disorder or breadth in the ring size distribution. Consequently, we refer to $\sigma^2$ as the pore disorder.

For partial pore formation, with $\mu < 1$, the least disordered structure would have $\sigma^2 = \mu$ (i.e. $12\mu < 12$ heptagons and no other non-hexagonal rings). Any other structure would necessarily have $\sigma^2 > \mu$. Thus we also consider the ratio $\mu/\sigma^2$ as a metric of pore quality; pores or partial pores formed with the minimal number of excess bonds will have $\mu/\sigma^2 = 1$ and those formed with an unnecessarily broad distribution of rings will have $\mu/\sigma^2 < 1$.

### 2.3 Results and Discussion

Upon impact with the graphene bilayer, an Ar atom may be reflected from the surface, penetrate through both layers of the surface, or be trapped between them. The probability of these three outcomes vary, of course, with the impact energy and angle. The original expectation was that these values would provide some indication of what conditions were more favorable for pore formation. Figure 2.3 shows that for impacts at shallow angles, Ar tends to reflect off the graphene surface, even at high energies. Fully 100\% of the 15- and 30-degree impacts were reflected, and roughly 90\% of the 45-degree impacts are reflected, even at energies up to 5 keV. (Note that even these reflected impacts can lead to successful pore formation, as the Ar atom transfers its momentum to C atoms that are then ejected from the surface, contradicting our earlier assumption that reflection would be an indication of non-productive collisions.) At steeper angles, trapping of the Ar between the graphene sheets becomes possible; this occurs in roughly 20 to 50\% of 60-degree impacts over a broad range of energies from 1 keV to 5 keV. For normal and near-normal incidence, penetration of both layers is the most likely outcome above 500 eV, and reflection becomes very unlikely.
The cross-sectional area of a pore is one of the most important characteristics of a nanoporous surface in applications such as separations or electrode materials, as it determines the type of species that can pass through the pores as well as the rate at which they can be transported. These cross-sectional areas are reported in Figure 2.4 for each combination of impact energy and incident angle. As seen in Figure 2.4, the area for increasing impact energy eventually plateaus at a maximum corresponding the angle of impact. Those impacts that are normal to the surface create the largest pores, whereas shallow angle impacts lead to smaller pores. For the shallowest angles of 15 and 30 degrees, the effective area is limited to 2 Å², which plateau for impact at keV energies.
energies higher than 500 eV. Pore areas for larger angles of 45 and 60 degrees appear to plateau around 5 Å² at impact energies of at least 3000 eV. The largest angles of 75 and 90 degree angles plateau at approximately 8 Å² at impact energies of at least 2000 eV. To get an idea for how the areas seen for these pores compare to sizes for commonly used molecular sieves, we can approximate the shape of the pore as a circle and apply $A = \pi r^2$. The smallest commercially available sieve is model 3A which has a diameter of 3 Å.[40] This molecular sieve would have a pore area of approximately 7 Å². This size can be achieved using impact energies of at least 2000 eV and angles of 75 and 90 degrees. Sizes comparable to molecular sieves of larger sizes do not appear to be possible using Ar as the impacting particle.
Ideally, after sufficient annealing, the cross-links created by bombardment of Ar should arrange themselves to form a $sp^2$ network between the two graphene sheets. Going on this assumption, the negative curvature required to form this network between sheets would need twelve 7-membered rings among the 6-membered rings found in graphene. We use the ring counting algorithm previously discussed to determine what size rings are present in each of our simulations. Figure 2.5 shows an example of both the distribution of these rings for a single simulation and for the average over twenty simulations for a particular angle and energy (it would be burdensome to include all of these). Generally, these graphs show a large amount of 6-membered rings as expected, along with several 5-membered and 7-membered rings. Larger rings are found occasionally, corresponding to the openings of the pores and incomplete cross-linking between sheets. On average, between five and seven 7-membered rings are present, with between two and five 5-membered rings also present. These 5-membered rings induce positive curvature, which reduces the negative curvature induced by the 7-membered rings. Rings larger than seven induce more negative curvature, which can account for the positive curvature induced by the 5-membered rings. It should be noted that the size of the pores created in these simulations are too small to utilize twelve 7-membered rings to induce the required negative curvature. Future studies will require impact atoms to be larger than Ar, most likely molecules instead, to create a sufficiently large pore.

We consider a pore to be "complete" if it contains 6-membered rings along with twelve 7-membered rings. Quantitative measurement of completeness follows from Eq. 2.1. Application of this equation are shown in Figure 2.6. A value near zero corresponds to a system where no damage has occurred to either graphene sheet. A value of one corresponds to the correct amount of negative curvature needed for a "complete" pore. In an effort to understand how changes in angle and impact energy
Figure 2.5: Example of distribution of average ring sizes for 20 separate impact simulations for a specific impact energy and specific angle. Inset figure shows distribution of ring sizes for a single impact simulation for a specific impact energy and specific angle.
affect this measurement, we choose to fit an equation to the completeness data. The line plots in Figure 2.6 represent the fit of raw data using the equation $a - be^{-x/c}$, where $a$, $b$, and $c$ are fitting parameters and $x$ is the raw completeness value. We can see in Figure 2.6 that the fit produces a plateauing completeness value for each angle as energy becomes large. The maximum completeness value obtained for these angles is shown in Figure 2.7. From this figure, we can see that a 45 degree impact angle results in the highest completeness value, suggesting this would be the optimal bombardment when a clean pore is desired.

Even though a 45 degree impact obtains a completeness value close to 1, we still need to consider the disorder of the formed pore. As stated earlier, disorder
Figure 2.7: The maximum completeness value obtained from the fit in the previous figure, expressed as a function of angle.
Figure 2.8: Pore disorder expressed as a function of impact energy for varying angles. Allows us to quantify the variation of ring sizes making up the pore. We can see in Figure 2.8 that there is a broad distribution in ring sizes occurring for impact angles where higher completeness values are found. If we consider pore quality, the ratio of completeness and disorder, we can see in Figure 2.9 that these pores have formed with a broad ring distribution, since $\mu/\sigma^2 < 1$. This indicates that the high completeness values are likely due to the presence of 8 and 9-membered rings (and the lack of 3, 4, and 5-membered rings to induce a corresponding positive curvature), and not the desired 7-membered rings. This supports our previous speculation that larger impact particles will be necessary for pores large enough to incorporate the necessary 12 7-membered rings.
Figure 2.9: Pore quality expressed as a function of impact energy for varying angles. Pore quality is the ratio of pore completeness and pore disorder.
2.4 Conclusions

The bombardment of bilayer graphene by Ar was studied using molecular dynamics simulations using a variety of impact kinetic energies and impact angles. The Ar atoms were found to reflect, penetrate, and become trapped between the bilayer, based on impact energy and angle. In cases where the Ar atom is sufficiently energized, a pore is formed in the bilayer. It was discovered that pores could still be formed, even if the Ar atom reflected off of or became trapped in the bilayer. Pore size is observed to increase as impact energy increases, eventually reaching a plateau at a specific energy. Results show that shallow impact angles form smaller pores, whereas impact angles closer to being normal to the graphene bilayer produce larger pores.

Topological measures were derived to determine how the distribution of different ring sizes affects the formation of pores. Analysis of the pore completeness found that the most complete pores were found for 45 degree impact angles. Pore disorder values for more complete pores are larger relative to less complete pores, indicating a broader ring distribution for more complete pores. Pore quality is found to be roughly the same for all impact angles, indicating that the broader ring distribution is the cause for high completeness values, rather than the sole presence of 7-membered rings. The next chapter will utilize a larger impacting particle, a C_{60} molecule, in an attempt to improve the pore quality.
Chapter 3

C\textsubscript{60} Molecular Bombardment of a Graphene Bilayer

3.1 Introduction

Carbon materials such as graphitic nanomaterials are ideal for use as molecular sieves.\textsuperscript{[41–44]} Defect-free carbon materials are capable of withstanding high temperatures, making them the preferred choice over other inorganic molecular sieves. They also have the benefit of remaining stable in acidic conditions. Tuning of the pore size of these molecular sieves can be accomplished through the several methods, including opening via oxidative burnoff and closing via exposure to high temperature in a vacuum\textsuperscript{[45]}. Another method for tuning pore size is to use an energized particle to impact sieve material, creating a pore dependent on the size of the particle. This was the goal of Chapter 2. However the size of the hole in the graphene bilayer was too small to properly form the sidewalls necessary for a pore.

Collision studies similar to those in Chapter 2 are performed in this work with C\textsubscript{60} instead of Ar as the projectile. There were two main issues with using Ar as the
bombarding particle. The first was the size of the atom compared to the desired pore size. By selecting a larger particle, we can potentially achieve the goal of forming a hole large enough to allow for complete pore.

The other issue with Ar was that multiple carbon atoms were removed from the graphene bilayer upon impact. Instead of an atom penetrating or reflecting off of a graphene bilayer, a \( \text{C}_{60} \) molecule has the potential to incorporate some of its carbon atoms into the graphene bilayer as it breaks apart from the collision. The \( \text{C}_{60} \) molecule, also known as a Buckminsterfullerene, is a spherical fullerene molecule consisting solely of \( sp^2 \)-hybridized carbon atoms. This fullerene molecule is stable even at high temperatures and pressures, allowing it to be used as bombarding particle. The \( \text{C}_{60} \) atoms that incorporate into the graphene bilayer can then arrange themselves with the graphene bilayer’s atoms to form the desired pore walls. This leads to there not being enough carbon atoms to form the sidewalls of the pore. With these two issues in mind, a \( \text{C}_{60} \) molecule is used instead of an Ar atom.

In this paper, we study the impact of an energized \( \text{C}_{60} \) molecule on a graphene bilayer. The results of these impacts are then analyzed using methods that quantify the geometry of the resulting graphitic nanostructure formed from the rearrangement of the carbon atoms and the properties of the “pore” formed by the impact. Simulations with and without annealing are presented to show the effect annealing has on bond rearrangement. A method for visualizing properties of these systems is also presented, along with the results of applying this visualization method.

### 3.2 Methods

Impacts were performed by modeling collisions between a \( \text{C}_{60} \) projectile and a graphene bilayer substrate. The system was modeled with rectangular periodic
boundary conditions in the two dimensions parallel to the graphene sheets, with side lengths of 66.45 Å along the [100] direction and 63.95 Å along the [120] direction. Each graphene sheet contained 1620 carbon atoms. The C$_{60}$ molecule kinetic energies were varied between 5 keV and 10 keV, at 500 eV intervals. Two angles of impact were used, 45$^\circ$ and 90$^\circ$, measured as the angle between the argon velocity vector and the surface plane (i.e. 90$^\circ$ corresponds to normal impact). Twenty separate impacts were performed for each combination of energy and angle, so that statistical analysis of the impacts could be performed. During the impact, each system was integrated with unconstrained (microcanonical) dynamics for 10 ps. Because of the relatively large variation in timesteps required during the energetic collision phase ($\sim$ 0.05 fs) and subsequent energy dissipation phase ($\sim$ 0.25 fs), a variable-timestep integrator was used to integrate the dynamics.

After an initial 10 ps of impact dynamics, the system was equilibrated in the canonical ensemble at a temperature of 3000 K for 1.2 ns using a Langevin thermostat with a time constant of 100 fs. This annealing period introduces extra energy to the system to allow for some slower bond rearrangement dynamics that are important in restructuring the pore geometry. Alternatively, after the initial 10 ps of impact dynamics, some systems were equilibrated in the microcanonical ensemble for 5 ns. All interatomic interactions were modeled with the AIREBO potential.

All C$_{60}$ impacts at the energies given above generate pores in the bilayer graphene surface, and the cross-sectional area of the pore is perhaps the most important characteristic in assessing the suitability of the pore for practical applications.

We define the pore cross-sectional area, $A$, to be the geometrical area of the largest contiguous region in the surface plane that is at least one carbon–carbon bond length ($r_{CC} = 1.42$ Å) from all carbon atoms, when they are projected into this surface plane. This is illustrated in Figure 2.1 for several pore sizes. In our analysis,
the value of $A$ is determined numerically, by integrating the cross sectional area with a rectangular grid with spacing 0.033 Å.

Note that by projecting all atoms into the surface plane, this definition implicitly assumes that the pore is perpendicular to the surface plane. It would consequently be unreasonable for angled or sinuous pores in thick substrates, but is a reasonable approximation for bilayer graphene. An example of a pore formed via $C_{60}$ bombardment is shown in Figure 3.1.
The pores generated by impact and subsequent thermal annealing will not be simple vacancies, as in Figure 2.1. Some of the dangling bonds, broken during the initial impact, will be reformed, either by crosslinking the graphene layers or reconstructing within the layer. These reconstructions are crucial to forming the pore wall, and in producing functional nanoporous materials. Thus, another important characteristic of the pores generated by impacts is the degree to which the graphitic structure has been maintained in the pore.

As a measure of how fully formed a given pore is, we define a measure

$$\mu = \frac{1}{12} \sum_{i=3}^{9} n_i (i - 6), \quad (3.1)$$

where $n_i$ is the number of $i$-membered rings, or $i$-gons, in the system. This measure can be understood intuitively in the following manner. The summation

$$\sum_{i=3}^{9} n_i (i - 6) \equiv \Delta b \quad (3.2)$$

that appears in Eq. 3.1 can be interpreted as a count of the number of excess bonds in the system: each hexagon ($i = 6$) in purely graphitic material contributes nothing to $\Delta b$, while each heptagon ($i = 7$), for example, contributes exactly one excess bond to $\Delta b$. Equation 3.1 gives a value of $\mu = 0$ for undamaged graphene layers, and $\mu = 1$ for an ideal pore with exactly 12 heptagons. Values of $\mu > 1$ indicate more than 12 excess bonds in the structure; more than would be needed to generate a single, ideal pore. For a detailed derivation of Equation 3.1, please see Section 2.2.

Ignoring the normalization coefficient in Eq. 3.1, $\mu$ can be viewed as an average deviation from, or first moment about, the 6-member rings of a purely hexagonal
We analogously define a second moment, \[ \sigma^2 = \frac{1}{12} \sum_{i=3}^{9} n_i (i - 6)^2. \] (3.3)

The coefficient 1/12 is chosen so that \( \sigma^2 = 1 \) for an ideal pore with 12 heptagons. While \( \mu \) corresponds to the mean excess ring size, \( \sigma^2 \) corresponds to the variance of the ring size distribution about six, and will be minimized in an ideal pore. At a given value of \( \mu \) (pore completeness), lower values of \( \sigma^2 \) indicate less disorder or breadth in the ring size distribution. Consequently, we refer to \( \sigma^2 \) as the pore disorder.

For partial pore formation, with \( \mu < 1 \), the least disordered structure would have \( \sigma^2 = \mu \) (i.e. \( 12\mu < 12 \) heptagons and no other non-hexagonal rings). Any other structure would necessarily have \( \sigma^2 > \mu \). Thus we also consider the ratio \( \mu/\sigma^2 \) as a metric of pore quality; pores or partial pores formed with the minimal number of excess bonds will have \( \mu/\sigma^2 = 1 \) and those formed with an unnecessarily broad distribution of rings will have \( \mu/\sigma^2 < 1 \).

### 3.3 Results and Discussion

We begin by discussing the cross-sectional area of the pores that are important for applications in separating components, as the size of the pore dictates what can pass through it and also how fast transport occurs. Figure 3.2 shows the average cross-sectional areas formed at each impact energy and incident angle under both NVE and NVT dynamics. The thermostat used during NVT dynamics causes faster bond rearrangement compared to NVE dynamics, however this annealing leads to smaller pore areas for some impact energies (both NVE and NVT dynamics fall within the same standard error for other impact energies) at the expense of a a wider distribution.
of ring sizes, which we will discuss in more detail later. At a given impact energy, the 45° impacts cause larger pore areas compared to the 90° impacts. Since our goal is to use these pores as molecular sieves, it is important to compare the results in Figure 3.2 to sizes commonly used in molecular sieves. Based on observing the general shape of these pores, we may approximate the pore’s shape as a circle and use $A = \pi r^2$ to approximate the diameter of the pore. Using this approximation, we estimate that the pores obtained using the 90° impacts are 10–11.2 Å in diameter, which compares to the commercially available sieves made from porous glass or activated carbon.\[40]\] The 45° impacts are capable of producing a pore diameter between 12–15 Å. This range of sizes also falls between the commercially available sieves consisting of porous glass or activated carbonszostak1992handbook. Although it is possible to select a specific pore size with varying impact energy and angle in the simulations performed here, it is also possible to select very specific pore sizes using porous glass, which can produce pores of 10 Å and higher.

After impacting the graphene bilayer with the C$_{60}$ molecule, crosslinks begin to form a $sp^2$ network between the two graphene sheets using the remaining carbon atoms from both sheets and the bombarding molecule that were not ejected from the system. As time progresses in both NVE and NVT conditions, bond rearrangement continues to occur, creating crosslinks between the layers of graphene. We recall that twelve 7-membered rings among the hexagonal rings are necessary to induce enough negative curvature to properly form the pore between layers. The ring counting algorithm, described in Section 2.2, is used to find how many rings of each size make up each system. For example, Figures 3.3 and 3.4 show the distribution of ring sizes over twenty simulations for a 10 keV impact energy and 90° angle where NVE dynamics and NVT dynamics were used, respectively. As we expect, a large number of 6-membered rings are present in both systems, accounting for the undamaged graphene...
Figure 3.2: Average pore area expressed as a function of impact energy for 45° and 90° impact angles, for both 5 ns NVE and 1.2 ns NVT post-collision dynamics. Error bars show standard error.
Figure 3.3: Example of distribution of ring sizes for 20 separate impact simulations for a 10 keV impact energy and 90° angle under NVE post-collision dynamics.

lattices. In general, we see a broader ring distribution for the simulations under NVT dynamics, compared to those using NVE dynamics. This is due to the higher temperature introduced by the Langevin thermostat, allowing energy barriers to be crossed for bond rearrangement that does not occur under the cooler NVE dynamics. This allows for larger rings to form, even though they are not as energetically favorable compared to rings sizes closer to 6-membered rings. Both Figures 3.3 and 3.4 show the necessary amount of large rings, defined as 7, 8 and 9-membered rings, for a complete pore, enough to overcome the positive curvature induced by the small rings, defined as 3 and 5-membered rings. This solves the issue of incomplete pores being formed by the Ar impacts in Chapter 2.

Next, we consider pore completeness as calculated from Equation 3.1. Fig-
Figure 3.4: Example of distribution of ring sizes for 20 separate impact simulations for a 10 keV impact energy and 90° angle under NVT post-collision dynamics.
Figure 3.5: Pore completeness expressed as a function of impact energy for varying angles for both NVE and NVT post-collision dynamics.

Figure 3.5 shows the calculated completeness values for both NVE and NVT simulations. We can see from this figure that all completeness values are greater than one, indicating there are more large rings than small rings. As impact energy increases, the completeness value also tends to increase, except for the 45° impacts using NVE dynamics where the completeness value tends to fluctuate, perhaps decreasing slightly with impact energy. This fluctuation is due to significant differences in ring distributions for different impact energies and there not being enough time allowed for bond rearrangement. We also see that 45° impacts result in formation of more large rings compared to the 90° impacts.
We have noted that there is a broader ring distribution for simulations using NVT dynamics compared to those using NVE dynamics, as seen in Figures 3.3 and 3.4. To quantify this, we calculate pore disorder using Equation 3.3. Pore disorder will have the same value as pore completeness when forming an ideal pore, and greater than the completeness value if the ring distribution is broader than needed. Figure 3.6 shows that the disorder values are, in fact, significantly larger than the completeness values in Figure 3.5. Additionally, the trend that the disorder in the NVT equilibration is larger than for NVE equilibration is quite general, at most impact conditions. The pore disorder for 45° impacts using NVE dynamics also appears to slightly decrease with higher energies, possibly due to the formation of less large rings or more small rings.

To account for how the broader ring distributions relate to pore completeness, we calculate pore quality, the ratio of pore completeness over pore disorder, as shown in Figure 3.7. The 45° impacts result in higher pore quality values than the 90° impacts for simulations using both NVE and NVT dynamics. The pore quality values are improved compared to the Ar bombardment simulations by between 0.05 and 0.10. It is also apparent that the faster bond rearrangement enabled by the higher temperature in NVT dynamics leads to broader ring distributions compared to systems using NVE dynamics. This suggests that future simulations where formation of specific ring sizes is important should rely on the microcanonical ensemble for bond rearrangement after an impact.

3.4 Conclusions

The bombardment of a graphene bilayer by a C_{60} molecule was studied using molecular dynamics simulations with both microcanonical and canonical post-collision
Figure 3.6: Pore disorder expressed as a function of impact energy for varying angles for both NVE and NVT post-collision dynamics.
Figure 3.7: Pore quality expressed as a function of impact energy for varying angles for both NVE and NVT post-collision dynamics. Pore quality is the ratio of pore completeness and pore disorder.
equilibration for a range of impact energies and two different impact angles. An impact angle of 45° off the surface normal was found to result in formation of large pores that are accessible via common commercially available molecular sieves. These bombardment simulations achieve much higher pore diameters, between 5 Å and 7.5 Å, compared to Ar bombardment simulations, which achieve a maximum pore diameter of 3 Å. This limits the use of C\textsubscript{60} molecular bombardment of a graphene bilayer as a molecular sieve, since porous glass is already thoroughly researched for this application.

Bond rearrangement favors broader ring distributions when using the higher temperature equilibration. This, in turn, causes smaller pore areas for simulations using NVT dynamics. Previously derived topological measures are used to describe the ring distributions in these pores. Calculation of pore completeness suggested that simulations using NVT dynamics result in simulating better pores. However, when considering pore disorder, the negative affect the broader ring distributions of NVT simulations have on variance of the ring size distributions, we find that presence of 8 and 9-membered rings and the absence of 5-membered rings leads to incomplete pores. Although the pores formed from these bombardment simulations are incomplete, they are 0.05 to 0.10 higher quality than the pores formed through Ar bombardment in the previous chapter. Therefore pores created through C\textsubscript{60} bombardment result in higher quality pores when compared to Ar bombardment-created pores, but are too large to be considered as an alternative to commercially available molecular sieves.
Chapter 4

Intercalation of Li and Ca in Graphite

4.1 Introduction

Graphite is capable of intercalating atoms between each pair of graphene sheets. This creates what is known as an intercalation compound, where one species is reversibly adsorbed/absorbed onto/into another material. One use for these intercalation compounds is as a battery electrode, where the lithium intercalated graphite is used as an anode.

Lithium-ion batteries have become popular because of their high energy density compared to other rechargeable batteries. By intercalating lithium atoms into graphite, it is possible to create a material that behaves like a lithium metal anode, without the safety risk associated with metallic lithium. To make a quantitative comparison between metallic lithium and various Li-intercalation compounds, each material’s specific charge capacity, the load current a battery can deliver over time per substrate mass, can be used. The specific capacity for Li-intercalated graphite
is 372 mAh/g, which is quite low compared to the capacity of metallic lithium, 3860 mAh/g.\cite{5} It is possible to increase specific charge capacity by increasing the amount of intercalated lithium in graphite.

The amount of intercalated lithium can be improved through the use of other metals as co-intercalants. An experimental study have found that introducing other metals such as calcium can increase the amount of Li intercalated into materials like graphite. By using a Li$_2$Ca alloy, Pruvost et al.\cite{46} were able to synthesize a Li intercalation compound with formula Li$_{3.1}$Ca$_{2.1}$C$_6$. This work attempts to calculate how the introduction of calcium influences the lithium binding energy and the structure of the graphite by utilizing density functional theory (DFT) calculations, with the goal of increasing the amount of intercalated lithium.

### 4.2 Methods

A graphite supercell, consisting of two layers of graphene, was constructed. Each layer contained 48 carbon atoms for a total system size of 96 atoms. The plane spanned by each graphene sheet measured 17.04 Å by 7.38 Å. Periodic boundaries are used to simulate infinite graphene planes with no edge effects. The interlayer space distance measures 3.33 Å for a total length of 6.66 Å orthogonal to the graphene planes. A periodic boundary is also used in this dimension to simulate an infinite bulk system.

Lithium and calcium atoms were inserted randomly into the interlayer space between graphene sheets. The atom coordinates parallel to the graphene plane were chosen randomly from a uniform distribution. The orthogonal coordinate is fixed as the mean distance between the two planes. Because two interlayer spaces exist in the supercell, the atoms were inserted in a 50%/50% ratio between the two layers. In
the event that an atom is inserted within 2.0 Å to another atom then the new atom is removed and a new position is chosen.

All calculations performed in this work utilized density functional theory, as implemented in the Vienna *ab initio* simulation package (VASP). The projector-augmented-wave method is used to reduce the cost associated with the rapidly oscillating valence wave functions associated with each atom, transforming them into smoother, more computationally efficient wave functions. The exchange-correlation functional uses the generalized gradient approximation, as discussed in Chapter 1. Specifically, the Perdew-Burke-Enzernhof (PBE) method is used here. The kinetic energy cutoff was varied for a geometry optimizations of the clean graphite system until a cutoff of 400 eV was found to be appropriate for the calculations in this work. DFT does poorly at modeling dispersion forces, yet these interactions are important for interlayer interactions in graphite and also its intercalation compounds. Consequently, we use the vdW-DF2 method to account for these forces.

The adsorption energy of lithium into a carbon material is calculated using the equation

\[
E_{ads}(n) = \frac{nE(Li) + E(X) - E(Li-X))}{n}. \tag{4.1}
\]

In this equation, \(n\) is the total number of adsorbed Li atoms, \(X\) is the carbon material, in this case graphite, and \(E(Li)\), \(E(X)\) and \(E(Li-X)\) are the energies associated with a single Li, a clean, defect-free carbon material, and the interacting Li–X system.

The adsorption energy, \(E_{ads}\), is dependent on the lithium concentration. Lithium will prefer to adsorb to itself, rather than graphite, once the adsorption energy falls below 1.6 eV. We refer to this value as the lithium cohesive energy limit. The adsorption of lithium to graphite is favorable for adsorption values above this limit. To
validate the DFT model, the adsorption energy for a single Li atom in graphite was calculated and found to be 0.64 eV/Li, comparing favorably to the literature value of 0.67 eV/Li.\[16\]

In order to determine the adsorption energy of lithium after the addition of calcium, a modified expression is necessary. The adsorption energy for lithium into a calcium-decorated carbon material is calculated as

$$E_{\text{Li}}^{\text{ads}}(n) = (nE(Li) + mE_{\text{Ca}}^{\text{ads}}(m) + E(X) + mE(Ca) - E(Li_{m}\text{-Ca}_{m}\text{-X}))/n.$$  \hspace{1cm} (4.2)

In this equation, \(m\) is the total number of adsorbed Ca atoms, \(E(Ca)\) is the adsorption energy of a single calcium, \(E(Li_{m}\text{-Ca}_{m}\text{-X})\) is the energy of the calcium-lithium intercalated system, and \(E_{\text{ads}}^{\text{Ca}}(m)\) is the adsorption energy of calcium into the carbon material. The latter quantity, \(E_{\text{ads}}^{\text{Ca}}(m)\), can be found using an equation similar to Equation 4.1:

$$E_{\text{ads}}^{\text{Ca}}(m) = (mE(Ca) + E(X) - E(Ca\text{-X}))/m.$$  \hspace{1cm} (4.3)

We can see that in the absence of calcium, Equation 4.2 reduces to Equation 4.1.

An alternative method can also be used to calculate adsorption energy. When using Equations 4.1, 4.2, and 4.3, we assume that when loading the \(n\)th lithium atom, it will have an adsorption energy equal to the average adsorption energy for all \(n\) lithium atoms. Instead of calculating the adsorption energy for lithium into graphite using this average total energy, we can instead calculate the adsorption energy by differentiating total energy of the lithium-intercalated system with respect to the amount of lithium added. This equation is written as

$$E_{\text{ads}}(n) = \frac{\partial E(Li_{\varsigma}\text{-X})}{\partial \varsigma},$$  \hspace{1cm} (4.4)
where $\varsigma$ is evaluated at $n$, the number of lithium atoms. In practice, we can express Equation 4.4 as a linear approximation of the function at the value $n$ using

$$E_{\text{ads}}(n) \approx \frac{\Delta E(Li_n^-X)}{\Delta n}. \quad (4.5)$$

This equation will allow us to calculate the adsorption energy of the $n$th lithium atom, rather than the average.

Lithium atoms were intercalated into the graphite supercell in the range of 1, 4-20 atoms, at 4 atom intervals. For each lithium concentration, ten geometry optimizations were performed with different configurations of lithium atoms in order to account for variance in energy minimums. All geometry optimizations used the conjugate gradients algorithm for relaxing atoms toward the energy minimum. The supercell lattice constants were also allowed to relax anisotropically during optimizations to allow the interlayer space to expand to accommodate intercalants. Each geometry optimization was terminated once the total energy change and band structure energy change between two steps were less than a cutoff of $10^{-4}$ eV. The resulting total energies from each of the 10 optimizations were averaged to calculate the mean total energy for that specific lithium concentration. These mean total energies were then used to determine specific concentration adsorption energies, $E_{\text{ads}}(y)$, of a lithium atom onto the graphite.

Calcium atoms were intercalated into the graphite supercell in the range 2-16 atoms, at 2 atom intervals. For each amount of calcium, lithium was also intercalated into the graphite supercell in the range of 12-22 atoms, at 2 atom intervals. The lithium concentration range was chosen based on the previous lithium-intercalated graphite work that showed the maximum lithium concentration in graphite is LiC$_6$. For each of these systems, ten optimizations were performed using different atom
configurations. The conjugate gradient method was once again used to relax the system/atom positions and anisotropic supercell lattice constant relaxation was allowed. A coarse geometry optimization was first performed using a total energy change cutoff of $10^{-2}$ eV. More accurate geometry optimizations were then completed using the results from the course optimizations until the total energy change between two steps was less than the $10^{-4}$ eV cutoff. This was necessary due to computational limits preventing the more accurate optimizations from converging within imposed time constraints. The ten total energies obtained from the optimizations for each distinct lithium-calcium combination were averaged to obtain a mean total energy. This total energy was used to calculate adsorption energy, $E_{\text{ads}}$, using Equation 4.2 and values from Table 4.1.

### 4.3 Results and Discussion

Optimizations were performed using two different graphite stacking patterns, AA and AB. Figure 4.1 shows the structure of these two stacking patterns prior to insertion of intercalants. Adsorption energies were calculated from Equation 4.1 using values from Table 4.1. The stacking patterns lead to different $E(X)$ and $E(\text{Li–X})$ values, but does not change the $E(\text{Li})$ value. When obtaining the total energy of the AA-stacked and AB-stacked graphite, a set of geometry optimizations were performed on the graphite supercell and a lattice scaling vector of 1.009 was found to give the lowest total energy for both systems.

Figure 4.2 shows adsorption energy as a function of lithium concentration in graphite for both AA stacking and AB stacking. There is a decreasing adsorption energy trend for both systems, eventually crossing below the lithium cohesive energy limit, shown as the horizontal line in Figure 4.2. Based on these results, we find that
Figure 4.1: Image of AA-stacked graphite (left) and AB-stacked graphite (right). Materials are shown slightly off normal to show multiple layers.

<table>
<thead>
<tr>
<th>Material</th>
<th>Total Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E\text{(Li)}$</td>
<td>0.61686269</td>
</tr>
<tr>
<td>$E\text{(AA graphite)}$</td>
<td>-722.905548</td>
</tr>
<tr>
<td>$E\text{(AB graphite)}$</td>
<td>-723.4092994</td>
</tr>
<tr>
<td>$E\text{(Ca)}$</td>
<td>1.85655779</td>
</tr>
<tr>
<td>$E_{\text{Ca}}^{\text{ads}}(1)$</td>
<td>1.58750621</td>
</tr>
</tbody>
</table>

Table 4.1: Calculated total energies for various materials necessary for adsorption energy calculations.
Figure 4.2: Lithium adsorption energy values as a function of intercalated lithium concentration in graphite. The lithium cohesive energy is also plotted.

Li intercalation into graphite is unfavorable, energetically, once there is more than one lithium atom per six carbon atoms, LiC$_6$. This agrees with previous experiments that have determined the maximum lithium intercalation in graphite to be LiC$_6$.$^{[16]}$

We also note that there is a higher adsorption energy for lower amounts of lithium in AB graphite compared to AA graphite. Because the carbon atoms in adjacent layers of graphene in AB graphite are off-registry, this prohibits the lithium atoms from occupying the space central to both hexagonal rings. This also causes a slight increase in interlayer space due to the proximity of the intercalant to the carbon atoms. The increased layer space appears to be more favorable for lithium
Table 4.2: Average adsorption energies for different lithium concentrations, Li$_y$C$_6$, in AA-stacked graphite and AB-stacked graphite.

intercalation in the AB-stacked graphite rather than the ability to occupy the central space between both hexagonal rings in AA-stacked graphite.

We next consider the geometry optimizations including calcium as a cointercalant. Early testing found that AA-stacked graphite systems failed to optimize within reasonable time constraints, so only AB-stacked graphite was used. Figure 4.3 shows the adsorption energies for lithium in calcium-decorated AB-stacked graphite. We can see a general trend where an increase in calcium concentration leads to a higher adsorption energy value for lithium up to a point, and then begins to decrease. Around Ca$_{0.875}$Li$_y$C$_6$, increasing calcium concentration is observed to begin to overfill the interlayer space of the graphite, leading to lower lithium adsorption values. We also notice that the adsorption energy values are mostly above the lithium cohesive energy limit, save for the lowest and highest calcium concentrations.

We can fit the adsorption energy data in Figure 4.3 to estimate where the maximum lithium concentration will occur. To do this, we can use a power function, which is expressed as

$$E_{ads}^{max}(y) = ay^b$$  \hspace{1cm} (4.6)
Figure 4.3: The adsorption energy values as a function of intercalated lithium concentration in graphite for different concentrations of calcium. The lithium cohesive energy is also plotted.
and fit this equation using least squares. In this equation, $y$ is the amount of lithium and $a$ and $b$ are fitting parameters. We then set $E_{ads}^*(y) = E_{coh}$, where $E_{coh}$ is the Li cohesive energy, and solve for $y$. Figure 4.4 shows the fit of the maximum lithium concentration as a function of the calcium concentration. From this figure, we can see that highest achievable lithium concentration occurs between $\text{Ca}_{0.25}\text{Li}_{1.72}\text{C}_6$ and $\text{Ca}_{0.375}\text{Li}_{1.70}\text{C}_6$. The least squares fit for the $\text{Ca}_{0.25}\text{Li}_y\text{C}_6$ data had an $R^2$ value of 0.78, due to noise present in this data set, whereas the $\text{Ca}_{0.375}\text{Li}_y\text{C}_6$ data had an $R^2 = 0.96$ (all other data had $R^2 > 0.95$). Therefore, we can view the fit for the $\text{Ca}_{0.375}\text{Li}_y\text{C}_6$ data as more statistically valid, and not suggest that the true maximum lithium concentration would occur at $\text{Ca}_{0.25}\text{Li}_{1.72}\text{C}_6$. This shows that it is possible to achieve a higher intercalated lithium concentration in graphite by using calcium.

The primary use of these intercalated materials is as an anode in a Li-ion battery. Batteries must be small enough to use in electronics, so expanding the size of the anode without increasing its specific capacity relative to size increase is not useful. It is also harmful to the battery for the anode to expand and contract upon cycling, so limiting the size increase of the material is important. Therefore, it is useful for us to compare the lithium adsorption energy to the interlayer distance change.

<table>
<thead>
<tr>
<th>Ca ($x$)</th>
<th>0.125</th>
<th>0.25</th>
<th>0.375</th>
<th>0.5</th>
<th>0.625</th>
<th>0.75</th>
<th>0.825</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li ($y$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.75</td>
<td>2.013</td>
<td>2.120</td>
<td>2.529</td>
<td>2.760</td>
<td>2.835</td>
<td>3.108</td>
<td>3.192</td>
<td>3.138</td>
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<tr>
<td>0.875</td>
<td>1.886</td>
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<td>2.681</td>
<td>2.791</td>
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<td>1.766</td>
<td>1.841</td>
<td>2.224</td>
<td>2.282</td>
<td>2.254</td>
<td>2.447</td>
<td>2.313</td>
<td>2.273</td>
</tr>
<tr>
<td>1.125</td>
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<td>1.909</td>
<td>2.024</td>
<td>2.050</td>
<td>2.068</td>
<td>2.104</td>
<td>2.140</td>
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<td>1.25</td>
<td>1.599</td>
<td>1.675</td>
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<td>1.987</td>
<td>1.960</td>
<td>1.955</td>
<td>1.816</td>
<td>1.814</td>
</tr>
<tr>
<td>1.375</td>
<td>1.569</td>
<td>1.789</td>
<td>1.840</td>
<td>1.838</td>
<td>1.761</td>
<td>1.713</td>
<td>1.593</td>
<td>1.550</td>
</tr>
</tbody>
</table>

Table 4.3: Average adsorption energies for different lithium concentrations and different calcium concentrations, $\text{Ca}_x\text{Li}_y\text{C}_6$, in AB-stacked graphite.
Figure 4.4: The maximum lithium concentration that is achievable as a function of the intercalated calcium concentration for $\text{Ca}_x\text{Li}_y\text{C}_6$. 
We first calculate the interlayer distance change using a difference equation,

\[ \tau = \frac{Z_f(x) - Z_{gr}}{Z_{gr}}. \] (4.7)

Here, \( Z_{gr} \) is the length of the box in the dimension of the interlayer distance of the non-intercalated graphite system and \( Z_f \) is the length of the box in the dimension of the interlayer distance after optimization.

While the addition of calcium has increased the graphite’s ability to intercalate lithium, it has also increased the interlayer distance between graphene layers. This increase in interlayer distance results in a 9%–25% expansion of the material, as seen in Table 4.4.

To show how the interlayer distance varies with the maximum lithium concentrations plotted in Figure 4.4, we fit the interlayer distance change, \( \tau \), for each concentration of calcium (shown in Table 4.4) with a linear function,

\[ \tau(y) = my + c, \] (4.8)

where \( y \) is the lithium concentration and \( m \) and \( c \) are fitting parameters. We then evaluate Equation 4.8 at the maximum lithium concentration, \( y_{max} \) for each cal-

<table>
<thead>
<tr>
<th>Ca ((x))</th>
<th>0.125</th>
<th>0.25</th>
<th>0.375</th>
<th>0.5</th>
<th>0.625</th>
<th>0.75</th>
<th>0.825</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li ((y))</td>
<td>interlayer distance change</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>0.75</td>
<td>0.093</td>
<td>0.117</td>
<td>0.158</td>
<td>0.178</td>
<td>0.195</td>
<td>0.212</td>
<td>0.232</td>
<td>0.247</td>
</tr>
<tr>
<td>0.875</td>
<td>0.094</td>
<td>0.122</td>
<td>0.154</td>
<td>0.175</td>
<td>0.197</td>
<td>0.214</td>
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<td>0.156</td>
<td>0.178</td>
<td>0.204</td>
<td>0.221</td>
<td>0.227</td>
<td>0.237</td>
</tr>
<tr>
<td>1.25</td>
<td>0.104</td>
<td>0.126</td>
<td>0.156</td>
<td>0.183</td>
<td>0.206</td>
<td>0.218</td>
<td>0.232</td>
<td>0.223</td>
</tr>
<tr>
<td>1.375</td>
<td>0.111</td>
<td>0.131</td>
<td>0.160</td>
<td>0.186</td>
<td>0.202</td>
<td>0.213</td>
<td>0.211</td>
<td>0.228</td>
</tr>
</tbody>
</table>

Table 4.4: Increase in interlayer distance change, \( \tau \), for different lithium concentrations and different calcium concentrations, \( \text{Ca}_x\text{Li}_y\text{C}_6 \), in AB-stacked graphite.
Figure 4.5: The interlayer distance for each maximum lithium concentration obtained using a least squares linear fit of Table 4.4.

cium concentration. This gives us $\tau(y_{max})$, the interlayer distance at each maximum lithium concentration, as seen in Figure 4.5. With the information in this plot, we can choose our lithium and calcium concentrations based on our concerns about expansion of the graphite layers. In the event that we want to minimize the expansion of the graphite layers, then we will choose a lithium concentration with the smallest interlayer distance in Figure 4.5. Thus, we would pick $Ca_{0.125}Li_{1.28}C_6$ in this case. If we do not consider the expansion of the substrate important, then we would pick the largest lithium concentration, disregarding the interlayer distance. We would choose $Ca_{0.25}Li_{1.72}C_6$ as our intercalated material.
Using our alternative method for calculating adsorption energy, we calculate the adsorption energy of lithium into graphite using Equation 4.6 with the data in Table 4.2. Note that the $E_{ads}$ in Table 4.2 is normalized using the number of lithium atoms for each concentration before applying Equation 4.6. A plot of adsorption energy calculated using this manner is presented in Figure 4.6. In this figure, we can see that the adsorption energy for lithium in AB-stacked graphite falls below the lithium cohesive limit at a concentration of $\text{Li}_{0.4}\text{C}_6$. We also see that the lithium adsorption energy for AA-stacked graphite fluctuates around the lithium cohesive limit until a concentration around $\text{Li}_{0.9}\text{C}_6$. Although this method of calculating adsorption energy suggests that lithium will prefer not to adsorb into graphite at these concentrations, we know from experiment that a concentration of $\text{LiC}_6$ is possible. To better estimate adsorption energy using Equation 4.6, future work should rely on smaller changes in the amount of intercalated lithium to better approximate Equation 4.4.

### 4.4 Conclusions

This work has considered the use of calcium to improve the intercalation of lithium into graphite. Calculations have been performed using DFT to determine the adsorption energy values for various concentrations of lithium in graphite and lithium and calcium in graphite. The lithium in graphite calculations found a maximum concentration of $\text{LiC}_6$ is possible before the adsorption energy falls below the lithium cohesive energy limit. The lithium and calcium intercalation calculations found that a higher maximum lithium concentration was possible.

The interlayer space between graphene layers tends to expand after intercalating calcium, which allows for more lithium atoms to occupy this space. However, minimizing size is important when considering batteries. Therefore, the increased
Figure 4.6: Lithium adsorption energy values as a function of intercalated lithium concentration in graphite calculated using Equation 4.6. The lithium cohesive energy is also plotted.
lithium intercalation must be considered alongside the expansion of the graphene layers to see if there is an actual benefit to using calcium. This work found that increasing the interlayer distance by 10.5% gives a maximum lithium concentration of $\text{Ca}_{0.125}\text{Li}_{1.28}\text{C}_6$. At a higher interlayer distance increase of 13.8%, the highest lithium concentration found in this study is obtained, $\text{Ca}_{0.25}\text{Li}_{1.72}\text{C}_6$. This shows that as high as 72% more lithium can be intercalated into graphite when using a calcium dopant. This results in a specific capacity of 516.6 mAh/g for $\text{Ca}_{0.25}\text{Li}_{1.72}\text{C}_6$, compared to 372 mAh/g for $\text{LiC}_6$, also a 72% improvement.
Chapter 5

Intercalation of Li and Ca in Graphyne

5.1 Introduction

Carbon materials have become popular as adsorbents in energy storage materials. Of particular interest is that graphite has been found to intercalate lithium atoms, making it useful as an anode in Li-ion batteries. However, graphite has a relatively low specific capacity, 372 mAh/g, compared to pure lithium, 3860 mAh/g. In search of a higher specific capacity, a carbon material called graphyne, shown in Figure 5.1, a theoretically proposed two-dimensional network of carbon with both $sp$ and $sp^2$-hybridized bonds, has been proposed as a superior adsorbent.

In the last few years, there have been many computational hours used toward researching this new carbon material and its ability to intercalate lithium, among other elements. Previous theoretical studies have shown that this material has the ability to intercalate more lithium atoms per carbon atom than all other known carbon materials. Though this material intercalates more Li than other carbon...
materials, there is still room for improvement. Experimental studies have found that introducing other metals such as calcium can increase the amount of Li intercalated into materials like graphite.\textsuperscript{[46]} Chapter 4 also shows that calcium can be used to improve lithium intercalation in graphite. This chapter uses density functional theory (DFT) calculations to calculate how the adsorption energy of lithium is affected by the intercalation of calcium into graphyne in an attempt to further increase lithium concentration.

5.2 Methods

A graphyne supercell, consisting of two layers was constructed. Each layer contained 24 carbon atoms for a total system size of 48 atoms. The supercell lattice constants were also allowed to relax anisotropically to reach an energy minimum. The plane spanned by each graphyne sheet measured 11.82 Å by 6.82 Å. Periodic boundaries are used to simulate infinite graphyne planes with no edge effects. The interlayer space distance measures 3.385 Å for a total length of 6.77 Å orthogonal to the graphyne planes. A periodic boundary is also used here to simulate an infinite bulk system. This graphyne system is shown in Figure 5.1.

Lithium and calcium atoms were inserted randomly into the interlayer space between graphyne sheets. The atom coordinates parallel to the graphyne layer plane were chosen randomly from a uniform distribution. The orthogonal coordinate is fixed as the mean distance between the two planes. Because two interlayer spaces exist in the supercell, the atoms were inserted in a 50%/50% ratio between the two layers. In the event that an atom is inserted within 1.5 Å to another atom then the new atom is removed and a new position is chosen.

All calculations performed in this work utilized density functional theory, as
The projector-augmented-wave method \cite{51} is used to reduce the cost associated with the rapidly oscillating valence wave functions associated with each atom, transforming them into smoother, more computationally efficient wave functions. The exchange-correlation functional uses the generalized gradient approximation, as discussed in Chapter 1. Specifically, the Perdew-Burke-Ernzerhof (PBE) method \cite{4} is used here. The kinetic energy cutoff was varied for a geometry optimizations of the clean graphyne system until a cutoff of 400 eV was found to be appropriate for the calculations in this work. DFT does poorly at modeling dispersion forces, yet these interactions are important for interlayer interactions in graphite and also its intercalation compounds. Consequently, we use the vdW-DF2 method \cite{52–56} to account for these forces.

The adsorption energy of lithium into a carbon material is calculated using
the equation

\[ E_{ads}(n) = \frac{nE(\text{Li}) + E(X) - E(\text{Li} \cdots X))}{n}. \quad (5.1) \]

In this equation, \( n \) is the total number of adsorbed Li atoms, \( X \) is the carbon material, in this case graphyne, and \( E(\text{Li}), E(X) \) and \( E(\text{Li} \cdots X) \) are the energies associated with a single Li, a clean, defect-free carbon material, and the interacting Li–X system.

The adsorption energy, \( E_{ads} \), is dependent on the lithium concentration. Lithium will prefer to adsorb to itself, rather than graphyne, once the adsorption energy falls below 1.6 eV. We refer to this value as the lithium cohesive energy limit. The adsorption of lithium to graphyne is favorable for adsorption values above this limit.

In order to determine the adsorption energy of lithium after the addition of calcium, a modified expression is necessary. The adsorption energy for lithium into a calcium-decorated carbon material is calculated as

\[ E^{\text{Li}}_{ads}(n) = \frac{nE(\text{Li}) + mE_{ads}^{\text{Ca}}(m) + E(X) + mE(\text{Ca}) - E(\text{Li}_{n} \cdots \text{Ca}_{m} \cdots X))}{n}. \quad (5.2) \]

In this equation, \( m \) is the total number of adsorbed Ca atoms, \( E(\text{Ca}) \) is the adsorption energy of a single calcium, \( E(\text{Li}_{n} \cdots \text{Ca}_{m} \cdots X) \) is the energy of the calcium-lithium intercalated system, and \( E_{ads}^{\text{Ca}}(m) \) is the adsorption energy of calcium into the carbon material. The latter quantity, \( E_{ads}^{\text{Ca}}(m) \), can be found using an equation similar to Equation 5.1:

\[ E_{ads}^{\text{Ca}}(m) = \frac{mE(\text{Ca}) + E(X) - E(\text{Ca} \cdots X))}{m}. \quad (5.3) \]

We can see that in the absence of calcium, Equation 4.2 reduces to Equation 5.1.

For the lithium-only systems, between 4 to 32 Lithium atoms were intercalated into the graphyne supercell at 4 atom intervals. For the calcium-lithium systems, calcium atoms were intercalated into the graphyne supercell in the range 1-4 atoms, at
1 atom intervals. For each amount of intercalated calcium in this system, lithium was also intercalated into the graphyne supercell in amounts of 16, 24, 28, and 32 atoms. The lithium concentration range was chosen based on the distortions found in the previous lithium-intercalated graphyne systems and the fact that there is no benefit to adding calcium for lower lithium concentrations, since those were found to be stable. Ten geometry optimizations were performed for each concentration of lithium and/or calcium, each with a different configurations of lithium atoms and/or calcium atoms, to account for statistical variation. All geometry optimizations used the conjugate gradients algorithm for relaxing atoms toward the energy minimum. The supercell lattice constants were also allowed to relax anisotropically during optimizations to allow the interlayer space to expand to accommodate intercalants. Each geometry optimization was terminated once the total energy change and eigenvalue change between two steps were less than a cutoff of $10^{-4}$ eV. The resulting total energies from each of the 10 optimizations were averaged to calculate the mean total energy for that specific lithium concentration. These mean total energies were then used to determine concentration-dependent adsorption energies, $\tilde{E}_{ads}^{Li}(y)$, of a lithium atom onto the graphyne, where $\tilde{E}_{ads}^{Li}(y) = \frac{E_{ads}^{Li}(n)}{8}$.

### 5.3 Results and Discussion

Energies of the pure materials appear in Table 5.1. Adsorption energies were calculated from Equation 5.1, shown in Table 5.2. Figure 5.2 plots the lithium adsorption energy values for different concentrations of lithium in graphyne. We see that the adsorption energy values decrease as lithium concentration increases, though these values do not reach the lithium cohesive energy limit even at a concentration of Li$_{4.0}$C$_6$. 
Table 5.1: Calculated total energies for various materials necessary for adsorption energy calculations.

<table>
<thead>
<tr>
<th>Material</th>
<th>Total Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E(\text{Li})$</td>
<td>0.61686269</td>
</tr>
<tr>
<td>$E(\text{Graphyne})$</td>
<td>-340.7964216</td>
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<tr>
<td>$E(\text{Ca})$</td>
<td>1.85655779</td>
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<tr>
<td>$E_{\text{ads}}^{\text{Ca}}(1)$</td>
<td>-1.3306894</td>
</tr>
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</table>

Table 5.2: Average adsorption energies for different lithium concentrations, $\text{Li}_y\text{C}_6$, in graphyne.

<table>
<thead>
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<th>Li Concentration $y$</th>
<th>$E_{ads}(y)$ (eV)</th>
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</thead>
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<td>2.111</td>
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</tr>
<tr>
<td>4.0</td>
<td>1.744</td>
</tr>
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</table>

We can fit the data from Table 5.2 with least squares using an exponential function,

$$E_{\text{ads}}^{\text{Li}}(y) = ae^{by}.$$  \hspace{1cm} (5.4)

We then set $E_{ads}^{\text{Li}}(y^*) = E_{coh}$, where $E_{coh}$ is the Li cohesive energy, and solve for $y^*$. This results in a maximum lithium concentration of $\text{Li}_{4.59}\text{C}_6$ in graphyne. Based only on this calculation, it appears that graphyne is much better at intercalating lithium compared to graphite, which reaches its maximum lithium concentration at $\text{LiC}_6$. However, further analysis of these lithium-intercalated systems will show that this comes at a cost.

In Chapter 4, we observed an increase in interlayer space distance for graphite.
Figure 5.2: Lithium adsorption energy values as a function of intercalated lithium concentration, $y$, for structure Li$_y$C$_6$ in graphyne (blue curve). The lithium cohesive energy is also plotted (red line).
Table 5.3: Increase in interlayer distance change, \( \tau \), for different lithium concentrations in graphyne.

<table>
<thead>
<tr>
<th>Li Concentration ( y )</th>
<th>interlayer distance change</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.037</td>
</tr>
<tr>
<td>1.0</td>
<td>0.038</td>
</tr>
<tr>
<td>1.5</td>
<td>0.039</td>
</tr>
<tr>
<td>2.0</td>
<td>0.047</td>
</tr>
<tr>
<td>2.5</td>
<td>0.058</td>
</tr>
<tr>
<td>3.0</td>
<td>0.065</td>
</tr>
<tr>
<td>3.5</td>
<td>0.062</td>
</tr>
<tr>
<td>4.0</td>
<td>0.079</td>
</tr>
</tbody>
</table>

when both lithium and calcium atoms were intercalated. We can observe similar behavior for lithium-intercalated graphyne. Again, we can calculate interlayer distance change using a difference equation,

\[
\tau = \frac{Z_f(x) - Z_{\text{gry}}}{Z_{\text{gry}}},
\]

where \( Z_{\text{gry}} \) is the length of the box in the dimension of the interlayer distance of the non-intercalated graphyne system and \( Z_f \) is the length of the box in the dimension of the interlayer distance after optimization, for each lithium concentration \( x \).

Table 5.3 shows the average interlayer space distance increase for the lithium-intercalated graphyne systems shown in Table 5.2. From this data, we can see that there is 3.7\%–7.9\% increase for these lithium-intercalated systems. Compared to the interlayer distance increase observed for the calcium-lithium-intercalated graphite systems in Chapter 4, this is too small of a size increase to account for the much higher lithium concentrations obtainable with graphyne. We now look to graphyne’s structure for an explanation of the higher lithium adsorption compared to graphite.

We can see in Figure 5.1 that graphyne contains larger rings compared to graphene, consisting of both 12-membered and 6-membered rings. These larger rings,
along with the larger interlayer space distance, were suspected to allow for higher concentrations of intercalated lithium, as we have found in Figure 5.2. However, we can see that distortions begin to occur as lithium concentration increases. A system loaded with the same lithium concentration as the maximum concentration found for graphite in Chapter 4, LiC$_6$, can be seen in Figure 5.3. In this image, the two layers of the material still appear mostly planar.

The graphyne layers continue to distort as lithium concentration increases, as we can see in Figures 5.4, and 5.5. Although this material has a $\pi$-bonding network similar to graphene, it lacks the same rigidity as graphene due to the acetylenic chains (–$C\equiv C$–). These acetylenic chains can distort (become non linear), which allows each layer of the substrate to deform to fit around the intercalant. We mentioned in Chapter 4 that it is important for a battery anode to not expand and contract too much when cycling. The anode should also not deform under cycling, as this could lead to lower battery life due to exfoliation or chemical degradation of the layered material. Based on the distorted bonding observed in graphyne for lithium concentrations of Li$_2$C$_6$ and higher, it is probable that an anode made from this material with these concentrations would not have as long of a life as a lithium-intercalated graphite anode if loaded at concentrations of Li$_2$C$_6$ or higher.

After seeing the distortions in graphyne caused by the lithium intercalant, we can conjecture that one of two, or potentially both, outcomes can be expected with the addition of calcium as a cointercalant. The calcium could (and most likely will) cause the $sp$-bonded atoms to distort, similar to the effect of the lithium intercalant. Intercalation of the comparatively larger calcium atom could also result in an expansion of the interlayer space without distorting the $sp$-bonded atoms. To determine which of these outcomes will dominate, we now move to the geometry optimizations including calcium as a cointercalant.
Adsorption energies were calculated from Equation 5.2, shown in Table 5.4. $E_{\text{ads}}(\text{Ca})$ for graphyne is found to be negative for graphyne, shown in Table 5.1, meaning the energy of the system is higher when calcium is intercalated. This results in the lower adsorption energies when including calcium as a cointercalant which we see in Figure 5.6, compared to those shown in Figure 5.2 where no cointercalant is present. A concentration of approximately $\text{Ca}_{0.125}\text{Li}_3\text{C}_6$, as well as $\text{Ca}_{0.25}\text{Li}_{3.7}\text{C}_6$, fall below the lithium cohesive limit, while the others remain higher for the plotted concentrations.

The lower adsorption energies are potentially acceptable, if the calcium atoms allow for less distortion of the graphyne layers. We observed significant distortion in the acetylenic chains for $\text{Li}_2\text{C}_6$ as seen in Figure 5.4. When the calcium cointercalant is present, we again see significant distortion in these acetylenic chains. As the amount of calcium increases, the distortion tends to also increase, which can been
Figure 5.4: Visualization of a Li$_2$C$_6$ graphyne system where the lithium atoms are represented by purple spheres and carbon atoms by gray spheres.

<table>
<thead>
<tr>
<th>Ca ($x$)</th>
<th>Li ($y$)</th>
<th>$E_{ads} (y)$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.125</td>
<td>1</td>
<td>1.985</td>
</tr>
<tr>
<td>0.25</td>
<td>3</td>
<td>1.573</td>
</tr>
<tr>
<td>0.375</td>
<td>3.5</td>
<td>1.536</td>
</tr>
<tr>
<td>0.5</td>
<td>4</td>
<td>1.576</td>
</tr>
</tbody>
</table>

Table 5.4: Average adsorption energies for different lithium concentrations and different calcium concentrations, Ca$_x$Li$_y$C$_6$, in graphyne.
Figure 5.5: Visualization of a Li$_4$C$_6$ graphyne system where the lithium atoms are represented by purple spheres and carbon atoms by gray spheres.
Figure 5.6: Lithium adsorption energy values as a function of intercalated lithium concentration in graphyne for different concentrations of calcium. The lithium cohesive energy is also plotted.
Figure 5.7: Visualization of a Ca$_{0.125}$Li$_2$C$_6$ graphyne system where the lithium atoms are represented by purple spheres, the calcium atoms by green spheres, and carbon atoms by gray spheres.

seen in Figures 5.7 and 5.8. Distortions the lead to bond breakage occur at a concentration of Ca$_{0.125}$Li$_4$C$_6$, shown in Figure 5.9. This bond-breaking trend continues for higher concentrations of calcium, for concentrations of Ca$_{0.25}$Li$_4$C$_6$, Ca$_{0.375}$Li$_3.5$C$_6$, and Ca$_{0.5}$Li$_3.5$C$_6$. Figure 5.10 is given as an example of these higher calcium concentrations to show the evolution of layer distortion and bond breaking.

Because the same distortions are observed in the lithium-intercalated systems and calcium-lithium systems, calcium prefers to cause the $sp$-bonded atoms to distort rather than expand the interlayer distance. We can expect a battery anode to deform under cycling as much or more in these calcium-lithium-intercalated sys-
Figure 5.8: Visualization of a Ca$_{0.5}$Li$_2$C$_6$ graphyne system where the lithium atoms are represented by purple spheres, the calcium atoms by green spheres, and carbon atoms by gray spheres.
Figure 5.9: Visualization of a Ca$_{0.125}$Li$_4$C$_6$ graphyne system where the lithium atoms are represented by purple spheres, the calcium atoms by green spheres, and carbon atoms by gray spheres. A red dotted line indicates the broken bond inside of the highlighted red square.
Figure 5.10: Visualization of a Ca$_{0.5}$Li$_{3.5}$C$_6$ graphyne system where the lithium atoms are represented by purple spheres, the calcium atoms by green spheres, and carbon atoms by gray spheres.
tems compared to the lithium-intercalated systems. Consequently, there appears to be no obvious advantage to using calcium as a cointercalant in lithium-intercalated graphyne.

5.4 Conclusions

This work has considered the use of calcium to improve the intercalation of lithium into graphyne. Calculations have been performed using DFT to determine the adsorption energy values for various concentrations of lithium in graphyne and lithium and calcium in graphyne. The maximum concentration of lithium in graphyne without calcium was found to be $\text{Li}_{4.59}\text{C}_6$. However, lithium concentrations of $\text{Li}_2\text{C}_6$ and higher tend to distort the acetylenic chains of graphyne. These distortions have the potential to cause chemical degradation of the material if used as an anode in a lithium-ion battery.

Calcium was investigated as a cointercalant with the conjecture that it may improve the intercalation of lithium into graphyne by limiting the distortions found in lithium-intercalated systems by instead increasing the distance between layers of the material. It was found that calcium increases the energy of the graphyne system upon intercalation, resulting in a lower adsorption energy for calcium-lithium-intercalated graphyne compared to lithium-intercalated graphyne. Distortion of the planar graphyne layers was again found to occur when including a calcium cointercalant along with lithium. These distortions were found to be as prominent, if not worse, as the calcium concentration increased as those found in lithium-intercalated graphyne. Therefore, this work cannot suggest the use of calcium as a way of increasing lithium intercalation in graphyne.
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