Computational Investigations of the Adsorption of Molecular Hydrogen on Graphene-Based Nanopore Model

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Computational Investigations of the Adsorption of Molecular Hydrogen on Graphene-based Nanopore Model

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science

By

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Abstract

Duncan, Jared Michael  M.S., Department of Chemistry, Wright State University, 2012. Computational Investigations of the Adsorption of Molecular Hydrogen on Graphene-based Nanopore Model

Computational modeling using classical grand canonical Monte Carlo simulations and first-principles calculations were carried out to study the adsorption of molecular hydrogen on nanoporous carbon modeled by the slit-pore geometry. It has previously been shown that hydrogen adsorption on pristine porous carbon has dependence on pore size and that an optimum pore size, which exhibits the maximum mass uptake, exists. There have been suggestions that doping graphitic nanocarbon structures with Pd enhances their adsorption capacity. The pore-size dependence of this change in adsorption brought about by Pd and the conditions at which improvement in adsorption can occur have not been extensively addressed to date. In this work, we perform computational modeling to examine hydrogen adsorption on pristine carbon and Pd-doped carbon nanopores. First-principles calculations were used to generate minimized configurations of the sorbent system while grand canonical Monte Carlo simulations modeled the finite temperature and pressure adsorption of hydrogen. We perform simulations at 298 K and pressures of 0.01 MPa, 1 MPa, and 5 MPa for systems with Pd to C ratios of 1:32, 1:18 and 1:8. Among the
systems examined, pristine carbon at 5 MPa exhibited the highest mass uptake at 4.2 wt% adsorption capacity. This is consistent with the expectation that as the gas reservoir pressure increases, the adsorption capacity also increases.

The presence of Pd resulted in enhancement in adsorption only at 0.01 MPa, the lowest pressure investigated. For the maximum adsorption of 4.2 wt% at 5 MPa, the heat of adsorption was calculated to be 8 kJ/mol. The target heat of adsorption value for hydrogen storage materials is 25 kJ/mol, and this was achieved for the 1:8 Pd:C ratio at a pore size of 6 Å, but the system showed a lower adsorption capacity of 1.5 wt%.
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Chapter 1

Introduction

Research involving alternative energy has received major attention in recent years, and enthusiasm towards this research has been driven primarily by the need to lessen dependence on foreign oil, and the need for cleaner energy options to reduce greenhouse gas emissions. According to statistics compiled in 2008, the United States consumed, on average, 20 million barrels of petroleum, with 57% dependence on net petroleum imports. At that time, crude oil prices had reached $94.04 per barrel, and the average for motor gasoline retail price had reached more than $3 per gallon(1). After that one barrel of oil has gone down to about $70, and gasoline fluctuated between $2 to $3 per gallon, on average(2). To date, the price of gasoline has risen back up, sometimes reaching more than $4 per gallon. The need for an efficient, alternative energy resource is becoming more and more imperative. Net petroleum imports have decreased since 2008, and the projection through 2035 shows a continued decreasing trend. The improved energy consumption in the U.S. has been due to several factors including the increased use of renewables as a source of energy, the use of energy efficient cars, household appliances, and equipment,
and energy conservation awareness both for industry and consumers. Hydrogen is currently one of the most highly researched sources of alternative energy. Interest in using hydrogen as a fuel source partially stems from its ability to act as a clean energy. A clean energy is one that is renewable and has little to no impact on the environment. Categorized as clean energy sources include wind, biomass, and solar energy. Hydropower is considered a clean energy because it gives off zero emissions. Hydrogen itself can be produced from many different sources such as animal feedstock, biomass, fossil fuels, and water. Thermochemical process is a technique needed to produce hydrogen from biomass, coal, petroleum, natural gas, and other fossil fuels. Nuclear, wind, and sunlight are all sources from which power can be generated in order to produce hydrogen in an electrolytic fashion. Sunlight has enough power to force photolytic production of hydrogen from water when photobiological and photoelectrochemical processes are incorporated(3).

Figure 1 shows a schematic diagram of a fuel cell, where molecular hydrogen is the fuel source. On the anode side of the fuel cell, the hydrogen molecule is oxidized and dissociates into two electrons and two $H^+$ ions. The electrons go to an electrically conducting wire passing to an external circuit to supply power, and then making their way to the positively charged cathode. The $H^+$ ions pass through a porous electrolyte membrane and go towards the cathode. On the cathode side of the fuel cell, is a source of oxygen, and this $O_2$ combines with $H^+$ ions and electrons to produce water. As seen from the schematic diagram, water is the only by-product.
Research on hydrogen as a fuel received a major boost in 2003 through the Hydrogen Fuel Initiative announced by former President George W. Bush in the 2003 State of the Union Address. This is a $1.2 billion plan to be exercised over a five year period. The idea behind these plans was to accelerate research in the field of hydrogen fuel cells in order to make hydrogen-based vehicles a real and practical option. A product of this initiative was the Energy Hydrogen Program, which is designed to reach the 2015 goals of commercialization of these hydrogen-based vehicles. Currently the goal of mass-market penetration is set for the year 2020 mainly involving the introduction of vehicles powered solely by hydrogen fuel(4). Transportation is a key focus of hydrogen research because transportation vehicles account for over two-thirds of daily oil
consumption. In 2008, for example, U.S. motor gasoline accounted for 71% of the daily oil consumption(1).

The DOE has set forth several standards and goals to be met by certain years including gravimetric capacity, volumetric capacity, and system cost. By the year 2015, the goals laid out by the DOE include: a gravimetric capacity of 0.09 kg H₂/kg system, a volumetric capacity of 0.081 kg H₂/L, and a system cost of $2/kWh(5). Also, a heat of adsorption goal of approximately 15-30 kJ/mol, with some agreement at 25 kJ/mol, has been set as a goal as well(6). The 25 kJ/mol heat of adsorption value represents a moderate adsorption strength that is intermediate between physisorption and chemisorption. The desired heat of adsorption is that of a strong physisorption for sufficient mass uptake, but weaker than that of a chemisorption so that a large amount of energy is not required to carry out the desorption process.

1.1 Significance of the Study

Hydrogen fuel cell research is considered a three-stage effort, as schematically depicted in Figure 2. These stages are: production and delivery, storage, and fuel cells. The work presented here involves hydrogen storage. Presently, storage is an area proving to be exceptionally challenging. An acceptable storage medium should be lightweight and stable, as well as display
favorable kinetics and thermodynamic properties. Reversibility is also an important factor. On the thermodynamic front, storage capacity and heat of adsorption are two key factors to consider in a hydrogen storage medium. In determining the applicability of a system as a storage medium, the initial stage involves examining these thermodynamic properties. If the thermodynamic requirements are satisfied, then further kinetics and reversibility studies would be carried out. This work presented covers the initial stage of identifying a good storage medium by determining the hydrogen mass uptake and heat of adsorption of the sorbent material under investigation.

Figure 2. Three stages in hydrogen fuel cell research: production and delivery, storage and fuel cell research.

Carbon based systems have drawn interests as hydrogen storage materials due to their strength and lightweight nature. They have several different forms that possess various adsorption properties, and in addition, can be tuned by substitution or doping. Also, most carbon nanostructures are porous materials, providing for an element of adjustability of the pore size on the
nanoscale, which could be useful for storage capacity improvement. Currently, the major drawback to using carbon structures as a storage medium is that they do not provide ample mass uptake of hydrogen(7).

Metal-based systems have drawn interest like carbon, but for very different reasons. While also being stable, metals are generally much heavier than carbon. Hydrogen has a strong affinity for metals and this affinity is what draws such high interest in metal materials as well as what proves to be the downfall of metal-based systems. While exhibiting larger weight percents, the metal media require too much energy in order to remove the hydrogen from the system, thus rendering the hydrogen useless(7).

Some research has been done with the effort to incorporate the most favorable properties of both carbon and metal-based systems. This research will contribute to the atomic level understanding of such efforts that attempt to increase the mass uptake of carbon-based systems by metal doping. Improvement in hydrogen adsorption capacity brought about by doping with various metals has been shown for porous carbon-based materials, such as carbon nanotubes(8), pillared carbon materials(9), and graphene(10) using computational investigations. In this study, we particularly focus on the studying the effect of Pd on hydrogen adsorption. The role of Pd to potentially improve hydrogen storage has been of interest as palladium has the capacity to absorb large amounts of hydrogen(11). In addition, recent experiments have shown that adding Pd to porous carbon has the potential to improve mass uptake at some of the conditions investigated(12,13). Of particular interest in this thesis is
the molecular modeling of the pore-size dependence of hydrogen adsorption on porous carbon with varying amounts of palladium to carbon ratios. We use computational techniques, including first principles calculations and classical grand canonical Monte Carlo simulations to carry out the simulation studies. In our simulations the carbon nanopore is modeled by the slit-pore geometry. This model essentially takes the distance of two planar structures to represent the pore size. The planar structures will consist of graphene layers incorporating different Pd:C ratios.

Studies of hydrogen adsorption on pure carbon slit-pores, also known as expanded graphite, have been reported previously using various potential models for carbon-hydrogen interaction. The potential energy interactions in this work are based on the covalent-valence force field (cvff), and there have been no previous reports on hydrogen adsorption on pristine carbon using this force field. In order to perform meaningful comparisons between pristine and Pd-doped carbon, it is necessary to model both pristine and doped using the same force field, and thus we do simulations on pristine carbon slit-pore as well.

This research consists mainly of three parts. The first part of the study involves investigating the hydrogen storage uptake of pristine carbon slit-pores at different pore sizes by grand canonical Monte Carlo simulations employing cvff as forcefield. The second and third parts explore the possibility of any adsorption benefits associated with metal doping of carbon systems, with Pd being chosen in particular for this study. The second part consists of first-principles calculations to generate optimized structures of graphene with Pd. The
optimized structures are then used to build the carbon sorbate with various levels of Pd additions. The third part evaluates pore-size dependence of storage capacity on carbon nanopores with Pd modeled by the slit-pore geometry using GCMC simulations. Simulations are performed at room temperature and moderate pressures. From the GCMC simulations, the strength of interaction is also determined through evaluation of heats of adsorption.

The thesis is organized as follows. In the next section, the main objective and specific aims will be outlined. Following this is a literature review section on previous studies that explored various types of hydrogen storage materials. Particular focus is given to porous carbon-based systems, which is the type of system investigated here. Some literature review on metal hydrides and metal organic frameworks, or MOFs, are also presented. In Chapter II, a description of computational modeling is presented. General considerations in carrying out simulations are briefly described. Particular focus is given to the grand-canonical Monte Carlo (GCMC) simulation technique, which is the commonly used method for finite temperature and pressure adsorption simulations. An integral part of classical simulations, such as the GCMC technique, is the choice of empirical potential energy expressions to model various interactions in the system investigated. Some expressions for the potential energy used to describe the interactions in atomic and molecular simulations, specifically for carbon and hydrogen, are also discussed in Chapter II. Chapter III gives details for the set-up of structures and various parameters used in the modeling studies performed. In Chapter IV, results for hydrogen mass uptake and the effects of the presence
of Pd on adsorption are discussed. We also report the pore-size dependence of this mass uptake, and the resulting optimum pore size for maximum adsorption. To gain insight on the degree of adsorption interaction, heats of adsorption calculations are also presented. Finally, a summary and conclusion of the research are presented in Chapter V.

1.2 Objectives

The primary objective of this study is to evaluate the effects of the presence of Pd on the adsorption of molecular hydrogen on a slit-pore model of carbon using computational techniques. Specific aims are as follows:

(i) Determine hydrogen storage uptake on pristine carbon slit-pores by grand canonical Monte Carlo simulations employing the constant valence force field (cvff).

(ii) Use first-principles calculations for geometry optimization of a palladium atom introduced onto a graphene layer.

(iii) Investigate the Pd-doped carbon system as a hydrogen storage medium, with focus on factors including pore-size dependence, optimum pore size, heat of adsorption, and dependence of adsorption on varying levels of palladium to carbon ratios.
1.3 Literature Review

Hydrogen storage has presented one of the biggest challenges in the effort to maximize utilization of hydrogen in fuel cells. Several different mediums are currently being studied, and these can be divided into three major groups: chemical hydrides, metal hydrides, and nanoporous materials. Cryogenic and high-pressure tanks and several other media are being studied as well. One of the most difficult challenges with hydrogen storage is the balance between weight percent and kinetic/thermodynamic properties. Media that provide favorable kinetic and thermodynamic properties tend to have lower-than-acceptable weight percents. Media that favor high absorption numbers tend to present difficulty with the ability to remove the hydrogen from the medium, which is a vital part of the hydrogen fueling process. Presented here is a literature review of some hydrogen storage media, such as carbon nanotubes, and other porous carbon-based structures, and metal-organic frameworks, which fall under the nanoporous structures category. Also presented are some works that have been done on metal hydrides. These reviews demonstrate both the favorable and unfavorable characteristics of each medium.

1.2.1 Carbon Nanotubes

In 1991, Iijima introduced and described a new structure of carbon called carbon nanotubes(14). These carbon nanotubes are shaped by rolled graphite
sheets and contain an inner diameter ranging from 0.7 nm to several nanometers\(^1\). The nanotubes are capped on both ends by half of a fullerene. If a single graphite layer creates the tube then it is called a single-wall nanotube. These single-wall nanotubes are inclined to collect and form bundles of multiple nanotubes. Carbon nanotubes are chemically stable and have low mass density.

There have been several reports advocating the use of carbon nanotubes as a storage medium for hydrogen adsorption. Single-walled nanotubes provide the benefits of having a large theoretical surface area and very narrow pore size distribution\(^2\). Pore sizes can be varied to tune the adsorption properties.

One problem is that the inconsistencies in the reported results by all the different laboratories are so massive, that no conclusive evidence can be drawn to make a correlation to the real hydrogen storage capacity of single-wall nanotubes (SWNT)\(^3\). Anson \textit{et al.} suggested that another problem is that there is no sample containing SWNTs consisting of no other carbon forms. This makes it difficult to account accurately for any carbon materials that are not forming nanotubes. Also, it is difficult to control several attributes of the SWNTs, such as, bundle size, nanotube diameter distribution, and orientation of the tubes.

Dillon \textit{et al.} were among the first to measure H\(_2\) adsorption capacity of SWNTs\(^4\). They used an as-prepared soot that possessed approximately 0.1 to 0.2 wt\% SWNTs at 133 K. They then used an extrapolation method to predict that SWNTs could have an adsorption capacity of 5 to 10 wt\%. They also
predicted that SWNTs containing a diameter between 1.63 and 2 nm could come close to reaching a 6.5 wt% uptake density. However, the hydrogen desorption was measured to only be 0.01 mass% of the sample and the content of the SWNT in the sample was approximately 0.2 mass%. Also, it was assumed that the SWNTs were the only contributing factor to the hydrogen uptake. Since the original measurement was made on such a dilute sample, further analysis called for a sizeable correction on the 99.8% of material that was considered to be inert(15).

Zuttel et al. reported a model where condensation of hydrogen as a monolayer at the surface of nanotubes as well as bulk gathering in the cavity is assumed. Using this model, they found that a 3.3 wt% could be obtained on the surface of the SWNT as a monolayer. In the cavity, a potential absorption of 1.5 wt% was calculated. All together, the model suggests that the SWNTs could have the potential to absorb 5 wt% of hydrogen(15).

Liu et al. has reported an H₂ uptake of 4.2 wt% at ambient temperature and pressures around 10 MPa, with 80% of the adsorbed H₂ capable of being released at room temperature(19). These results may appear to imply that SWNTs can be a promising storage medium for H₂ at room temperature. However, the 4.2 wt% still falls short of the DOE goal and a fairly high pressure of 10 MPa is required to reach such adsorption capacity.
1.2.2 Other Porous Carbon Structures

Several advantages to using carbon based materials as a hydrogen storage medium stem from the fact that they are lightweight, strong, and have many different forms that present various adsorption properties. Carbon has the ability to covalently bond to hydrogen, resulting in a very strong bond. This is not a useful trait for hydrogen storage because the bonding is fairly irreversible. Solid carbon, such as amorphous carbon, diamond, fullerenes, and nanotubes display the ability to physisorb molecular hydrogen. This is a much weaker attraction and is almost fully reversible. However, the physisorption of H$_2$ on graphene-based systems is only about 16 kJ/mol, which is below the predicted 25 kJ/mol ideal heat of adsorption(6).

The interaction between the graphene layers and the non-polar hydrogen molecules in a graphite system is primarily a London dispersion interaction. It was reported, that at room temperature, an individual graphene layer provides only a 60% increase in H$_2$ uptake. This enhancement was found not change drastically when temperature was decreased, or pressure was increased(20).

A possibility for graphite as a storage medium involves expanding the graphene layers. In graphite, the sheets typically have an interlayer spacing of 3.3 Å. This does not provide enough room for the hydrogen molecules to be adsorbed. Expansion of the layers is necessary in terms of volume requirement for H$_2$ molecular adsorption, but this expansion requires a significant amount of energy. Thus, artificial expansion of the layers is necessary. This can be
achieved by inserting molecular spacers, by metal intercalation, or created due to the presence of defects in the graphite lattice. Computational investigation for the expanded graphite system has been done by Aga and coworkers(6). The study revealed that the optimum interlayer spacing between graphene sheets is approximately 6.2-6.4 Å. At this interlayer spacing, the maximum uptake for the graphite system is 2.3 wt% at 298 K and 5 MPa, short of the DOE goals for on-board hydrogen storage. The expanded graphite system is a model for activated carbon fibers, which possess a substantial amount of porosity, and whose pore size can be tuned through variations in the sample preparation.

One of the goals in designing materials for improved hydrogen storage is to increase the surface area to enhance surface interactions. Pore sizes are an important factor to consider, directly affecting hydrogen adsorption capacities. Studies involving the role of porosities have gained attention, and various structures to model porosity, in addition to the expanded graphite system, have been computationally investigated to this end. Carbon nanofoam structures, whose pore sizes can be varied by varying the nanotubes fused to create the nanofoam, have been proposed (21, 22). A porous framework consisting of nanotubes and phenyl spacers have also been examined for its stability and potential for enhancing hydrogen storage and diffusion (23). Fullerene, serving as spacers in graphene layers, have been evaluated (24). Another porous network, called pillared graphene, whose design allows for tuning the pore size and surface area, has also been investigated (25).
1.2.3 Metal Hydrides

Metal hydrides are concentrated single-phase compounds consisting of the host metal and hydrogen(26). Two phases are generally formed between metal and hydrogen; the α-phase, where only some hydrogen is absorbed, and the β-phase, where the hydride is completely formed(27). Hydrides can be categorized in more distinct terms as: covalent hydrides, wherein hydrogen will share the electron pair with similarly electronegative atoms or non-metals, ionic hydrides, wherein hydrogen exists as H\(^+\), or metal hydrides, wherein hydrogen performs as a metal and are mostly formed with transition metals. Metal hydrides show potential as an effective hydrogen storage medium due to their high storage capacities at low pressures, while also preserving volumetric densities similar to that of liquid hydrogen(26).

Complex hydrides, such as borohydrides, as well as alanates, have all been of interest in the search for the most advantageous hydride storage material. Schüth et al. reported sodium alanate as a promising system with a theoretical reversible storage capacity of 5.5 wt%(28). Seayad et al. reported multiple desorption peaks for borohydride complexes with the total amount of hydrogen desorbed being 9 wt% at 600 °C(27). Schüth et al. incorporated doping their alanate with a catalyst to speed up adsorption and desorption processes. It was shown that titanium based materials provided the most favorable kinetics and the best reversible storage capacity(28).
Light metals have been intensively studied because of their low weight and favorable hydrogen to metal atom ratio. In some cases, the ratio is on the order of 2:1. Sakintuna et al. explored magnesium-based metal hydrides as a possible candidate (27). Magnesium proved beneficial showing high storage capacity coupled with low cost. Magnesium hydride exhibited the highest energy density for reversible hydrides valid for hydrogen storage with an H$_2$ capacity of 7.7 wt%.

An important factor for the adsorption of hydrogen by a metal is the metal surface, which triggers dissociation of H$_2$ molecules and permits simple diffusion of hydrogen into the bulk (27). With the belief that diffusion through the hydride layer is the rate-limiting step, Sakintuna et al. employed a ball-milling process to establish fresh surfaces during processing. The ball-milling process results in a higher surface area, creates defects on the surface and in the interior of the material, and forms a micro/nanostructure. Sakintuna et al. reported that, through milling, a decrease in the desorption temperature was found. For MgH$_2$, a 100 °C decrease in the onset of desorption was found.

Despite the favorable mass uptake associated with metal hydrides, this storage medium has disadvantages as well. Kinetic and thermodynamic limitations are a concern going forward. The hydrides require higher than acceptable temperatures for desorption of hydrogen. Problems are also associated with regeneration abilities. Some hydrides have cost concerns as well as the need for heating cycles due to the unfavorable kinetics (26). Further research is being conducted in an effort to address many of these issues, but
until a more favorable desorption temperature can be reached, metal hydrides may not meet DOE criteria for on-board vehicle application.

1.2.4 Metal-Organic Frameworks

As was mentioned in the studies previously described, metal hydride systems and several carbon-based adsorbents have been of interest as a hydrogen storage material. There are a number of problems associated with metal hydrides, but these are dominated primarily by the high heat of adsorption and required high desorption temperatures. Studies on carbon-based adsorbents have displayed promising outcomes at times, but have been plagued by mixed results. It is now accepted that the interaction, which is of physisorption in nature, occurring in pristine carbon-based systems in not enough to support a high mass uptake and gives a weak sufficient heat of adsorption. Metal-organic frameworks, or MOFs, could provide a blending of these two media, with an effort to find a middle ground, resulting in favorable storage characteristics.

MOFs consist of multidentate ligands with coordinate bonds between them, as well as metal atoms or small metal-possessing assemblies that are often called secondary building units, or SBUs. Many MOFs have three-dimensional structures containing uniform pores and a system of channels. Guest species, often a solvent from synthesis, fill the channels and pores. If the
guest species is removed, the framework usually collapses. In some cases, the framework does not collapse and the empty spaces remain, making possible the adsorption of other guest molecules(30).

In May 2003, Rosi, et al. reported what may be the first measurements that involve using a MOF for hydrogen adsorption. At 77 K and pressures at or less than 1 atm, an uptake of 4.5 wt% was reported. At 20 bar and room temperatures, 1.0 wt% was reported(29). While these values were later adjusted and found to be lower upon further study, MOFs have since been extensively evaluated for their abilities to store hydrogen. Since 2003, over 60 different MOFs have been studied(30).

Several methods have been considered while trying to optimize hydrogen adsorption in MOFs. Such methods include, but are not limited to: high porosity with suitable pore size, impregnation, interpenetration, catenation, the energetics of physisorption open metal sites, SBU adsorptive sites, MOFs of light metals, and functionalized linkers(31).

Latroche, et al. performed a study on a commonly tested MOF named MOF-5(32). Their findings concluded that there are four sites for H$_2$ adsorption. Two positions were reported as being filled initially: one being at the center of the three ZnO$_3$ triangular faces and the other on top of the individual ZnO$_3$ triangle. One of the other two locations exists above the two oxygen ions and the last is located at the pinnacle of the hexagonal linkers. It was found that the
primary site for adsorption was the metal oxide cluster while the organic linker was involved in a more minor role.

The phenomenon known as hydrogen spillover is another reason why MOFs are considered to be good candidates for hydrogen storage. Hydrogen spillover is where, after physisorption of molecular hydrogen on the metal occurs, atomic hydrogen adsorbs onto the surface of the support. The support is believed to be the main receptor of atomic hydrogen(33).

The best storage capacities involving MOFs have been reported using temperatures of 77 K and pressures as high as 90 bar. Dincă *et al.*(34) reported that if a fuel tank were to be kept at 77 K and 90 bar, their MOF would show a hydrogen uptake of 6.9 wt%. Wong-Foy *et al.* reported that the MOF they tested displayed adsorption of 7.0 wt% and is thought to have the potential for even better uptake at 60 bar and 77 K(35). These temperature and pressure are unfit by DOE criteria. At room temperature, and 20 bar, Han *et al.* reported a hydrogen uptake of 3.89 wt%, which was the best reversible, ambient temperature hydrogen-storage capacity found at that time(36).

Much like carbon-based structures, such as expanded graphite and nanotubes, MOFs demonstrate good H₂ by mass ratio, but they suffer from weak adsorption and inconsistent results. As suggested by Bathi and Myers, in order for a medium to have the capability to store hydrogen and ambient pressure and temperature, the heat of adsorption of hydrogen should be 15.1 kJ/mol(37). For MOFs, cryogenic temperatures are necessary in order to
achieve considerable H₂ uptake. Dincă and Long reported that H₂ binding energies of up to 9.5 kJ/mol can be observed if frameworks are developed with extremely narrow pores, resulting in overlapping potentials from multiple pore walls acting together with an individual H₂ molecule(38). A promising note is that engineering the pores of MOFs on the atomic scale is a possibility. This would provide some control with regard to the H₂ binding interaction(39).
Chapter 2

Computational Modeling

Many problems can be solved analytically or numerically to give straightforward approximations with the use of mathematical and physics-based equations. With the increasing complexity of systems that are now of interest, many problems cannot simply be solved by straightforward analytical or numerical solutions. Computational modeling is an invaluable tool in tackling complex problems.

Computational modeling comes with both advantages and disadvantages. The disadvantages primarily stem from the limitations of computational modeling. The results of simulations depend largely on the input model for the system being simulated, and thus the accuracy of the results have dependence on how simple or how complex the model is, and how close it is to the actual system of interest. Thus, the results can only be as accurate as the input model. Simulations are also limited by the number of particles that can practically be included as of part of the simulation box defining the system. Bulk properties are typically easier to simulate as compared to interfacial properties, for example. One mole consists
of $6.02 \times 10^{23}$ particles. Simulations performed are orders of magnitudes less than this.

Computer simulations have several advantages. Simulations come into play to test theories that would otherwise prove impossible to implausible to test with physical experimentation. Simulations provide an experimenter with a method of testing that is more economically and fiscally efficient. If a particular experimental system, design or model proves to be unsuccessful, materials, labor cost, and time can all be saved. On the other side, if a model does show success, it can then be compared to physical experimentation. Besides being useful for new or innovative ideas, simulations can also prove a useful tool for presenting insight into already studied theories.

Computer simulations also open up possibilities of testing conditions that may be difficult to create in normal physical experimentation. For example, extreme temperatures and pressures can be difficult or dangerous to create in real experimentation, especially if the result is not already known to be successful; but with simulations, these environments can be tested with much more ease. Simulations can prove useful when needing to study behaviors on the microscopic, as well as atomic.
2.1 General Considerations

In carrying out atomic or molecular computer simulations, a number of factors, including interaction potential, simulation method, number of particles in the system and use of periodic boundary conditions, need to be taken into consideration. A detailed description of computer simulation methods can be found elsewhere (40, 41). A brief description of these factors follows.

2.1.1 Classical Simulation Methods: MD and MC simulations

Molecular dynamics (MD) is used when time propagation of the system is required to derive time-dependent properties. Monte Carlo (MC) simulation is used when one is interested in finding states of the system that satisfy a set of parameters. With the use of statistical mechanics, the physical properties of the simulated system can be obtained.

In molecular dynamics, time propagation of the positions and momenta of the particles in the model system is carried out. For a continuous potential energy interaction, positions and momenta as a function of time are determined by solving a set of $3N$ coupled Newton's equations of motion, where $N$ is the number of particles or interaction sites in the system. In MD simulations, the equations of motion are discretized so that they can be integrated numerically on
a computer. A time step is chosen for the advancement of positions and momenta. An algorithm to carry out the integration scheme is also chosen.

Monte Carlo simulations do not involve time propagations, but involve the search for configurations or states that satisfy the given conditions. The simplest of which involves a simulation with constant number of particles ($N$), volume ($V$) and temperature ($T$), which is known as the constant NVT or canonical ensemble. Monte Carlo moves in this case only consist of random displacements of a particle, which is also randomly selected. The displacement is assigned as follows:

$$ r_n \rightarrow r_o + \Delta r_{\text{max}} \left( \text{Ranf} - 0.5 \right). $$

Here, $r_n$ is the new position and $r_o$ is the old position. The term $\text{Ranf}$ is a function that outputs a random number from 0 to 1. If $\text{Ranf} = 0$, then the particle is displaced by $-0.5\Delta r_{\text{max}}$ as calculated from Equation 1. At the maximum value, $\text{Ranf} = 1$, the particle is displaced by $0.5\Delta r_{\text{max}}$. This means that for every Monte Carlo move, a randomly chosen particle is given a trial displacement, which is generated randomly, within the range $-0.5\Delta r_{\text{max}}$ to $0.5\Delta r_{\text{max}}$. Thus, the maximum displacement is set by $\Delta r_{\text{max}}$ and it is chosen to yield an acceptance ratio typically in the range 30-50%.

Because of a particle displacement, each Monte Carlo trial move results to a new energy of the system, $U(r_n)$. For each move, the difference between the energy of the new configuration, $U(r_n)$, and the energy of the old configuration,
$U(r_0)$, is evaluated. The trial move is rejected or accepted based on the following expression for the acceptance probability:

$$\text{acc}(r_o \rightarrow r_n) = \min\left(1, \exp\{-\beta[U(r_n) - U(r_o)]\}\right),$$

(2)

where $\text{acc}(r_o \rightarrow r_n)$ is the acceptance probability for the trial move from the old position to the new position, and $\beta$ is $1/k_B T$. Here, $k_B$ is Boltzmann’s constant and $T$ is the temperature of the system. If the new position is lower in energy than the old position, the exponential term is a positive number greater than 1. The minimum between 1 and this exponential term is 1. Thus, from Equation 2, we see that whenever the new position results in a lower energy configuration, the move is always accepted as its acceptance probability is 1. If the trial move results in a higher energy, the acceptance probability, as given by Equation 2 becomes less than 1, and is equal to the resulting value of the exponential term.

In the work presented here, the grand canonical Monte Carlo (GCMC) technique is implemented. The GCMC technique is appropriate for adsorption simulations since the chemical potential is kept constant, rather than the number of particles. This will be discussed in further detail in Section 2.2.
2.1.2 System Size, Energy Cut-off and Periodic Boundary Conditions

The length of a simulation run is mostly determined by the number of particles in the system. Most of the computer time is consumed calculating interparticle interactions and in the case of molecular dynamics, integrating the coupled equations of motion. A balance of accuracy and simulation time length is considered in choosing the number of particles to simulate.

There are tricks implemented in order to address the finite system size issue in simulations. For example, in calculating the interactions among particles in a system, periodic boundary conditions and minimum image convention are employed. Computer simulations are carried out for particle numbers on the order of $10^2$-$10^6$, a very small system size compared to Avogadro's number, the number of particles in one mole. Imposing periodic boundary conditions on the system significantly minimizes finite size effects. A series of simulations with varying system sizes can be done to determine the appropriate system size at which finite size effects no longer affect the results. The simplest periodic boundary condition is when the simulation box has cubic or rectangular symmetry. With cubic or rectangular periodic boundary conditions, the two ends of the simulation box in each of the Cartesian directions, $x$, $y$, and $z$, are considered connected.

To contribute to simulation time efficiency, an energy cut-off in the interaction calculation is imposed. Typically, the energy cut-off is set to 12 to 16
Å for van der Waals interactions. This means that for interparticle distances beyond this length, the interaction vanishes and need not be explicitly calculated anymore. For Coulombic interaction, a technique called Ewald summation may be used. In addition, interaction potentials do not have to treat every atom as an interaction site. It is common for simulations involving large systems, such as proteins, lipids and polymers, to have a group of atoms be treated as one interaction site instead of having individual atomic interaction sites. A set of atoms may also be constrained to move if their expected change in configuration can be considered negligible.

### 2.2 Grand-Canonical Monte Carlo Simulations

The study presented here uses a method called grand canonical Monte Carlo (GCMC) method. GCMC is the appropriate simulation technique to carry out such that at equilibrium, the chemical potential of the absorbed hydrogen molecules is identical to that of the surrounding gas.

In the constant NVT (canonical) Monte Carlo method discussed earlier, there is only one type of Monte Carlo move involved, and this move consists of particle displacements. Grand Canonical Monte Carlo method evaluates more than one changing variable. For example, in this H$_2$ adsorption study, both
number of H$_2$ molecules in the system and the positions of the H$_2$ molecules are evaluated with regard to their effect on the chemical potential of the system.

With the GCMC ensemble, two kinds of trial moves are needed for sampling the distribution. The first kind of trial move involves the displacement of particles already accepted as part of the system. A particle is randomly selected and a new position is assigned. The displacement move is then accepted or rejected based on Equation 2, as in the canonical ensemble.

Since the number of adsorbed particles is varied to make the chemical potential of the reservoir molecules and the adsorbed molecules equal, insertion and removal of adsorbed particles is the other kind of trial move involved in the GCMC procedure. With this trial move, a particle is inserted at a random position in the simulation box or an adsorbed particle that is randomly selected is removed(40). The condition for accepting an additional adsorbed molecule at a randomly generated position is detailed in the equation below.

$$\text{acc}(N \rightarrow N+1) = \min \left[ 1, \frac{V}{A^3(N+1)} \exp \left\{ \beta \left[ \mu - U(N+1) + U(N) \right] \right\} \right]$$ (3)

In this equation, $N$ is the number of particles already adsorbed prior to the insertion move, so $\text{acc}(N \rightarrow N+1)$ gives the acceptance probability for increasing the number of adsorbed particles from $N$ to $N+1$. The potential energy of the system with $N$ adsorbed particles is $U(N)$, and after insertion of an additional particle the new energy is $U(N+1)$. The volume of the system is given by $V$. The volume is held constant throughout the progress of the simulation. The
equilibrium chemical potential of the adsorbed particles and the gas reservoir is 
\( \mu \), \( \Lambda \) is the thermal de Broglie wavelength, and \( \beta \) is \( 1/k_B T \), where \( k_B \) is Boltzmann’s constant and \( T \) is the temperature of the system.

As mentioned, in addition to insertion of particles, removal of already adsorbed particles must also be a part of the Monte Carlo moves in GCMC to attain the desired chemical potential. An adsorbed particle is selected at random, and whether this removal move should be accepted or rejected is based on the condition below.

\[
\text{acc}(N \rightarrow N-1) = \min \left[ 1, \frac{\Lambda^3 N}{V} \exp \left\{ -\beta [\mu + U(N-1) - U(N)] \right\} \right],
\]

(4)

where \( N \) is the number of particles already adsorbed prior to the deletion, \( N-1 \) is the resulting number of particles after a random particle deletion. The term \( \text{acc}(N \rightarrow N-1) \) gives the acceptance probability for this move, which involves decreasing the number of adsorbed particles from \( N \) to \( N-1 \). The old energy is \( U(N) \), and after deletion the new energy is \( U(N-1) \). The other terms have the same definitions as those in Equation 3.

At finite temperatures, the entropy change when an \( \text{H}_2 \) transitions from a gas phase to an adsorbed phase, becomes important. This change in entropy is related to the hydrogen uptake of the system. So, in adsorption studies the isosteric heat of adsorption is a quantity of interest. This is the amount of heat liberated upon adsorption. Nicholson and Parsonage(42) have derived a fluctuation formula for evaluating the heat of adsorption as follows,
\[ q_{st} = -\frac{\langle NU \rangle - \langle N \rangle \langle U \rangle}{\langle N^2 \rangle - \langle N \rangle^2} + k_b T \]

In this equation, \( q_{st} \) is the isosteric heat of adsorption, \( U \) represents the total energy of the system, \( N \) represents the number of adsorbed particles, \( k_b \) is Boltzmann's constant, and \( T \) is the temperature. The brackets represent the average quantity. For example, the term \( <NU> \) is the average of the product of the number of particles and potential energy taken over several Monte Carlo moves. Using this expression, the heat of adsorption can be calculated from GCMC simulations since such simulations allow for the measurement of fluctuations in the number of adsorbed particles and potential energy of the system. For hydrogen storage purposes, the target value for the heat of adsorption is around 25 kJ/mol. GCMC allows for the calculation of this quantity and a comparison to the optimum target value can then be made.

### 2.3 Modeling Atomic and Molecular Interactions

An important component in computer simulations is a description of how the particles in a system interact with each other. Also, if an external field is present, then a description of how the system interacts with the external field should also be given. Thus a potential energy function has to be defined in
computational modeling. The potential energy function allows for the calculation of energies of the system, as well as the forces in the system. In modeling the interactions, each atom may be considered as an interaction site. However, for the simulation of large molecules, a functional group may be considered as one site. If the simulation involves solute-solvent interactions, the solvent can be considered as a continuum model.

In classical simulations of hydrogen adsorption on carbon, potential energy functions for the $H_2$-C and the $H_2$-$H_2$ interactions are needed. Since in adsorption simulations, the sorbent system is typically constrained to move, and maintains the same initial position, and it is not necessary to define a C-C potential energy function. We show here examples of potential energy interactions used to model hydrogen adsorption on carbon. These are presented in Figure 3. The figure shows two separate potential energy equations to account for the $H_2$-C interaction. Both interactions are available in the literature. One was proposed by Patchkovskii and coworkers(20), and the other was proposed by Wang and coworkers(43). From the figure, the difference in binding energies can be seen. The Patchkovskii et al. potential exhibits a stronger binding energy between carbon and molecular hydrogen, while the Wang et al. potential has a weaker binding energy. Modeling hydrogen adsorption using these two interactions have been reported previously(6).
The C-H\textsubscript{2} potential energy interaction proposed by Patchkovskii and coworkers\cite{20}, shown in red in the figure, is given below.

\[ u(r) = Ae^{-r\alpha} - C_6r^{-6} \]  \hspace{1cm} (6)

The potential energy \( u(r) \) is a function of the distance \( r \) between the carbon atom and the center of mass of an H\textsubscript{2} molecule. The parameters \( A, C_6, \) and \( \alpha \) were chosen to fit \textit{ab initio} results for an H\textsubscript{2} molecule on a coronene system, and have the following values: \( A = 1099.40 \) eV/molecule, \( C_6 = 17.3621 \) eV Å\textsuperscript{6}/molecule, and \( \alpha = 3.5763/\text{Å}. \)

Figure 3. Potential energy interactions used in hydrogen adsorption simulations previously reported in the literature.
The other C-H\textsubscript{2} interaction used, proposed by Wang and co-workers\cite{38}, shown as green in the figure, is as follows:

\[
U(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] \tag{7}
\]

Like the potential energy expression in Equation 6, this expression represents a pair-wise interaction between the carbon atom and the hydrogen molecule. The potential energy \(U(r)\) has the Lennard-Jones form and is a function of only the distance \(r\). The Lennard-Jones parameters \(\varepsilon\) and \(\sigma\) represent, respectively, the potential well depth and the inter-particle distance at which the interaction is zero. In this equation, these parameters have values of \(\varepsilon = 3.69\) meV/molecule and \(\sigma = 2.97\) Å, which were chosen to fit the energy spectra from scattering experiments of H\textsubscript{2} physisorbed on graphite.

To model the molecular hydrogen interaction, the Silvera-Goldman potential\cite{44} is shown as an example. This potential energy function treats each molecule as one interaction site with spherical symmetry, ignoring the rotational degrees of freedom of the molecules. The form of the interaction is shown below:

\[
U(r) = e^{-(\alpha - \beta r - \gamma r^2)} \left( \frac{C_6}{r^6} + \frac{C_8}{r^8} + \frac{C_{10}}{r^{10}} \right) \times \exp \left[ -\left( \frac{1.28 r_m}{r} - 1 \right)^2 \right] \tag{8}
\]
In this equation $u(r)$ is the potential energy as a function of the inter-particle distance $r$. The constants on the exponential term, $\alpha$, $\beta$, and $\gamma$, are equal to 1.713, 1.5671, and 0.00993 atomic units, respectively. The constants $C_6$, $C_8$, and $C_{10}$, are equal to 12.14, 215.2, and 4813.9 atomic units, respectively, and $r_m$ is the well minimum.

The potential energy interactions in the Pd-doped graphene system are much more complicated, and thus cannot be modeled by a simple form, such as that of a Lennard-Jones type alone. The consistent-valence force field, or cvff, was used instead. Dauber-Osguthorpe et al. provided the parameters for water, amino acids, and several functional groups in the cvff (45). The augmented cvff was later developed to include more atom types. This force field is available in the Materials Studio Sorption package, used to carry out the grand canonical Monte Carlo adsorption simulations. The form of the cvff forcefield is as follows:

$$u(r) = \sum_b D_b \left[1 - e^{-\alpha(b-b_o)}\right] + \sum_\theta H_\theta (\theta - \theta_o)^2 + \sum_\phi H_\phi \left[1 + s \cos(n\phi)\right] + \sum_{X} H_x \chi^2$$

$$+ \sum_b \sum_{b'} F_{bb'} (b-b_o)(b'-b_o) + \sum_\theta \sum_{\theta'} F_{\theta\theta'} (\theta - \theta_o)(\theta' - \theta'_o)$$

$$+ \sum_b \sum_{\theta} F_{b\theta} (b-b_o)(\theta - \theta_o) + \sum_{\phi} F_{\phi\phi} \cos(\theta - \theta_o)(\theta' - \theta'_o)$$

$$+ \sum_{X} \sum_{\chi} F_{X\chi} + \sum_{X'} \sum q_i q_j \frac{e^{r_i r_j}}{r_{ij}^{11}}$$

The potential energy is given by $u(r)$ and $r$ is the inter-particle distance. The values of the parameters in the equation depend on the type of atom being modeled. The first four terms in the potential energy expression relate to the
energy of deformation. Term 1 corresponds to bond lengths, term 2 to bond angles, term 3 to torsion angles, and term 4 represents out-of-plane interactions. Terms 5 to 9 correspond to couplings between internal coordinates and deformation. The purpose of these terms is to duplicate experimental vibrational frequencies with accuracy. By doing so, the terms reproduce the dynamic properties of molecules. Non-bonding interactions are accounted for by terms 10 and 11. The van der Waals interactions are represented by a Lennard-Jones function in term 10, and electrostatic interactions are given by the Coulombic term in 11.

2.4 Equilibration and Sampling

The length of a simulation run consists of two parts: the equilibration stage, then the sampling stage. The total length of the simulation can run from several thousands to billions of molecular dynamics (MD) time steps or Monte Carlo (MC) trial moves. The equilibration stage involves letting the system propagate through time in the case of molecular dynamics, or sample configurations as in the case of Monte Carlo until the properties of the system, such as energy, temperature, pressure, or number of particles have reached an equilibrium value and are now just fluctuating around this equilibrium value. When the system has reached equilibrium, sampling run is performed, over
which various averages are taken to calculate various properties of the system that are of interest.

In the case of the adsorption studies specifically performed in this work, equilibrium in the system is monitored by looking at the number of adsorbed molecules. The number of Monte Carlo trial steps to equilibrate the system varied with pressure, with higher pressures requiring longer simulation runs. When the number of adsorbed molecules is stable, that is, it fluctuates about an average value, the sampling stage is next carried out. To demonstrate this concept, we show in Figure 4 the number of adsorbed molecules as the simulation progresses. This is a sample output from the Sorption module in Materials Studio. The blue curve shows the instantaneous number of adsorbed H₂ molecules, while the red curve shows the average number of adsorbed molecules. As seen from the figure, the number of adsorbed molecules stabilizes after $2 \times 10^5$ steps, and sampling can then be done from $2 \times 10^5$ to $1 \times 10^6$ steps for this particular simulation run.
Figure 4. Number of adsorbed molecules as a function of Monte Carlo steps carried out as the simulation progresses. This is a sample output from the Sorption module of Materials Studio.

In Monte Carlo simulations, choosing the appropriate value of maximum trial displacement is important in achieving efficiency of the MC run. Recall that the displacement given to a random particle is randomly generated according to Equation 1, where $\Delta r_{\text{max}}$ sets the maximum trial displacement. The value of $\Delta r_{\text{max}}$ is adjusted during the course of the simulation. Typically, $\Delta$ is adjusted to achieve an acceptance probability that falls between 30%-50% for the translational moves. Note that if the maximum displacement were too large, most of the moves would likely be rejected, resulting in a very low acceptance probability and the efficiency of the sampling would be compromised. If the
maximum displacement were too small, the acceptance probability becomes too high, and this time, resulting in poor sampling of the configuration space. A moderate acceptance probability is therefore required to achieve an efficient Monte Carlo sampling of the configurational space.
Chapter 3

Simulation Details

The computational techniques used in this study are grand canonical Monte Carlo simulations and first principles calculations. The GCMC simulations implement the consistent-valence forcefield (cvff), as described in Equation 9, to model atomic interactions, and the first principles calculations are based on density functional theory approximations. There are three major tasks in this study. The first consists of evaluating the hydrogen storage capacity of a slit-pore model of carbon. Even though studies for this have been reported previously, there have been no previous reports on simulations employing the cvff forcefield. To make our comparisons with Pd-doped carbon meaningful, simulations should be carried out for the pristine carbon case employing the same cvff forcefield. The second task involves studying interactions of Pd and C to investigate adsorption capacity improvements through Pd-doping using first-principles calculations. Optimized Pd-doped graphene structures are also generated in this task. The third involves pore-size dependence studies for the Pd-doped carbon nanopore model. As in the case of the pristine nanopore, a
simple slit-pore geometry is used. This section describes simulation details associated with these three major tasks.

### 3.1 Slit-pore Model of Pristine Carbon Nanopore

To study the effects of metal-doping on adsorption properties, it is first necessary to perform calculations on a pristine carbon system to serve as a baseline. To simulate a porous carbon material, we used the slit pore geometry, which consists of two layers of graphene, with the interlayer separation representing the pore size.

Prior to constructing the slit-pore, the geometry of a graphene layer is first optimized. In modeling, first-principle calculations are those that begin at the stage of already-determined laws of physics, mathematics, and chemistry. In contrast to classical simulations, which use empirical potentials, no parameters are fitted to describe the particle interaction. First-principle, or *ab initio*, calculations start directly with the properties of the atoms in question and then begin to derive the properties of larger systems. Due to minimized imposition of assumptions and parameter fitting, first-principles calculations are computationally much more expensive than classical simulations, and so only a few atoms are typically used to carry out such calculations. Here, a 2x2 unit cell of graphene, containing eight carbon atoms, was optimized using density
functional theory (DFT) with the generalized gradient approximation (GGA). This was carried out using Materials Studio CASTEP simulation package. The resulting optimized geometry of graphene has a C-C distance of 1.44 Å.

Classical simulations often follow after first-principle calculations, with the intent of increasing the system size and incorporating parameters such as pressure and temperature. For the GCMC simulations, a larger system size can be simulated. From the optimized geometry, an 8x8 supercell is created to form a graphene layer with 512 atoms. The slit-pore geometry is constructed from two parallel graphene layers. Overall, the adsorbate consists of 1024 carbon atoms.

Figure 5. The carbon slit pore model showing the simulation box with vacuum slab onto which periodic boundary conditions are applied.

The resulting system has dimensions of 39 Å in the x and y directions. The z dimension depends on the slit pore size. Shown in Figure 5 is the set up for the slit pore model of pristine carbon. A vacuum slab of along the z direction is
added so that periodic boundary conditions can be applied in the $z$ direction as well, in addition to $x$ and $y$ periodic boundary conditions.

The GCMC simulations were carried out at room temperature, 298 K, and at pressures 0.1 MPa, 1 MPa and 5 MPa. The pore size, or interlayer spacing, was varied from 5.6 Å to 11 Å. Simulations were carried out using the Materials Studio Sorption package. The cvff forcefield, which is available in Sorption was used. A potential cutoff of 14 Å was imposed on both van der Waals and Coulombic interactions. An acceptance probability of 30%-40% was the criteria set for the translational Monte Carlo moves. Particle exchange was chosen to occur randomly every one MC cycle, which consists of $N_{av} + 1$ MC steps. The value of $N_{av}$ varies for different pressures and pore sizes because this number is chosen to be close to the number of adsorbed $\text{H}_2$ molecules. The equilibration period was done anywhere from $2 \times 10^5$ to $5 \times 10^6$ steps, depending on the pressure and pore size. A typical adsorption capacity output is shown Fig. 4 in the previous chapter. Note that the adsorption capacity rises from zero to an average adsorption capacity value. When the system is equilibrated, averaging or sampling runs are carried out. Sampling runs are set to $2 \times 10^6$ steps long.
3.2. Optimized Structure of Graphene with Pd

Change in the hydrogen adsorption capacity of porous carbon-based materials brought about by metal doping, Pd-doping in particular, is of interest in this study. To carry out adsorption simulations on slit-pores of carbon with Pd, it is first necessary to determine the structure of Pd-doped graphene. The goal is to find the preferred adsorption site of a Pd atom on graphene. A palladium atom was introduced into the previously optimized 2x2 graphene unit cell described in the previous section. Geometry optimization using Materials Studio CASTEP package was used to minimize the energy of the configuration.

Charge density difference calculations were also done in order to gain insight into the electron density change that occurred due to the interaction of Pd and carbon. Once this graphene-palladium system was established, H$_2$ molecules were introduced. To study how each H$_2$ molecule is affected by the presence of a Pd atom, and how adsorption is affected the already present H$_2$ molecules, the molecules have been introduced one after the other. Geometry optimization was performed after each molecule addition. Changes in bond length and positions relative to the graphene plane were determined.
3.3. Slit-pore Model of Carbon Nanopore with Palladium

With the optimized 2x2 unit cell of the graphene-palladium system, a slit-pore model, similar to that of the pristine carbon system, was created from two Pd-doped layers. The size of the system was increased by making an 8x8 supercell. Similar to the pristine carbon system, the total number of carbon atoms is 1024. The system size is $39.4 \times 39.4 \times 37.8 \, \text{Å}^3$. The GCMC simulations were carried out at the temperature, pressures, and interlayer spacings that matched the pristine carbon system runs. Other simulation parameters, such as forcefield, potential energy cutoff, and acceptance probabilities were also set similar to the pristine carbon system. Varying amounts of palladium have been added to the system. Simulations have been carried out for systems with Pd:C ratios of 1:32, 1:18 and 1:8.
Chapter 4

Results and Discussion

This chapter includes three sections covering the three tasks performed in this computational investigation. Results for the pore size dependence of hydrogen mass uptake, in terms of H$_2$ wt%, are first presented. The second section presents the geometry optimization of Pd on graphene and the adsorption of hydrogen on this Pd-graphene system using ab initio calculations. Lastly, we discuss results of grand canonical Monte Carlo simulations of molecular hydrogen adsorption on the slit-pore model of carbon with Pd.

4.1. Hydrogen Mass Uptake on Pristine Carbon Slit-pore

Figure 6 shows the dependence of hydrogen mass uptake in the pristine carbon system at a temperature of 298 K and at a pressure of 0.01 MPa. An optimum pore size, where a maximum in the adsorption occurs, is seen at
around 6.4 Å. At this slit-pore size, a 0.116 wt% H₂ mass uptake was obtained. The 6.2 Å slit-pore size yielded a similar result of 0.114 wt% H₂ mass uptake.

Figure 6. Effect of slit-pore size on the hydrogen mass uptake of pristine carbon at T=298 K and P=0.01 MPa. The optimum slit-pore size occurs near 6.2 – 6.4 Å.

4.2. Adsorption of Hydrogen on Graphene with Pd

From ab initio calculations, we find that the Pd atom prefers to sit on top of the hollow site of a hexagonal array of carbon atoms. Figure 7 shows the minimized configuration for a Pd atom on a 2x2 unit cell of graphene. The figure shows the entire simulation box, where a vacuum slab was added in the z
direction, so that periodic boundary conditions in all three cartesian directions can be imposed. The calculations reveal that the optimized distance of the Pd atom from the closest neighboring carbon atoms are 2.18 and 2.19 Å, while its perpendicular distance from the graphene plane is 2.17 Å.

Figure 7. Geometry optimization result for a Pd atom on a 2x2 unit cell of graphene. The Pd atom sits 2.18-2.19 Å away from the nearest carbon atoms, and its perpendicular distance from the graphene plane is 2.17 Å.

Once we obtained an optimized structure for the Pd-carbon system, molecular hydrogen molecules were introduced one at a time. Geometry optimization is carried out after each H$_2$ addition. Figure 8 shows a plot of the adsorption energy of molecular hydrogen on the Pd-carbon system. The plot shows that as number of hydrogen molecules introduced into the system is increased, the average binding energy per molecule decreases. The first H$_2$ molecule experiences an adsorption energy of 1.06 eV/H$_2$ while when six molecules are introduced, the adsorption energy is decreased to 0.2 eV/H$_2$. 
Figure 8. Average adsorption energy per H\textsubscript{2} on the Pd-carbon system. The adsorption energy per molecule decreases as number of sorbate molecules increases.

The optimized geometry when one hydrogen molecule is adsorbed is shown on Figure 9. The preferred position of the H\textsubscript{2} molecule is right on top of the Pd atom. As shown in the figure, bond lengthening to 0.865 Å is experienced by the H\textsubscript{2} molecule, although in contrast to the case if bulk Pd were present, the H – H bond is not broken. The perpendicular distance of the H\textsubscript{2} molecule from the graphene plane is 3.7 Å, while that of the Pd atom is 2.1 Å.
Figure 9. Optimized position of $\text{H}_2$ on graphene with Pd. The hydrogen molecule bond is not broken, but the bond length increases to 0.865 Å.

Figure 10. Optimized geometry for three $\text{H}_2$ molecules on the Pd-graphene system. Two of the adsorbed molecules that are closer to the Pd atom increase in bond length, while the third molecule, preferring to be 5.0 Å in $z$-distance away from the Pd atom maintains a typical $\text{H}_2$ bond length.
Figure 10 shows the configuration when three hydrogen molecules are introduced. The optimized configuration shows that H – H bond lengthening to 0.853 Å and 0.845 Å occurs for two of the molecules. However, the third molecule is not anymore affected by the presence of the Pd atom, and its bond length is 0.756 Å.

The perpendicular distance (z-distance) of the Pd atom has increased to 2.3 Å, compared to the 2.1 Å when there was only one molecule adsorbed. As expected the molecules with that H – H bond lengthening are the ones closer to the Pd atom, and their z-distances are 3.0 Å and 3.2 Å. The third molecule with unchanged bond length has a z-distance 5.0 Å.

When two more molecules are added increase the number of H₂ to five, the two molecules originally closer to the Pd atom maintain their proximity and bond lengths, while the other three are unaffected by the Pd atom. Their bond lengths are all 0.753 Å. The optimized geometry for this is shown in Figure 11.
Figure 11. Optimized geometry for five H$_2$ molecules on the Pd-graphene system. As in the case for three adsorbed molecules, two H$_2$ molecules maintained close proximity to the Pd atom, and had bond lengthening. The other three all had a bond length of 0.753 Å, typical for H – H bond distance in an H$_2$ molecule.

To compare the geometry of the hydrogen molecules with and without the presence of a Pd atom, geometry optimizations were also performed for a pristine graphene system. Figure 12 shows a 2x2 unit cell of graphene with one adsorbed molecule.

Figure 12. Hydrogen molecule on pristine graphene. The optimized bond length is 0.754 Å, and z-distance is 3.4 Å.
Figure 13. Optimized configuration of three $H_2$ molecules on pristine graphene. The optimized bond length is 0.752 Å, and $z$-distance is 3.40 Å for all three.

The optimized position of the hydrogen molecule is 3.4 Å in perpendicular distance from the graphene plane. When the number of molecules is increased to three, all three molecules stayed on the plane, and again assumed $z$-positions of 3.4 Å. The optimized geometry is shown on Figure 13. We find that three $H_2$ molecules is the limit of the planar arrangement for this cell size. The addition of a fourth molecule disturbs this planar arrangement, and that is due to volume restrictions.

On pristine carbon, the bond lengths are not significantly different from each other, with values 0.752 Å and 0.754 Å. These values agree with the typical bond length for a hydrogen molecule. The $z$-distance of 3.4 Å also agrees with an expectation based on empirical C-H$_2$ potentials available in the literature.
Referring to Figure 3, the minimum in the C-H₂ potentials from Wang, *et al* and Patchkovskii *et al* is close to 3.4 Å.

When Pd is added to carbon-based materials, Pd can exist as either clusters or single atoms. The formation of clusters can be viewed as unfavorable in the sense that clusters decrease the available volume available for storage at significantly increases the mass of the sorbent material, and thus, decreasing the hydrogen storage capacity. However, it is also suggested that the presence of metal clusters on carbon-based system enhance adsorption as the clusters act as catalyst and increase hydrogen mass uptake via the spillover mechanism(46).

This current study investigates the effect of Pd existing as single atoms rather than as clusters. Even though the preparation of sorbent materials decorated with metals existing as single atoms presents experimental challenges, a recent imaging study has shown that some Pd can exist as single atoms in activated carbon fibers(13). When transition metals exist as single atoms, the interaction is proposed to be that of Kubas type(47). This interaction results to bonding of hydrogen molecules with an individual metal atom. Such mechanism is suspected to play a role in potentially increasing hydrogen mass uptake(13, 46). The presence of hydrogen molecules around the Pd atom, without the hydrogen undergoing dissociation, as shown, for example, in Figure 10 is consistent with Kubas type of interaction.
4.3. Hydrogen Mass Uptake on a Slit-pore Model of Carbon with Pd

In this section, results for hydrogen adsorption in the Pd-doped carbon are presented. Pore-size dependence using slit-pore geometry is compared for the pristine and doped system. Simulations have been carried out for pore sizes less than 12 Å. The temperature examined for all simulations is 298 K, and the pressures investigated are 0.01 MPa, 1 MPa, and 5.0 MPa.

Figure 14. Hydrogen mass uptake (wt% H\textsubscript{2} adsorbed) of slit-pores of pristine carbon and carbon with Pd at T=298 K and P=0.01 MPa. The adsorption capacity increases with increasing ratios of Pd content.
Figure 14 shows the hydrogen molecule wt% adsorption as a function of the slit-pore size at a temperature of 298 K and a pressure of 0.01 MPa. A maximum in the adsorption capacity is found to occur between 6.2 – 6.6 Å for all the systems investigated. Previous studies have reported optimum pore size around that range(6). We see from the figure that with Pd in the system, the maximum is shifted to a larger pore size as the amount of Pd is increased. Even though this trend is clearly depicted in the graph, the shift to larger pore sizes is only very small, and is still at less than 7 Å even for the highest doping investigated. Despite little to no effect on the optimum pore size for maximum adsorption, the effect of Pd on the adsorption capacity, however, is significant. The graph shows a clear increase in the adsorption capacity as the amount of Pd is increased, with a maximum wt % adsorption of 0.56 wt% for Pd:C ratio of 1:8. Comparing this with the adsorption for pristine carbon, whose maximum adsorption is at 0.11 wt%, the increase represents a five-fold improvement in the adsorption capacity. This observation is for 0.01 MPa pressure.

When the pressure is increased to 1 MPa, which is still a moderate amount of pressure, the exhibited trend is different. This is shown in Figure 15. Similar to adsorption on pristine carbon, the pore size corresponding to maximum adsorption is unchanged but only for the lowest doping of 1:32 ratio of Pd:C investigated. At a higher Pd ratio of 1:18, maximum adsorption occurs over a broad range, from 6.5 to 9 Å. At the highest Pd ratio investigated, 1:8, maximum adsorption is exhibited starting at about 8 Å. Similar to the 1:18 Pd:C ratio, the
maximum occurs over a broad range and is not well-defined peak such as the case for pristine carbon.

![Graph](image)

**Figure 15.** Hydrogen mass uptake at \(T=298\) K and \(P=1\) MPa. A crossover behavior on the effect of the degree of Pd content occurs near 8 Å.

While the pristine system maintained an optimum pore size of 6.2-6.6 Å, the optimum interlayer spacing for the systems with Pd appear to be favoring larger pore sizes as the ratio of Pd to C is increased. This new trend could be due to a need for more spacing in order to fit the hydrogen molecules and
palladium atoms in the system in order to maximize adsorption. This observation also agrees with the results of first principles calculations presented in Section 4.2. For the pristine graphene shown in Figures 12 and 13, the H$_2$ molecules maintained a perpendicular distance of 3.4 Å from the graphene plane. From this, an estimate that the expected optimum interlayer spacing would occur at around twice this value, which is around 6.8 Å, can be made. Now, for the graphene with Pd as shown in Figure 10, the two molecules closest to the Pd atom are about 3.1 Å z-distance from the plane, and the farther H$_2$ molecule has a 5.0 Å z-distance from the plane. Thus, the optimum pore size could be larger if Pd were present in the system. With a small amount of Pd, the maximum adsorption occurs near 6 Å, as seen for the 1:32 Pd ratio, while at higher ratios, the peak occurs at larger slit pore sizes. The first principles calculations support the presence of broadened peaks for the maximum adsorption as seen in Figure 15. The spread in the H$_2$ molecules z-position, ranging from 3 to 5 Å as a result of increased interaction in the presence of Pd, could be causing the broad range of pore sizes over which a maximum in the adsorption is attained. With these z-distances, the expected optimum pore size could be anywhere between 6 to 10 Å.

At a pressure of 1 MPa, the effect on hydrogen adsorption capacity is not a simple increasing trend as a function of Pd:C ratio as seen for the lower 0.01 MPa pressure. At lower pore sizes, the effect is opposite of that seen at 0.01 MPa, with the adsorption capacity decreasing as the Pd content is increased. Another difference between the two pressure systems is that with the 1 MPa
system, the pristine carbon layer results in the highest mass uptake. The pristine carbon system shows a maximum uptake of about 2.6 wt%, while the 1:8 Pd to C system yields only a 2.2 wt% adsorption for its highest mass uptake. Even though the number of molecules adsorbed increases with Pd content, the resulting wt % adsorption is not increased. This leads to the conclusion that at a higher pressure, the extra H\textsubscript{2} molecules adsorbed by the palladium atoms no longer sufficiently compensate for the extra weight from the palladium atoms. Note, however, though that at higher pore sizes the behavior shifts to increasing adsorption capacity as Pd content is increased. The crossover in the trend appears to be occurring at 8 Å.

Data collected on a 5 MPa system using GCMC simulations revealed a trend similar to that of the 1 MPa system in that the pristine carbon system presented the highest mass uptake. While the overall mass uptake was higher for each system due to the increased pressure, this again suggested that the added weight from the palladium atoms could not be compensated for by increased uptake of the number H\textsubscript{2} molecules. The results are shown on Figure 16. Over the range of pore sizes investigated, a crossover pore size similar to that seen for 1 MPa was not exhibited.
One notable feature in the adsorption results is that with this higher pressure of 5 MPa, the optimum interlayer spacing appears to be occurring between 9 to 11 Å for the pristine and the low Pd to C ratio of 1:32. For the systems with higher Pd content, it is possible that the hydrogen mass uptake will still increase with pore size increase, and a conclusive optimum pore size for the 1:18 and 1:8 Pd to C ratios at 5 MPa pressure cannot be suggested from this work. Notice that for the pristine carbon system, a lower peaked adsorption appears to be occurring below 7 Å. This is in addition to the clearly observed
maximum adsorption at 9.5 Å rather than the usual 6.2-6.6 Å. This lower peak could be due to a single layer of H₂ molecules, and the second higher peak observed could be due to two layers of molecules, whose formation now becomes more favorable at this higher 5 MPa pressure.

Figure 17. Heats of adsorption as a function of wt % hydrogen uptake at T=298 K and P=5 MPa. As the wt % uptake increases, the heat of adsorption decreases due to weakening of physisorption strength.

Determination of the heats of adsorption has been carried out for the adsorption simulations presented in Figure 16, which correspond to the system at 5 MPa. Calculations have been carried out using the fluctuation formula in Equation 5, and the results are presented in Figure 17. It can be seen from the
figure that the largest heat of adsorption of 25 kJ/mol occurs at about 1.5 wt% H₂ adsorption and is obtained for the highest Pd content. As the adsorption capacity increases, the heat of adsorption decreases.

Our simulation results show that the desired 6 wt% capacity with a heat of adsorption of 25 kJ/mol is not achieved even with Pd dispersed over the carbon nanopore system model considered here. Despite achieving a 25 kJ/mol value for the heat of adsorption, the corresponding mass uptake achieved is only 1.5 wt%. It is important to note that investigations presented here were done at reasonable operating conditions of 298 K and moderate pressure values. Significantly decreasing the temperature would of course significantly increase the adsorption capacity, but they would not represent practical operating conditions.
Chapter 5

Summary and Conclusion

The change in the adsorption capacity of a slit-pore carbon nanopore model brought about by the addition of Pd has been investigated in this study.

Computational methods involving first principles calculations and grand canonical Monte Carlo simulations are employed. First principles calculations were used primarily to study the adsorption energies using a small system consisting of a few unit cells. They have also been used to determine minimum energy configurations of the sorbent material, either pristine carbon or carbon with Pd. The configurations derived from first principles calculations have been extended to a larger sorbent system by constructing larger superscells. The larger sorbent system was then used in the grand canonical Monte Carlo simulations for carrying out finite temperature and pressure adsorption studies. In addition to investigating the adsorption capacity as a function of pressure and different levels of Pd additions, the use of the slit-pore model has enabled the study of the pore size dependence of molecular hydrogen adsorption.
Research on storage of hydrogen has received attention due to efforts in line with finding clean alternative sources of energy. Chemical storage, as opposed to compressed $\text{H}_2$, is sought with the goals of improving both mass and volumetric capacities. One of the candidates widely investigated in the literature consists of porous carbon-based materials to take advantage of properties such as light weight, stability, and tunability in both adsorption properties and surface area. The research performed here falls within this category, where a model of carbon-based porous material with Pd addition has been studied by computational modeling.

Results show that when Pd is added to graphene, the minimum energy configuration is such that the Pd atom is 2.2 Å away from the nearest carbon atoms. Hydrogen adsorption studies on the graphene sheet with Pd show that the adsorbed hydrogen molecules closest to the Pd atom undergo a lengthening of the bond length to 0.85 Å. The interaction observed appears to be consistent with proposed Kubas type of interaction, where a single transition atom interacts with hydrogen molecules (47). The interaction of single atoms with $\text{H}_2$ molecules not sufficient enough to cause dissociation of the molecules as is typically seen when bulk Pd is used in heterogeneous catalysis.

Only the molecules within the nearest neighbor shell have an increased bond length; other adsorbed molecules keep a bond length of 0.75 Å. For a 2x2 unit cell of graphene with one Pd atom, two $\text{H}_2$ molecules can take positions closest to the Pd atom, and these two molecules are found to have 3.0 Å and 3.2 Å perpendicular distances from the graphene plane. Comparing these results
with pristine carbon, the nearest H$_2$ molecules have a perpendicular distance of 3.4 Å from the graphene plane, and all maintain an H – H bond length of 0.75 Å.

Hydrogen adsorption capacity of both pristine carbon and that with Pd atoms at 298 K and moderate pressures of 0.01 MPa, 1 MPa and 5 MPa has been investigated by grand canonical Monte Carlo (GCMC) simulations. Simulations have been performed on different pore sizes ranging from 5 to 12 Å. With the slit-pore geometry model, the pore size corresponds to the interlayer spacing of the graphene planes. The amount of Pd dispersed over the graphene plane is set in terms of Pd to C atoms ratio. In this work, Pd to C ratios of 1:32, 1:18 and 1:8 have been studied. One of the important results we intend to obtain from this work is the optimum pore size. This is the pore size at which maximum molecular hydrogen adsorption is attained.

At the lowest pressure of 0.01 MPa investigated, we find that the optimum pore size occurs within 6.2 – 6.6 Å. The peak in adsorption for pristine carbon occurs closer to 6.2 Å, and a very slight shift towards increasing pore size is seen as the level of Pd content is increased. In addition, as the Pd to C ratio is increased, the adsorption capacity also increases. With pristine carbon, the maximum adsorption is 0.11 wt% of H$_2$ adsorbed, while at the highest level of Pd investigated, 1:8 Pd to C ratio, the maximum adsorption shows a five-fold increase to 0.56 wt%.

When the pressure is increased to 1 MPa pressure, a different trend is observed. The pore size dependence of the adsorption capacity can be divided
into two different regions, depicting opposite trends, with the crossover occurring near 8 Å. Below 8 Å pore sizes, the hydrogen mass uptake decreases with increasing amount of Pd content, while at pore sizes greater than 8 Å, the mass uptake increases with increasing Pd content. Examining the adsorption over all pore sizes, the maximum adsorption with Pd present is still less than the maximum adsorption for pristine carbon. The pristine carbon system shows a maximum uptake of about 2.6 wt% at a pore size of 6.4 Å, while the 1:8 Pd to C system shows a maximum uptake of 2.2 wt% at 9 Å.

The simulation results for 5 MPa pressure also show a decreasing trend in the adsorption capacity as the ratio of Pd to C content is increased. Even though the number of hydrogen molecules is increased due to the presence of Pd, the resulting wt% of H₂ adsorbed is not increased. The extra molecules adsorbed due to the presence of Pd no longer sufficiently compensate for the additional mass presented by the much heavier Pd atoms. For the optimum pore size, the results show a broad range of pore sizes for the maximum adsorption as opposed to the narrow peak exhibited in the low 0.01 MPa pressure. For the pristine carbon and the low Pd to C ratio of 1:32, the maximum adsorption occurs between 9 to 11 Å, and capacities are 4.2 wt% and 3.9 wt%, respectively. A maximum for the higher Pd to C ratios is not yet clearly seen for the simulations performed up to 11 Å pore size.

The highest mass uptake measured in this study is 4.2 wt% occurring at 5 MPa for pristine carbon. The corresponding heat of adsorption for this, however, is only 8 kJ/mol. This is very weak compared to the target value of 25 kJ/mol. A
heat of adsorption value, around 25 kJ/mol, is achieved for the highest Pd to C ratio of 1:8. However, the adsorption capacity for this point is only 1.5 wt%. A favorable hydrogen storage material should have a high storage capacity and at the same time exhibit a 25 kJ/mol heat of adsorption value. The simulations performed in this study have been limited to 298 K and moderate pressure values. Despite expected increase in adsorption capacity at lower temperatures and higher pressures, such studies were not done because of their deviation from reasonable operating conditions.
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