SUBSTRATE STRUCTURE AND DYNAMICS EFFECT ON SORPTION PROPERTIES: THEORY AND EXPERIMENT

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ABSTRACT

Adsorbent materials such as activated carbon and metal organic frameworks (MOFs) have received significant attention for their potential for storage of hydrogen and natural gas. Typically the adsorbent is assumed to consist of rigid slit- or cylindrical-shaped pores. Recent experimental adsorption measurements, however, suggest significant mechanical response breathing of the adsorbent in the presence of an adsorbate. In this thesis, I develop theoretical and computational models which predict high adsorbate densities in narrow carbon pores which give rise to a strong pressure on pore walls. I then present predictions of the mechanical response of the solid to this pressure, and the effect of this response on adsorption isotherms. Neutron scattering measurements of this mechanical response as well as the diffusion of the adsorbate in the breathing Graphene Oxide Framework (GOF) material is presented. In addition, calculations are presented which support a route toward enhancing the binding energy in carbonaceous adsorbates through boron doping via decaborane adsorption and subsequent decomposition.
Chapter 1

Introduction

The fear of “peak oil” and global warming has lead to substantial interest in alternative fuel technologies such as bio-diesel, non-fossil natural gas and hydrogen. Hydrogen and natural gas specifically are sought after as an alternative fuel source due to their abundance, energy density (by mass), and low emissions during burning. There are unfortunately major challenges which need to be addressed [1] before large-scale adoption of alternative fuel technologies for vehicular use. One of the more significant problems associated with using hydrogen and natural gas as a fuel source are the large volumes in which they occupy at ambient temperatures and pressures. Specifically, for methane or hydrogen stored at STP to deliver the equivalent energy of a standard vehicle tank of gas (60 liters) would require a 151,000 and 49,000 liter tank, respectively. Needless to say, tanks of this size would significantly reduce a vehicle’s cargo capacity and passenger comfort. Compressing the gas and/or cooling to very low temperatures can reduce the required tank size necessary. However, the added cost, weight, and low storage capabilities are prohibitive to the use in powering
vehicles [2, 3].

To address the issue of large required volumes, adsorbent materials are currently being studied in order to reduce the amount of pressure required to compress the gas and increase the feasible operating temperature. Although the adsorbent materials themselves take up space in the vehicle’s tank, van der Waals interactions attract the hydrogen and natural gas molecules to the adsorbent, becoming physically adsorbed (“physisorbed”) on the surface of the adsorbent and aggregate at densities much higher than without the presence of the adsorbent. In fact, densities exceeding twice the liquid density of hydrogen have been observed [4] in activated carbon samples. The performance of an adsorbent material is judged by the difference in the amount of gas stored in the presence of the adsorbent and the amount of gas stored in an equivalent volume with no adsorbent material, a quantity known as excess adsorption. Because it is also desirable for the adsorbent material to be lightweight, the excess adsorption is typically normalized by the mass of the adsorbent material. Thus, one seeks adsorbent materials which are both low weight and capable of storing large densities of gas. There are essentially two routes to high adsorption rates: large surface area (more binding sites) and high binding energy (strong binding at each site). The Alliance for Collaborative Research in Alternative Fuel Technology (ALLCRAFT) [5] at the University of Missouri have made significant advancements in hydrogen storage in activated carbon using these routes.

Activated carbon is an inexpensive and lightweight adsorbent material which is being studied for the storage of hydrogen and natural gas [4–11]. Abundant resources such as corn cobs, wood, coal, and other carbonaceous materials are “activated” to create a highly porous solid, composed of flakes of graphene-like structures with a
large specific surface area. The activation process involves heating the corn cob to 400-800°C to remove most of the volatile matter and leave a charred substance of 95-97% carbon. The char is then soaked in potassium hydroxide to eliminate most of the remaining oxygen and hydrogen from the solid and open up previously blocked pores. This activation with potassium hydroxide has been shown to produce carbons with a surface area of up to 3000 m²/g.

Once activated, the second route to high adsorption rate (high binding energy) is pursued on the activated carbon material by substitutionally doping the carbon flakes with boron. Previous theoretical work [12–15] has shown that this substitution results in an empty pₓ orbital near the boron, enhancing the interaction with the σ orbital of the H₂ molecule. In the work of Firlej et al. [14], it was shown that maximum deliverability of hydrogen is achievable through a 10% doping with boron. This previous work, however, neglected to study the feasibility of performing such substitutions. To dope the carbons, the ALL-CRAFT group uses decaborane (B₁₀H₁₄), which is deposited on the surface as a vapor, to transfer boron to the sample. The B₁₀H₁₄ is then heated above its decomposition temperature, depositing a film of boron atoms or boron hydrides. Substitution of carbon with a boron is then attempted through pyrolysis and high temperature annealing. Although current Fourier Transform Infrared Spectroscopy (FT-IR) and X-ray Photoemission Spectroscopy (XPS) [16] analysis gives good indication that boron has been incorporated into the carbon structure, the evidence that carbon substitution occurs is inconclusive; and the boron may simply be bound to the surface of the intact carbon.

Another route to producing materials with high binding energy is to synthesize the materials to have a majority of their pore volume in pores which are narrow (that
is, approximately the size of the adsorbate molecule). In narrow pores, the interaction potential due to each pore wall overlap to produce a deep potential well. The depth of the potential well is then sufficient to overcome the steric interactions between neighboring adsorbate molecules, allowing large densities in pores of this size. Since the van der Waals interaction potential decays with $1/R^6$, when pores are much larger than the size of the adsorbate molecule, the interaction potential is nearly zero and the density of the gas in these pores will be that of the bulk. As such, large pores do not contribute to the excess adsorption so that well-performing adsorbent materials must have only a minimum portion of their pore volume in the large pore regime.

To this end, adsorbent materials are characterized by two main methods. Both gravimetric and volumetric adsorption isotherms of the gas of interest are measured, and from these the binding energy can be calculated through fitting to appropriate models. Sub-critical $N_2$ isotherms are used to determine the distribution of pore sizes and total pore volumes of the materials. Each of these measurements assumes the adsorbent structure is rigid and remains static during the loading of adsorbate materials. Although Newton’s third law tells us that the force which the adsorbent wall applies on the adsorbate will come with an equal force on the adsorbent wall by the adsorbate, this static-adsorbent assumption is not entirely unreasonable due to the significantly larger mass of the solid compared to the adsorbed gas. However, with the high densities of adsorbate in the best performing adsorbent materials it is entirely possible for adsorption to put a non-negligible stress on the solid structure, leading to structural changes during adsorption. The effect of adsorption on the structure of the adsorbate is important to elucidate in order to revise the models of adsorption isotherms, binding energies, and pore size distributions.
In the following chapters, we will discuss the calculations and experiments addressing the issues of boron solubility in carbon and adsorbate-induced structural changes. Chapter 2 focuses on \textit{ab initio} calculations of B$_{10}$H$_{14}$ adsorption on carbon, B$_{10}$H$_{14}$ decomposition, and the energetics of boron doping. In Chapter 3, a model is developed for the structural response of a carbon structure due to H$_2$ adsorption. In Chapter 4, we discuss neutron and x-ray diffraction measurements of structural changes of a carbon adsorbent known as a Graphene Oxide Framework (GOF). In chapter 5, quasi-elastic neutron scattering measurements of the diffusion of H$_2$ in a GOF are discussed.

Figure 1.1 lists the current status of carbon-based adsorbents for the storage of hydrogen being developed by ALL-CRAFT. The volumetric adsorption is the mass of H$_2$ per \textit{volume} of carbon, while the gravimetric adsorption is the mass of H$_2$ per \textit{mass} of carbon. For a given temperature and pressure, the ALL-CRAFT sample known as 3K is the best performing sample, with an enhancement in volumetric storage capacity through boron doping. The sample HS;0B is an interesting sample; for, while it has a surface area less than a quarter of that of 3K, it performs just as well in terms of volumetric storage capacity. Discussions of activated carbon samples in this thesis will center on these two samples.
Figure 1.1: Current status of hydrogen storage capabilities of activated carbon samples developed through ALL-CRAFT, as reported in Ref. [8].
Chapter 2

Boron-doping Activated Carbon

2.1 INTRODUCTION

One potential pathway to achieving higher hydrogen binding energies and thus achieving a higher storage capacity [12] in carbonaceous materials is by substituting a fraction of the carbon atoms in the carbon matrix with boron (up to 1:10 B:C mass ratio) [17, 18]. Substitution of a carbon with a boron atom results in an electron deficiency (empty $p_z$ orbital) in the carbon matrix which increases the depth of the adsorbent - adsorbate interaction potential [19, 20]. Firlej [12] et al. have shown, through \textit{ab initio} calculations and Monte Carlo simulations, an increase in hydrogen heat of adsorption from 4-8 kJ/mol to 10-13.5 kJ/mol, leading to a potential storage capacity of 5 wt.% at room temperature and 100 bar, i.e., roughly double that of undoped activated carbon.

Boron-doped single walled carbon nanotubes [21] and boron-substituted carbon
scaffolds [22] have been previously fabricated. However, these materials have very low specific surface areas; 400 m$^2$/g in the case of carbon nanotubes and 900 m$^2$/g in the case of boron substituted carbon scaffolds. Although these materials have been shown to increase the hydrogen binding energy, they still have storage capacities much lower than the 2015 DOE target of 4.5 wt.% [23] due to their low surface areas.

A method of boron doping high-surface-area activated carbon is sought to provide both a strong binding and a large number of binding sites. Typical doping mechanisms occur during carbon synthesis [24–26] through an arc discharge process. By arcing graphite electrodes containing boron nitrate in inert atmospheres, boron is incorporated simultaneously with graphitization of the carbon nanotubes [26]. Doping during synthesis, however, seems to limit the surface area of the resulting carbon structure. Boron doping has also been achieved through deposition of various boron containing compounds through chemical vapor deposition. Boron trichloride (BCl$_3$) and diborane (B$_2$H$_6$) have successfully been used to dope materials with boron [27, 28]. However, because the amount of boron transferred to the sample per boron compound is low, a 1:10 B:C mass ratio is difficult to achieve via these boron compounds. Here we argue that incorporation of boron in a high-surface-area activated carbon is achievable through deposition of the unique boron containing compound decaborane (B$_{10}$H$_{14}$).

The benefits of using decaborane are the large number of borons in the compound and ease of dissociation. For this process, the decaborane is deposited on the sample as a vapor, followed by pyrolysis and high temperature annealing which is used to initiate the boron substitution. A typical doping process would begin with solid decaborane and the carbon sample in different containers at room temperature, separated by
a valve. The solid decaborane would then be heated to sublimation and the valve opened to allow the decaborane to enter the container with the carbon sample. To ensure efficient transport of boron into the sample, it is beneficial to perform this step at a temperature below the decomposition temperature. We are therefore interested in a range of deposition temperatures from 100 °C to below 300 °C.

In this chapter, we provide calculations in support of the following arguments:

1. Decaborane is strongly adsorbed on carbon surface. This strong adsorption provides a route to decaborane deposition without significant clogging of narrow pores;

2. Incorporation of boron in defected carbon structures is energetically favorable;

3. Replacing a carbon atom by a boron atom is only energetically favorable with an anionic boron;

4. Anionic-boron doped carbon structures produce a substantial increase in H₂ binding energy compared with undoped structures. This increase is primarily due to electrostatics.

### 2.2 COMPUTATIONAL METHOD

To determine the interaction energy between the adsorbate molecule (e.g. H₂, B₁₀H₁₄) and the adsorbent substrate for our microscopic system, we must solve the Schrödinger equation,

\[ H\Psi = E\Psi, \]  \quad (2.1)
where $E$ is the energy of the system, $\Psi$ is the wavefunction of the system, and $H$ is the Hamiltonian,

$$H = -\sum_i \frac{\hbar^2}{2m_e} \nabla^2_i - \sum_k \frac{\hbar^2}{2m_k} \nabla^2_k - \sum_{i<k} \frac{e^2 Z_k}{r_{ik}} + \sum_{i<j} \frac{e^2}{r_{ij}} + \sum_{k<l} \frac{e^2 Z_k Z_l}{r_{kl}}.$$  \hspace{1cm} (2.2)

In equation 2.2, $i$ and $j$ run over the system’s electrons, while $k$ and $l$ run over the system’s nuclei. $m_k$ is the mass of the $k$th nucleus, $m_e$ is the mass of an electron, $Z_k$ is the atomic number of the $k$th nucleus, $e$ is the charge on an electron, and $r_{ab}$ is the distance between particle $a$ and particle $b$. The first two terms are the kinetic energies of the electrons and nuclei, respectively. The last three terms are the potential energies due to the electron-nuclei, electron-electron and nuclei-nuclei interactions, respectively.

In equation 2.1, there are many eigenfunctions $\Psi_i$ for which there is an eigenvalue $E_i$ which solves the equation. We can build a complete eigensystem in which each of the eigenfunctions are orthonormal, i.e.

$$\int \Psi_i \Psi_j d\mathbf{r} = \delta_{ij}. \hspace{1cm} (2.3)$$

If we take equation 2.1 for one particular $\Psi_i$, multiply by $\Psi_j$ on the left, and integrate over all space we obtain

$$\int \Psi_j H \Psi_i d\mathbf{r} = E_i \delta_{ij}. \hspace{1cm} (2.4)$$

Equation 2.4 provides a route to determine molecular energies: once we have the system’s wavefunction, we simply apply equation 2.4 and we obtain the molecular energy.
Before we obtain the system’s wave function, we can apply a few approximations to the Hamiltonian. Because the mass of a nucleus is on the order of $10^3$ times the mass of an electron, under typical conditions the nuclei move much more slowly than the electrons. We can therefore decouple the motions of the nuclei and the electrons, and compute the electronic energies assuming fixed nuclear positions. This leaves the second term in equation 2.2 independent of the electrons, correlation in the third term is eliminated, and the fifth term is simply a constant for a given molecular geometry. We can therefore define the electronic Hamiltonian,

$$H = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_i \sum_k \frac{e^2 Z_k}{r_{ik}} + \sum_{i<j} \frac{e^2}{r_{ij}},$$

(2.5)

and the nuclear potential,

$$V_N = \sum_{k<l} \frac{e^2 Z_k Z_l}{r_{kl}}.$$  

(2.6)

The electronic Schrödinger equation is then

$$(H_{el} + V_N)\Psi_{el} = E_{el}\Psi_{el}.$$  

(2.7)

Since $V_N$ is constant for a given set of nuclear coordinates, and wave functions are invariant to constant terms in a Hamiltonian, we need only solve equation 2.7 without $V_N$.

At this point, we have a prescription (equation 2.4) for the molecular energy given the system’s wavefunction. We must still determine the system’s wave function. It can be shown that the electronic Hamiltonian, equation 2.5, obeys the variational principle. That is, for a given trial wave function, the energy from equation 2.4 is
greater than or equal to the true \textit{ground-state} energy. We can therefore determine good approximations to the ground-state wave function by guessing a trial wave function and applying the calculus of variations to find the wave function which minimizes the molecular energy.

One method of choosing a trial wave function was outlined by Hartree \cite{29}, in which the multi-electron wave function is built up as a product of single-electron wave functions, which is termed the “Hartree Product”,

\[ \Psi_{HP} = \psi_1 \psi_2 \cdots \psi_N. \] (2.8)

For each single-electron wave function, equation 2.7 is solved, with the last term replaced by the interelectronic potential of the form

\[ V_{ij} = \sum_{j \neq i} \int \frac{\rho_j}{r_{ij}} \, dr, \] (2.9)

where \( \rho_j \) is the probability density associated with electron \( j \). That is, the nuclei are treated as points while the neighboring electrons are treated as wave functions with a spread out charge. The equation 2.7 is then solved for each electron in the system in a self-consistent manner, until the energy converges. In this way, the interaction between one electron and the rest of electrons are approximated by the interaction between one electron and an average potential due to the rest of the electrons. Because the Hartree hamiltonian is separable, the energy eigenvalue of the multi-electron \( \Psi_{HP} \) is simply the sum of the one-electron eigenvalues.

The Hartree product lacks two physically relevant features of multielectron wave-functions. First, the Pauli exclusion principle tells us that the wavefunction must
be zero when any two single electron wavefunctions in the product with the same quantum numbers share the same physical space coordinates. Secondly, a Fermionic wavefunction must be antisymmetric. That is, the wavefunction must switch sign when two electrons are exchanged. Each of these issues can be resolved by expressing the multielectron wavefunction as a determinant, owing to the following properties of determinates:

- The determinant is antisymmetric to the exchange of two rows (each row determines a particle).
- The determinant is zero if there are two identical columns. This satisfies Pauli exclusion (the columns represent different orbitals.)

\[
\Psi_{SD} = \frac{1}{\sqrt{n!}} \begin{vmatrix} 
\chi_1(1) & \chi_2(1) & \cdots & \chi_n(1) \\
\chi_1(2) & \chi_2(2) & \cdots & \chi_n(2) \\
\vdots & \vdots & \ddots & \vdots \\
\chi_1(N) & \chi_2(N) & \cdots & \chi_n(N) 
\end{vmatrix},
\]

where \( N \) is the total number of electrons and \( \chi \) is now the spin-orbital,

\[ \chi = \psi \alpha, \]

where \( \alpha \) is the spin state of the electron.

The single-electron wavefunctions which form the Slater determinant are described mathematically by a “basis set”, a linear combination of basis functions. Physical wavefunctions have two properties which we desire of our basis functions: a cusp at the origin and a decay like \( \exp^{-r} \). One such basis function is the Slater-type orbital
\[
\psi(r, \theta, \phi, \zeta, n, l, m) = \frac{(2\zeta)^{n+1/2}}{[(2n)!]^{1/2}} r^{n-1/2} \exp^{-\zeta r} Y_l^m(\theta, \phi),
\]

(2.12)

where \( \zeta \) is an exponent depending on atomic number, \( n \) is the principle quantum number for the orbital and \( Y_l^m(\theta, \phi) \) is the spherical harmonic function, which depends on the angular momentum operators \( m \) and \( l \). Although STOs are intuitive in terms physical representation, their mathematical form can be unwieldy when the number of basis functions are large. Namely, STOs are not analytically integrable, and therefore require many computationally costly numerical integrations for a given calculation. Rather, we can get close to the same physical representation afforded by STOs, with analytically integrable functions, by building linear combinations of Gaussian Type Orbitals (GTOs):

\[
\phi(x, y, z; \alpha, i, j, k) = \left( \frac{2\alpha}{\pi} \right)^{3/4} \left[ \frac{(8\alpha)^{i+j+k}i!j!k!}{(2i)!(2j)!(2k)!} \right] \frac{1}{2} x^i y^j z^k \exp^{-\alpha(x^2+y^2+z^2)}
\]

(2.13)

\[
\psi(x, y, z; \alpha, i, j, k) = \sum_{a=1}^{M} c_a \phi(x, y, z; \alpha, i, j, k).
\]

(2.14)

Here the non-negative integers \( i, j \) and \( k \) are indices which describe the nature of the orbital. When all three indices are zero, the GTO has spherical symmetry and is termed an s-orbital. When the sum of the indices is one, the GTO is extended in space along \( x, y \) or \( z \) direction when the non-zero index is \( i, j \) or \( k \) respectively. This orbital is termed a p-orbital. When the sum of the indices is two, the GTO is a d-orbital. There are six such orbitals with index sum equal to two, corresponding to Cartesian prefactors \( x^2, y^2, z^2, xy, yz \) and \( xz \). Note that the main difference between STOs and GTOs is that the former has an \( e^{-\zeta r} \) term while the latter has an \( e^{-\alpha r^2} \) term.
The sum of the GTOs, each with different exponents $\alpha$, give an approximation to an STO of an exponent $\zeta$. STO orbitals are termed “single-$\zeta$” orbitals. Since most of chemistry occurs in the valence electrons, it is desirable for additional flexibility in the wavefunction to be afforded to the valence electrons, and therefore the valence electron orbitals are described by multiple STOs each with a different $\zeta$. Orbitals with multiple STOs formed by different exponents $\zeta$ are known as Pople split-valence basis sets. The nomenclature of Pople split-valence basis sets indicate the number of GTOs used to form each STO. For example, the 6-31g basis set has an STO for the core electrons formed by 6 GTOs, another STO for the valence electrons formed by 3 GTOs and one more STO with a different exponent $\zeta$ formed by 1 GTO. The radial dependence of the GTOs for hydrogen in the 6-31g basis set are shown in Figure 2.2.

Additional flexibility in orbital description is given by so-called polarization functions. These additional basis functions are formed by GTOs in the same fashion as before, with GTOs of one orbital principle quantum number higher than the valence electrons for the atom. The nomenclature for polarization functions the Pople split-valence basis set is shown, as an example, in the 6-31g(3d,3p) basis set. Here, in addition to the basis functions for 6-31g, two additional polarization functions are provided, formed by three d-type GTOs and three p-type GTOs.

Since adsorption interactions are primarily due to dispersion terms, the calculation of binding energies must properly include electron correlation energies. Møller-Plesset (MP$n$) and coupled cluster methods are suitable methods [30] for the job. Second-order Møller-Plesset (MP2) [31] provides adequate accuracy for this work (recoving 85% of the electron correlation energy) and is significantly less computationally in-
Figure 2.1: Radial dependence of the GTOs forming the valence orbital for hydrogen in the 6-31g basis set. The three unshaded functions sum to an approximate STO with one $\zeta$, while the shaded GTO approximates another STO with a different $\zeta$. 
tensive than coupled cluster methods. For this reason, the decaborane-carbon and decaborane-decaborane interaction potentials were calculated using MP2 theory using the Gaussian09 [32] software package. Calculations were done using a Pople split-valence double-zeta 6-31g(d,p) basis set, along with correlation consistent polarized valence-only double zeta (CC-pvdz) and triple zeta (CC-pvtz) basis sets. While the Pople basis sets are relatively inexpensive computationally, correlation consistent (CC) basis sets are computationally expensive but are designed to converge to the complete (infinite) basis set. Therefore, broad scans of the potential energy were done using the 6-31g(d,p) basis set while binding energies and vibrational frequencies were computed using a CC-pvtz basis set.

The graphene structure was modeled using a coronene (C\textsubscript{24}H\textsubscript{12}) molecule. Minimal energy coronene and decaborane nuclear structures were calculated in MP2/6-31g(d,p). During adsorption calculations, each of the two nuclear structures were held fixed and an energy scan was performed with respect to the distance between their respective center of masses (see Figure 2.3). For doping energetics calculations the effect of the limited size effects of the model carbon structures were studied by performing the calculations on increasingly large carbon structures, pyrene (C\textsubscript{16}H\textsubscript{10}), coronene (C\textsubscript{24}H\textsubscript{12}) and ovalene (C\textsubscript{32}H\textsubscript{14}) (see Figure 2.8). For the hydrogen adsorption calculations, the minimal energy doped and undoped carbons were used as well as a minimal energy H\textsubscript{2} structure, determined far from the carbon structure. As with the decaborane adsorption calculations, only the intermolecular center of mass distances were scanned, while the intramolecular structures were preserved.
Decaborane (B\textsubscript{10}H\textsubscript{14}) at room temperature is a white crystalline solid with a very low vapor pressure (on the order of 10\textsuperscript{-3} bar). The vapor pressure can be raised by increasing the temperature, up to the decomposition temperature, \( \sim 300 ^\circ C \). The triple point of decaborane occurs at 98.37\(^\circ\)C and 0.0243 bar. Furukawa [33] provided a liquid-gas coexistence curve and Miller [34] provided a solid-gas coexistence curve giving a phase diagram as shown in Figure 2.2. The low vaporization pressure at room temperature is a potential problem for efficient deposition in narrow pore spaces. Since liquid decaborane has the potential to clog pores [35], we must also ensure that the deposition is done at a pressure below the vapor pressure. Ignoring adsorption of decaborane on the carbon, the condition for the ability of decaborane to be entirely in the gas phase and contained in the pore space is given by the following condition on the vapor pressure of decaborane \( p_{\text{vapor}} \):

\[
p_{\text{vapor}}(T_f) > \chi_{DB} \frac{\rho_{\text{bulk}} \rho_s - \rho_{\text{bulk}}}{M_{DB}} RT_i + \frac{p_i T_f}{T_i} \tag{2.15}
\]

where \( T_i \) and \( T_f \) are the temperatures before and after doping, respectively, \( \chi_{DB} \) and \( M_{DB} \) are decaborane:carbon sample mass ratio and molar mass of decaborane, respectively. \( \rho_{\text{bulk}} \) is the density of bulk decaborane vapor and \( \rho_s \) is the carbon skeleton density. Because of the small vapor pressure of decaborane below its decomposition temperature, this limits \( \chi_{DB} \) and ultimately the amount of boron which can be delivered into the carbon in a given doping cycle. In order to determine the effect of adsorption on the amount of decaborane which can be delivered to the carbon sample we must model the adsorption isotherm. While there exist many isotherms with which
Figure 2.2: Decaborane phase diagram from data fits from Furukawa [33] and Miller [34]. Doping procedures begin with solid-phase decaborane which is then heated at low pressure to sublimation. It is important during the sublimation stage for the decaborane to remain under the liquid-gas coexistence curve. Once adsorbed, the decaborane is heated above its decomposition temperature.
Figure 2.3: Decaborane adsorbed on coronene (left). The MP2 energy versus the height of the decaborane molecule above the plane of the coronene molecule was calculated to determine the potential energy and extract parameters for the Langmuir isotherm. The in-plane vibrational frequency was taken from values of the decaborane-decaborane interaction potential, which was calculated by scanning over R as shown on the right.

to model the adsorption of decaborane on carbon, each relies on a determination of the binding energy. Low-pressure isotherms include Freidlich [36] and Langmuir [37]. The strong binding energy and large footprint of the decaborane model suggest saturation will occur at low pressure and the Freidlich isotherms will not be valid. Here we model the adsorption of decaborane using the theory of Langmuir [37]:

$$\theta = \frac{p_{\text{vapor}} \chi_{DB}}{1 + p_{\text{vapor}} \chi_{DB}}$$ \hspace{1cm} (2.16)

The Langmuir constant assuming localized adsorption is given by:

$$\chi_{DB} = \frac{e^{E_b/kT}}{\prod_{i=1}^{3} \sinh \left( \frac{h \nu_i}{2kT} \right)} \sqrt{\frac{\hbar^6}{(8\pi M_{DB})^3(kT)^5}}$$ \hspace{1cm} (2.17)

where $E_b$ is the binding energy of decaborane on coronene and $\nu_i$ are the frequencies of vibration in the three degrees of freedom (one out-of-plane and two in-plane degrees of freedom). The coronene-decaborane interaction potential is shown in Figure 2.4. The decaborane-decaborane interaction potential is shown in Figure 2.5. The binding
Figure 2.4: Decaborane - coronene interaction potential, with 6-31g(d,p) and CC-PVTZ basis sets as a function of the height of the decaborane molecule above the coronene plane, as measured from their respective centers of mass.

Energy $E_b$ is taken to be the minimum of the potential energy surface. The out-of-plane vibrational frequency was calculated from the potential energy scan by

$$\nu_z = \frac{1}{2\pi} \sqrt{\frac{\kappa_z}{\mu_{DB-Cor}}}$$  \hspace{1cm} (2.18)

where $\kappa$ is the curvature at position of minimum energy of $U_{DB-Cor}(z)$, the potential energy and $\mu_{DB-Cor}$ is the reduced mass of the decaborane-coronene system. Likewise, the in-plane vibrational frequencies are given by

$$\nu_x = \nu_y = \frac{1}{2\pi} \sqrt{\frac{\kappa_{xy}}{\mu_{DB-DB}}}$$  \hspace{1cm} (2.19)
Figure 2.5: Decaborane-decaborane potential energy scan with 6-31g(d,p) and CC-pvdz basis sets as a function of the center of mass to center of mass displacement, measured as shown in figure 2.3.

The binding energy and vibrational frequencies corresponding to the minimal energy configuration are presented in Table 2.1.

The binding energies computed from MP2/6-31g(d,p) and MP2/CC-pvdz are quite high ($\approx 70 - 80$ kJ/mol). The relatively weak decaborane–decaborane interactions indicate that adsorption of decaborane on the carbon surface will be highly localized. The size of each localized binding site can be determined from the decaborane-decaborane potential energy scan. Since the potential minimum occurs when the center-of-mass to center-of-mass distance is $r_{DB} = 7 \, \text{Å}$, the area of a single binding site (the decaborane “footprint”) is then $\alpha = (r_{DB}/2)^2 = 12.25 \, \text{Å}^2$. The relatively low frequencies of vibration in-plane with the carbon structure indicate that the interaction is longer range than for high frequencies of vibration, and have the effect of
Table 2.1: Binding energies and vibrational frequencies determined from MP2 potential energy calculations.

<table>
<thead>
<tr>
<th>Basis Set</th>
<th>$E_B$(DB-Cor) (kJ/mol)</th>
<th>$E_B$(DB-DB) (kJ/mol)</th>
<th>$\nu_{xy}$ (THz)</th>
<th>$\nu_{z}$ (THz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6–31g(d,p)</td>
<td>71</td>
<td>9.1</td>
<td>6.6</td>
<td>12</td>
</tr>
<tr>
<td>CC-pvtz</td>
<td>84</td>
<td>9.1</td>
<td>6.6</td>
<td>11</td>
</tr>
</tbody>
</table>

increasing the effective binding strength of the decaborane molecule.

Figure 2.6 shows the Langmuir adsorption isotherms, at $T = 100^\circ$C, $150^\circ$C, and $200^\circ$C, corresponding to the adsorption parameters in Table 2.1. For each isotherm there is a limit to the amount of decaborane which can be transferred to the sample while the pressure remains under the vapor pressure of decaborane. The red line indicates the coverage at the vapor pressure of decaborane for a given isotherm. Thus, for a given isotherm, we can keep the decaborane in the gas phase by doping only up to pressures left of the red line. The amount of decaborane on the surface of the carbon is limited to levels below the red line. The B:C weight percent ratio, assuming every boron atom from every decaborane molecule adsorbed on the sample becomes incorporated into the sample, is given on the right axis of the plot.

For a 10% coverage of boron:carbon, a decaborane coverage ratio $\sim 0.1 \frac{g_{DB}}{g_{C}}$ ratio is required. This is indicated by the horizontal dashed line in Figure 2.6. The high boron:carbon ratio is achievable for doping temperatures in which the isotherm crosses $0.1 \frac{g_{DB}}{g_{C}}$ before reaching the decaborane vapor pressure. As can be seen from the figure, this is easily manageable for all temperatures on the range of $100^\circ$C to $250^\circ$C.
Figure 2.6: Langmuir adsorption Isotherms at 100, 150, and 200 °C. The red line indicates the coverage at the vapor pressure of decaborane corresponding to the temperature of each isotherm. That is, adsorption isotherms for only three temperatures are shown in the plot. For intermediate temperatures, the red line depicts where that temperature’s isotherm crosses the vapor pressure at that temperature. In order for the decaborane to remain in the gas phase during adsorption, the coverage is limited to values below the red line. The right axis shows the corresponding B:C concentration, assuming all adsorbed B becomes incorporated into the sample.
2.3.1 Incorporation of boron in carbon structure

Once the decaborane is deposited onto the carbon surface, the sample will be annealed to a temperature well above the decaborane decomposition temperature (≈ 600 °C). During this annealing process, hydrogen gas will be produced, raising the vapor pressure in the cell. The remaining boron can remain adsorbed on the carbon surface, replace a carbon in the structure, or fill in a defected carbon surface. In order to determine the carbon sample’s ability to be doped to up to a 1:10 B:C ratio, we must understand the energetics of each scenario.

The earlier work of Firlej did not consider the feasibility of doping the carbon structure, but simply assumed such a structure would reasonably exist. There does exist, however, empirical evidence of boron doped carbon in the literature. Figure 2.7 shows various boron carbon materials reported in the literature. Lowell [38] in 1967 measured a maximum solubility of boron in carbon of 2.35 at.% at 2350 °C through pyrolysis with boron carbide. However, chemical vapor deposition methods have since produced boron-rich structures (BC₂, B₄C, B₈C, B₅₀C, B₅₀C₂, B₄₈C₃, B₅₁C, B₄₉C₃) [39–41]. Further, more moderate at.% structures have been synthesized; BC₃ has recently been produced through pyrolysis of benzene with BCl₃ at 800 °C [42] and BC₆ [43], BₓC₁₋ₓ for x < 0.25 and BC₅ [44,45] through CVD. Delhaës et. al [45] showed that boron-carbon mixtures dissociated into a biphasic mixture of carbon and B₄C above 1750 °C, as indicted by NMR which indicated the formation of B-B bonds.

Since boron-doped carbon structures have been produced through sub-1750 °C pyrolysis with concentrations higher than Lowell’s “solubility-limit”, it seems this limit is not applicable for lower pyrolysis temperatures, below the temperature of the biphasic phase formation temperature. Figure 2.7 also shows boron concentrations
of All-Craft synthesized materials as well as the concentrations modeled in the \textit{ab-initio} calculations in this section.

The original boron-doping calculations of Firlej used a pyrene molecule as a base carbon structure. With a single substitution of a carbon in the pyrene molecule with a boron atom, this structure corresponds to roughly 6.7 at.%. Larger base carbon structures coronene and ovalene with a single-doping correspond to 4.3 at.% and 3.2 at.%, respectively (Figure 2.8). We take as a reference energy the energy of a pristine carbon structure with a boron atom very far away, such that the interaction energy of the boron and carbon structure is negligible. The reaction process is imagined to be the boron atom approaching the carbon structure, pushing a carbon atom from its position and incorporating itself into the carbon structure, and the carbon atom moving very far away. During the process in which the boron incorporates itself into the carbon structure, the molecule will respond in a manner which minimizes its total energy.

The doping energy is then defined as:

\[
E_{\text{Doping}} = (E_{\text{BDopedCarbon}} + E_C) - (E_{\text{PrisineCarbon}} + E_B).
\]  

When comparing the MP2 energy of two systems as in Equation 2.20, large errors can arise when comparing two non-isoelectronic systems [30]. We therefore use the experimentally obtained ionization energies and e\(^-\) affinities when comparing non-isoelectronic systems. For the anionic boron-doped structure, the doping energy is

\[
E_{\text{Doping}}^- = (E_{\text{BDopedCarbon}}^- + E_C) - (E_{\text{PrisineCarbon}} + E_{B^-}) + E_{\text{B ionization}}.
\]
Figure 2.7: Reported boron solubility limits in carbon from the literature [4,5,38–45], as well as boron concentrations for boron-doped pyrene, coronene and ovalene. The boron solubility limit reported by Lowell was measured at very high processing temperatures which have been shown to produce biphasic mixtures, limiting boron solubility. More recently, higher boron concentrations have been produced via chemical vapor deposition.
Figure 2.8: Boron-doped pyrene, coronene and ovalene structures were studied. The structures shown are the MP2-energy optimized structures. The interactions with hydrogen were calculated by scanning the hydrogen center of mass displacement above the carbon structure plane. The low energy configuration of the hydrogen was found to always be with the axis of the hydrogen molecule perpendicular to the plane of the carbon structure.
Figure 2.9: The doping energy for anionic, cationic and neutral boron-doped pyrene, coronene and Ovalene. The doping energy is prohibitive for reactions involving neutral or cationic boron. The only feasible product of a boron incorporation reaction is a negatively charged boron-carbon structure. For small carbon fragments (pyrene), this reaction is endothermic while for larger more realistic fragments (coronene, ovalene) the reaction is slightly exothermic.

where \( E_{B\text{ ionization}} = 803 \text{ kJ/mol} \) is the boron ionization energy of boron. Likewise, the cationic doping energy is given by

\[
E_{\text{Doping}}^{+} = (E_{B\text{DopedCarbon}}^{+} + E_{C}) - (E_{\text{PristineCarbon}} + E_{B^{+}}) + E_{B\text{ ionization}} + E_{\text{Carbon e-affinity}}.
\]

(2.22)

where \( E_{B\text{ e-affinity}} = -27 \text{ kJ/mol} \) is the experimentally obtained electron affinity of boron [46] and \( E_{\text{Carbon e-affinity}} \) is the carbon structure’s electron affinity.

Figure 2.9 shows the relative energies of undoped, anionic-doped and cationic-
Table 2.2: The doping energy for anionic, cationic and neutral boron-doped pyrene, coronene and ovalene. For each “daughter” molecular configuration, the “parent” configuration was chosen in order to attempt to compare isoelectronic systems. The reference configuration was chosen to be the neutral, undoped configuration. The energy due to changes in configuration charge were taken to be their experimental values.

doped boron doped carbon. For each of the three carbon structures studied, the doping reaction is endothermic for the neutral and cationic reactions. Further, there is no entropy change between the two systems. Therefore, a spontaneous doping reaction will not occur. For the coronene carbon structure, the energy barrier for the neutral reaction is 205 kJ/mol, with an equivalent temperature of 24,460 K, well above any reasonable pyrolysis temperature. For cationic reaction the energy barrier is 635 kJ/mol, and the probability of a replacement reaction occurring happening even less.

The doping energies are listed in Table 2.2. For the anionic reaction the energy barrier is slightly positive for the pyrene structure (32 kJ/mol, 3850K) and negative for the coronene and ovalene structures (-40 kJ/mol, 4810K). For a doping procedure at 800 °C the probability of a reaction occurring during an Arrhenius type collision for an anionic structure is 2.7%. Reactions of anionic boron with the coronene and
ovalene structures are slightly exothermic and is therefore the likely mechanism for boron doping through carbon replacement. These calculations show the only feasible boron-doped carbon structure produced through the replacement of a carbon atom is one which comes with a negative charge.

Since the potassium hydroxide activation process produces a highly disordered and anisotropic material, it is reasonable to expect a significant number of defects in the activated carbon samples. For a coronene molecule, each type of reaction (neutral, cationic and anionic) is highly exothermic, with activation energies of -917 kJ/mol, -327 kJ/mol and -1561 kJ/mol, respectively. If a defect exists in the carbon structure already, the structure will readily accept a boron atom regardless of charge on the boron.

2.4 RESULTS: HYDROGEN INTERACTIONS WITH DOPED AND UNDOPED STRUCTURES

The interaction of hydrogen with the (charged and neutral) doped and undoped structures in the previous section was calculated in a similar fashion as the interaction of decaborane with coronene. That is, the interaction energy, as a function of center-of-mass to center-of-mass distance, is calculated as

\[ E_{Ads} = (E_{H_2}(R = \infty) + E_{Adsorbent}) - (E_{Adsorbent} + E_{H_2}(R)). \]  (2.23)

where \( E_{H_2}(R = \infty) \) is the energy of a hydrogen molecule, \( E_{Adsorbent} \) is the energy of the carbon structure and \( (E_{Adsorbent} + E_{H_2}(R)) \) is the energy of a hydrogen molecule.
Figure 2.10: Hydrogen interaction energy, as a function of center-of-mass height above the plane of the carbon structure, for coronene, boron-doped coronene, cationic boron-doped coronene and anionic boron-doped coronene.

at a distance R from the carbon structure. The interaction energy (Figure 2.10) shows a significant enhancement (nearly 2x) of the hydrogen-adsorbent interaction potential for an anionic boron-doped carbon (in this case, coronene), and virtually no differences between non-doped carbons and neutral or cationic B-doped variants.

Anionic boron-doped pyrene has the largest binding energy ($\approx 7.5$ kJ/mol) of carbon structures studied here. For both of the larger structures, the binding energy is $\approx 7.0$ kJ/mol (Figure 2.11). This indicates that the carbons with large surface area will retain such strong binding sites. Further, the longer range of interaction for anionic doped systems may lead to significant potential overlap in wider pores, thus enhancing storage capacity.

The enhancement of the interaction energy is due in large part to the static charge distribution of the boron doped carbon material. Figure 2.12 shows a cross section of the electric field produced by the neutral, cationic-doped, anionic-doped and un-
doped coronene structure. The equilibrium position of the hydrogen adsorbed on the surface is \( R = 3.2\,\text{Å} \). The electric field produced by the charge distribution for each charge configuration other than the anionic-doped structure decays significantly by this distance. For the anionic structure, the electric field decays only slightly up to approximately 6 Å. The small decay at distances comparable to the size of the carbon structure is consistent with a the charge distribution of uniformly charged disk. On the other hand for the cationic structure the significant decay of the electric field at small distances is consistent with a point charge.

It should be noted that the increase in binding energy for the undoped pyrene structure reported in the earlier work has not been reproduced here. Because in the earlier work the nuclear positions of the outermost carbons in the pyrene structures were not optimized, it is likely that the increase in binding energy reported was due to the fact that the structure was energetically frustrated, and the energy with the hydrogen adsorbed was not calculated with the true MP2 ground state of the system. In the current work we calculated the energy of each system using completely optimized nuclear positions and studied larger carbon systems to model the systems as realistically as possible. Further, the size of the basis sets used in this work were larger than those used in the earlier work, which typically improves the accuracy of calculations.

The calculations of decaborane adsorption reported in this chapter can be verified by monitoring the pressure of the decaborane during the doping process. The calculations predict the carbon adsorbent will readily adsorb a significant amount of the decaborane, resulting in decaborane pressures less than a tenth of a bar. The doping energetics calculations reported in this chapter can be experimentally verified
Figure 2.11: Hydrogen interaction potential, as a function of center-of-mass height above the plane of the carbon structure, for pyrene, coronene, ovalene, and their anionic counterparts.

through measurements of the chemical composition (e.g. via XPS) of the carbon structure after doping. The hydrogen binding energies can be experimentally verified through analysis of adsorption isotherms.
Figure 2.12: Cross-section of the electric field produced by the charge distribution for the neutral (a), anionic (b), cationic (c) boron-doped structures as well as the undoped structure. The vertical axis represents distance along a line bisecting the coronene molecule, such that the two halves of the molecule are into and out of the page. The horizontal axis represents distance from the coronene plane. The red line indicates the position of the boron, or the replaced carbon in the case of the undoped structure. The equilibrium position of the hydrogen molecule for each case is $\approx 3.2 \text{ Å}$. For each charge distribution except the anionic-doped coronene, the electric field decays significantly by $R = 3.2 \text{ Å}$. 
Chapter 3

Flexible Pore Walls in Activated Carbon

3.1 INTRODUCTION

Adsorbent materials such as activated carbon [6] and metal-organic frameworks (MOFs) [47] have received significant attention as potential low-pressure, high-capacity storage materials [1, 10]. Hydrogen and natural gas (methane) are desirable for energy storage as they result in zero (for H$_2$) or reduced (for CH$_4$) CO$_2$ emissions per unit energy when compared to gasoline [48]. However, the large volume these gases occupy at STP makes their application impractical without costly and heavy compression- or cryogenic-liquefaction systems. Adsorption into high-surface area, low-cost, low-weight materials has the potential to increase the performance of gas storage systems [48]. A significant effort has been devoted to increase the specific surface area of adsorbents [49], enhance the interaction potential between adsorbate and adsor-
bent [15], while increasing pore volumes in the nanometer scale range, where adsorp-
tion is strongest [6].

In the study of adsorption, it is typically assumed that the adsorbent material is structurally inert; its porous conformation remains unchanged by the adsorption process itself. This assumption underlies the majority of conceptual and theoretical frameworks utilized in the study of adsorbent materials. Further, experimental techniques for characterization of the material properties such as pore size distribution [50], surface area [51] and porosity [50] rely on the same assumption. The pore walls act, in this assumption, to provide a static potential energy $V(r)$, with a corre-
sponding force $-\nabla V(r)$, to the adsorbate molecules. Fundamentally, Newton’s third law assures us that the pore walls will feel a force equal in magnitude and opposite in direction (i.e. $+\nabla V(r)$). The fact that this assumption is often used is not so surprising; the argument in favor of the static pore wall assumption is that the large mass of the pore wall is sufficient to absorb this force with little effect on the structure. In addition, there is likely adsorption on each side of the pore wall which would give a zero net force on the pore wall. However, the adsorption-induced deformation of wet microporous materials has been observed for over 80 years [52,53]. Capillary condensation has been shown to both expand and contract nanopores [54], depending on bulk gas pressure. Recently a number of groups have produced experimental [55] evidence as well as statistical mechanics arguments [56–58] which demonstrate sorption strains due to large hydrostatic pressures generated by confined gases. Ancilotto [59] et. al. have shown that the very large hydrostatic pressures in a slit-shaped pore are due not only to the force due to the adsorbate, but a combined effect from the adsorbate and neighboring pore wall. This pressure is strong only in the case in which there is
significant overlap of the two pore walls’ potentials, i.e. in the narrow pore regime. In pores just wide enough to allow adsorbate to enter, but narrow enough for this potential overlap to occur, the conditions which satisfy the static pore assumption are no longer valid. It is no coincidence that such narrow pore sizes are also desirable for adsorption; the overlap of the walls’ potentials give rise to large adsorbate densities which in turn provide the substantial pressure on the pore walls. As advances in processing of carbonaceous adsorbents produce materials with larger and larger fractions of the total pore volume in the narrow pore regime, it is increasingly important to consider the structural response of adsorption in carbonaceous materials.

Calculated adsorption isotherms from Grand Canonical Monte Carlo (GCMC) simulations of hydrogen adsorbed in an infinite slit-pore of width varying with pressure compared to simulations performed with fixed width are shown in Figure 3.1 (top). For a comparison, the measured isotherms for ALL-CRAFT activated carbon sample 3K and saran-based carbon sample HS:0B are shown (bottom). Although at low pressure (up to 20 bar) the fixed-width and pressure-variant-width isotherms are nearly identical, at high pressure we notice a lack of the expected peak in the excess adsorption. A nearly linear increase is observed in the pressure-variant-width adsorption isotherm at pressures above the peak in the adsorption. This is due to the fact that as the pore is loaded with adsorbate it responds by making more room for more adsorbate. As the narrow pores expand slightly, the pore walls move into the space previously occupied by macropores. These macropores contain adsorbate at the same density as the bulk gas and do not contribute to the excess adsorption. In this way, we increase the total “beneficial” pore volume of the system while subsequently decreasing the volume of the system which contributes nothing to the excess
Figure 3.1: Hydrogen adsorption isotherm with a pressure-variant pore size (top, blue circles), in contrast to a hydrogen adsorption isotherm with constant pore size (top, black squares), calculated via Grand Canonical Monte Carlo simulations (top). The measured adsorption isotherm for sample 3K-600C (bottom, black squares), qualitatively resembles the calculated isotherm with constant pore size. The measured adsorption isotherm for sample HS:0B (bottom, blue circles) shows no peak in excess adsorption, a feature also seen in the calculated isotherm with pressure-variant pore size.
adsorption.

The calculated pressure-variant isotherm in Figure 3.1 shares features with the measured isotherm on HS;0B. While the two isotherms are quantitatively different, each has a distinguishing linear increase in the excess adsorption beyond the Henry’s law regime. In contrast, both the calculated constant-pore-size and measured 3K-600°C isotherms exhibit a peak. Comparison of the calculated and measured isotherms suggests pore expansion in the sample HS;0B.

Carbonaceous adsorbents are also typically assumed to be slit-shaped [60] with pore walls consisting of flat graphene-like sheets. Simulations of these materials typically model such pores with arbitrarily large lateral pore dimensions and pore widths. This view is, however, inconsistent with the mechanical properties of graphene. First, the Van der Waals attraction between two large, planar graphene sheets would tend to decrease the layer separation toward $H = 3.35$ Å, forming graphite. Second, stresses caused by atoms terminating the bonds on the edge of the graphene sheet have been shown to cause long range ripples [61]. Third, as the carbon materials used as adsorbents are significantly amorphous, the graphene sheets do not have such a preferred orientation suggested by the slit-pore model. As these sheets with random orientations lay over each other, inter-layer Van der Waals interactions can cause significant bending in the sheets. This effect is easily observed by High-Resolution Transmission Electron Microscopy HRTEM [62] images. Aso et. al. [62] used a combination of Temperature Programmed Oxidation (TPO), X-ray diffraction (XRD) and (HRTEM) to study the constituent sizes of polyvinyl chloride (PVC) and polyfurfuryl alcohol (PFA) based carbons. From their measurements they deduced three characteristic lengths: $L_{TPO}$, which used the C:H ratios determined through TPO and
Figure 3.2: Activated carbon pore model from Aso [62]. Although the carbon structure lengths are consistent with our model, the proposed terminating H bonds are replaced in our model by a curvature in the graphene structure itself.

model carbon structures: $L_{XRD}$, determined from powder XRD spectra using Scherrer’s Equation [63]; and $L_{TEM}$, determined through analysis of skeletonized HRTEM images (see Figure 3.2). $L_{XRD}$ provides a measurement of the planar, non-bended, regions of the carbon structure. $L_{TEM}$ provides a measurement of the overall size of each carbon sheet, including the bent regions. $L_{TPO}$ also does not distinguish between planar and bent regions, however the model carbon structures on which the analysis is based are assumed to be planar. Their proposed model was comprised of sheets of planar carbon with characteristic length $L_{XRD}$ connected, potentially out-of-plane, by other hydrogen bonds to neighboring planar carbon sheets. In this model, the total length of each structure was then $L_{TEM}$.

Schniepp [64] et. al., using the tip of an atomic force microscope to bend the edge
of a graphene sheet over on itself, determined a bending elasticity constant of $c = 1.2$ eV. Incorporation of this pore wall bending into models of carbonaceous adsorbents has shown to improve the calculation of $N_2$ adsorption isotherms required for BET analysis [65] over the slit-pore model.

In this chapter we propose a model for the bending of carbon pore walls and expand the calculations of the adsorbate-induced response of slit-shaped to curved pore walls. In Section 3.3 the general model which will be used to describe the bending of graphene in absence of an adsorbate is described, and the minimal energy pore structures in the model are solved for numerically. In Section 3.4, Molecular Dynamics simulations of the system are shown to verify the results of Section 3.3. Further, the system is studied in the presence of $H_2$. In Section 3.4.2, the molecular dynamics results are expanded via Perturbative Monte Carlo and the relative free energies of the system are calculated.

3.2 COMPUTATIONAL METHODS

3.2.1 Numerical Minimization Procedure

The unconstrained optimization problem can be stated as

$$\min \{ f(\mathbf{x}) : \mathbf{x} \in \mathbb{R}^n \},$$  \hspace{1cm} (3.1)

where $f : \mathbb{R}^n \to \mathbb{R}$ is assumed to be continuous and differentiable. The search for $\mathbf{x}_{min}$ is done through an iterative process. In the method of steepest descent, the search for a minimum starts at an arbitrary point $\mathbf{x}_0$. The choice for the direction of next step
in the iteration is chosen to be where \( f \) decreases quickest, i.e. the direction opposite the gradient with respect to \( x, \nabla f(x_0) \). The iterative procedure can be written

\[
x_{k+1} = x_k - \lambda_k \nabla f(x_k),
\]

(3.2)

where \( \lambda_k \) is the size of the step taken in the direction of steepest descent. We can optimize the step size by setting the derivative of \( f \) equal to zero:

\[
0 = \frac{d}{d\lambda_k} f(x_{k+1})
= \nabla f(x_{k+1})^T \cdot \frac{d}{d\lambda_k} x_{k+1}
= \nabla f(x_{k+1})^T \cdot \nabla f(x_k).
\]

(3.3)

That is, the step size should be chosen such that \( \nabla f(x_{k+1})^T \) and \( \nabla f(x_k) \) are orthogonal. This condition is equivalent to the search for a minimum along the line (a “line search”) given by Equation 3.2. The steepest descent with a line search algorithm, is then simply a sequence of line searches along the direction of the gradient at each new step. In the current work, the line search algorithm was done through the Newton-Ralphson method \[66\]

### 3.2.2 Molecular Dynamics Simulations

The non-bond potential used was a Lennard-Jones 12-6 potential.

\[
V_{\text{Non--bond}} = \epsilon \left[ \left( \frac{r_{\text{min}}}{r} \right)^{12} - 2 \left( \frac{r_{\text{min}}}{r} \right)^{6} \right],
\]

(3.4)
where \( \epsilon \) is the depth of the carbon-carbon interaction potential well and \( r_{\text{min}} \) is the equilibrium carbon-carbon displacement. Bond energies, \( V_{\text{Bond}} \), were assumed quadratic about the minimum bond distance

\[
V_{\text{Bond}} = K_b (b - b_0)^2. \tag{3.5}
\]

Like-wise for bond-angles, \( V_{\text{Bond-angle}} \),

\[
V_{\text{Bond-angle}} = K_\theta (\theta - \theta_0)^2. \tag{3.6}
\]

The dihedral angle potential, \( V_{\text{Dihedral}} \), is given by

\[
V_{\text{Dihedral}} = K_\chi (1 + \sin(2\chi)). \tag{3.7}
\]

Table 3.1 shows the values of the parameters from CHARMM [67] for the interaction potentials. Lorentz-Berthelot mixing rules were applied to determine the cross-species interaction parameters. The simulation was run for 750,000 timesteps of one femtosecond each.

Figure 3.3 shows a sample initial configuration for the MD simulations in this

<table>
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<th></th>
<th>( \epsilon ) (kcal/mol)</th>
<th>( r_{\text{min}} ) (Å)</th>
<th>( K_b ) (kcal/mol)</th>
<th>( b_0 ) (Å)</th>
<th>( K_\theta ) (kcal/mol)</th>
<th>( \theta ) (deg.)</th>
<th>( K_\chi ) (kcal/mol)</th>
</tr>
</thead>
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<td>305</td>
<td>1.38</td>
<td>40</td>
<td>120</td>
<td>3.1</td>
</tr>
<tr>
<td>H_2 – H_2</td>
<td>0.0697</td>
<td>2.96</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
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</tr>
</tbody>
</table>

Table 3.1: Interaction potential parameters for the molecular dynamics simulations using the CHARMM force field.
Figure 3.3: Simulation box for the molecular dynamics simulations. The blue box shows the periodic boundaries. The simulation box was chosen to be much larger than the carbon structure in order to measure the equilibrium gas pressure during simulation. This was done by calculating the average number of gas molecules in a volume far from the carbon structure and calculating the pressure from the ideal gas law.

Chapter. Periodic boundary conditions were used in the simulation. The simulation box, which is also the edge of the periodic cell, are shown in the figure.

3.2.3 Perturbative Grand Canonical Monte Carlo - Bennet’s Method

The problem of finding the free energy of a given \((\mu,V,T)\) macrostate reduces to that of evaluating the grand canonical configuration integral,

\[
\Xi = \int \exp \left[ -\beta U(q_1, \ldots, q_N) \right] \exp \left[ \beta \mu \right].
\]  

(3.8)
Here U is the potential energy, a function of the system’s N configurational degrees of freedom $q_1, q_2, \ldots, q_N$. Calculating the integral in Equation 3.8 is often infeasible due to the sheer number of degrees of freedom and because the largest contribution to the integral generally comes from a small but complicated portion of phase space. In the Monte Carlo (MC), the integral is approximated by sampling the phase space with a large, but finite number of steps. In order for this sampling to be done only on areas of phase space which contribute significantly to the integral, samples are pulled from probability distributions which are chosen to mimic the properties of the true probability distribution of the system of study. This is achieved through the use of the "Metropolis" algorithm. The algorithm works by proposing trial moves within phase space and accepting or rejecting the move based on some physically relevant parameter we wish our probability distribution to represent. In GCMC, the trial moves are the insertion, deletion or movement of a particle and the moves are accepted or rejected based on the change in energy of the system after the move. In this way, we can confine sampling of the integral in Equation 3.8 to preferentially include lower energy states. The probability a move is accepted is given by the the Metropolis function $M(x)$, defined as

$$M(x) = \min \left[ 1, \exp^{-x} \right]. \quad (3.9)$$

The Metropolis function is widely used in standard MC simulations as it has the property of detailed balance, i.e. $M(x)/M(-x) = \exp(-x)$. The large number of favorable states generated through this process are collectively known as a Markov Chain. The Markov Chain has the desirable qualities of the true probability function, and in Monte Carlo it is the Markov Chain which is sampled to calculate Equation
3.8. While this method is quite often effective by itself, it can often fail when there exist areas of the phase space which, while they contribute significantly to Equation 3.8, are sufficiently isolated to prevent a Markov Chain to access them. If one has an idea of the physically relevant regions of phase space, it is beneficial to calculate 3.8 for each isolated region of phase space.

Bennet’s Acceptance Ratio (BAR) method relies on the fact that it is often possible to calculate ratios between two integrals, defined by two different potential energy functions, $U_0$ and $U_1$, acting on the same phase space $(q_1,q_2,...,q_N)$. To see how this calculation can be done, we use as an example the Metropolis function, though other distributions may be used. In MC, Boltzmann-weighted acceptance probabilities are assigned to trial moves through $M(x)$. That is, a move which would change the energy by $\Delta U$ would be accepted with the probability $M(\beta U)$. If we consider a move which keeps the same configuration space $(q_1,...,q_N)$ but switches the potential function between $U_0$ and $U_1$ or vice versa, the acceptance probabilities for the pair of trial moves must satisfy

$$M(U_1 - U_0) \exp(-U_0) = M(U_0 - U_1) \exp(-U_1). \quad (3.10)$$

Integrating this over configuration space and multiplying by the factors $Q_0/Q_0$ and $Q_1/Q_1$ we have

$$Q_0 \int \frac{M(U_1 - U_0) \exp(-U_0)}{Q_0} dq_1...dq_n = Q_1 \int \frac{M(U_0 - U_1) \exp(-U_1)}{Q_1} dq_1...dq_n \quad (3.11)$$

The quotient on the left hand side is just a canonical average of the metropolis
function as calculated from system 0 while the right hand side is the average calculated from system 1. We can write Equation 3.11 as

\[
\frac{Q_0}{Q_1} = \frac{\langle M(U_0 - U_1) \rangle_1}{\langle M(U_1 - U_0) \rangle_0}
\] (3.12)

Equation 3.12 implies that we can calculate the ratio of the configuration integral of a system of interest and a reference system (L.H.S.) by computing the distribution of configurations as they are sampled in a MC simulation which includes a potential-switching step (R.H.S). The usefulness of Equation 3.12, however, is that the potential-switching steps need not be taken. We can accurately calculate the ratio simply by calculating the averages in Equation 3.12, which are just averages over separately generated U_0 and U_1 ensembles.

In the derivation of Equation 3.12, it is not necessary for the weighting function to be defined by the Metropolis function. If we let W be any finite-everywhere function of coordinates, then a generalized quotient formula is given by

\[
\frac{Q_0}{Q_1} = \frac{Q_0 \int W \exp(-(U_0 - U_1))}{Q_1 \int W \exp(-(U_1 - U_0))} = \frac{\langle W \exp(-U_0) \rangle_1}{\langle W \exp(-U_1) \rangle_0}
\] (3.13)

It has been shown by Bennet [68] that, in the limit of large sample sizes, the weighting function which minimizes the expected error in the free energy difference is the Fermi function,

\[
W(q_1...q_N) = \text{const} \times \left( \frac{Q_0}{n_0} \exp(-U_1) + \frac{Q_1}{n_1} \exp(-U_0) \right)^{-1}
\] (3.14)
This, into Equation 3.13 gives

\[
\frac{Q_0}{Q_1} = \frac{\langle f(U_0 - U_1 + C) \rangle_1}{\langle f(U_1 - U_0 - C) \rangle_0}
\]  

(3.15)

with the shift constant

\[
C = \ln \frac{Q_0 n_1}{Q_1 n_0}.
\]  

(3.16)

Since \(C\) depends on the unknown quantity \(\frac{Q_0}{Q_1}\), we must solve Equation 3.15 and 3.16 by adjusting \(C\) until the two become self-consistent. The change in the free energy can then be determined by solving

\[
\Delta A_{est} = \ln \left( \frac{\langle f(U_0 - U_1 + C) \rangle_1}{\langle f(U_1 - U_0 - C) \rangle_0} \right).
\]  

(3.17)

and

\[
\Delta A_{est} = C
\]  

(3.18)

in a self-consistent manner.

The error in \(\Delta A_{est}\) can be estimated through inspection of the numerator and denominator of BAR. When either the numerator or the denominator are small compared to unity, the largest contribution to the error is the possibility that configurations in which the probability of occurrence in the Markov chain is low, yet the configuration is highly energetically favorable, may not be sampled at all. The effect of this undersampling will be to underestimate the expectation of the free energy. Since the numerator is monotonically decreasing as a function of \(C\), while the de-
nominator is monotonically increasing, one can choose a \( C \) value such that either the numerator or denominator is equal to one. When the numerator/denominator is equal to one, the denominator/numerator is small compared to one and these undersampling errors get pushed to the denominator/numerator. The \( C \) value for which the numerator/denominator is equal to one gives an over/underestimate of the expectation of the free energy. Bennet’s method is particularly useful for studying systems in which trial moves are prohibitively unlikely to be accepted during a Monte Carlo step. Here, rather than attempting to build one Markov Chain through unlikely trial moves, separate Markov Chains are built for each trial move and the ratio of their respective acceptance probabilities calculated. For the system described in 3.4, trial moves of the pore wall in the presence of adsorbate are highly unfavorable due to the steep wall-adsorbate interaction potential at distances below the equilibrium distance. Attempts to study such a system with the standard MC algorithm are infeasible, as an exceedingly small portion of trial changes in pore wall structure are likely to be accepted when in the presence of a dense adsorbed film. In reality, however, it is this dense adsorbed film which will tend to move the pore wall. With BAR, the trial changes are not necessary to actually perform.

The steps toward estimating the free energy, as well as the associated error in the calculation are as follows:

1. Define a series of systems with different pore wall shapes. These systems represent the range of potentials \( (U_0, U_1, \text{ etc.}) \) used in Equation 3.13.

2. Perform standard GCMC simulations on each system, weighing changes via the Metropolis function.
3. For each member of the Markov chain, calculate the ratio in Equation 3.17 over a range of C values. The intersection of the $\Delta A$ vs. C plot and the C vs. C plot gives the estimate of the change in free energy.

4. A lower bound, $\Delta A_{\text{low}}$ and an upper bound $\Delta A_{\text{high}}$ can be determined by inspection of the numerator and denominator of BAR and the $\Delta A$ vs. C plot.

### 3.3 RESULTS: PORE WALL CURVATURE

#### 3.3.1 Ground State

In the slit-shaped pore model, pores are formed by two flat, parallel graphene sheets separated by a pore of width H. The slit-shaped pore model neglects the attractive Van der Waals interactions between each pore wall in a real material, which would cause the distance between each sheet to collapse to $H = 3.35 \, \text{Å}$, forming graphite. In reality, the pores are formed in the voids caused by steric interactions between each carbon layer. An improved model for a pore consists of a layer of graphene which is separated from another pore wall, by a distance H, by intercalated graphene sheets which are a lateral distance L apart (Figure 3.4,B and C). The dimensions of the pore formed is then L x H.

In the slit-shaped pore model, the energy required to bend one of these graphene sheets is assumed to be much larger than the Van der Waals attraction between the two pore walls. This assumption is contradictory to TEM images, which show carbon structures similar to those depicted in Figure 3.4A. To study the degree of pore curvature we model the bottom two layers as part of the larger bulk structure and
Figure 3.4: TEM images of activated carbon show significant curvature in the constituent graphene sheets (modeled on top). An improvement over the slit-shaped pore model should include the curvature induced by the interaction with neighboring sheets (middle). The interaction between carbon structures of this type and adsorbed hydrogen is studied as in the model on the bottom figure.
therefore held fixed. The top layer is completely free to move. The top layer interacts with the bulk graphite below through a potential \( V[z(x)] \) where \( z(x) \) is the height of the top layer at the horizontal position \( x \). The energy of such a configuration is

\[
E = E_{\text{Bend}} + E_{VdW} = \int 2c(\nabla^2 z(x))^2 + V[z(x)]dx = \int F[z(x)]dx,
\]

where \( c = 1.2 \text{ eV} \) is the bending energy \([64]\). The parameter \( c \) is empirical and contains all microscopic details of the graphene sheet including bond length, bond angle and dihedral angle interactions between the constituent carbon atoms. The minimal energy shape of the top layer sheet of graphene is thus the result of the competition between the energy required to keep the sheet flat and the attraction of the bulk graphite material. From calculus of variations, we obtain the sheet shape \( z(x) \) which minimizes the functional in Equation 3.19 as the solution to the Euler-Lagrange Equation \([69]\)

\[
0 = \left( \frac{\partial F}{\partial z} \right) - \frac{d}{dx} \left( \frac{\partial F}{\partial z'} \right) + \frac{d^2}{dx^2} \left( \frac{\partial F}{\partial z''} \right) = 4cz^{(4)}(x) + \frac{\partial V[z(x)]}{\partial z(x)}.
\]

The solution to Equation 3.22 requires the specification of boundary conditions at \( x = [0, L] \). We propose two limiting cases for these boundary conditions. For the case in which the interaction between graphene sheets is strong enough to pin down the graphene at the edges of the gap, the sheet outside the gap will be flat and
the slope of the graphene sheet at the edge will be zero. For the case in which the interaction is too weak to pin down the graphene sheet, bowing will occur near the edge and the slope of the sheet at the edge will be allowed to take on the value which minimizes the energy within the gap. We will study each case individually. The former will henceforth be referred to as the “constrained” solution, while the latter will be referred to as the “relaxed” solution.

We first treat the exactly solvable case in which the graphene-graphene interaction is harmonic about an equilibrium displacement $z_0$. We have then

$$E_{VdW} = \frac{K}{2} \int (z(x) - z_0)^2 dx,$$

where $K = 148 \text{ meV/Å}^4$ was determined by expanding Equation 3.26 about the potential minimum. From Equations 3.22 and 3.23 we have, then

$$F[z(x), z''(x)] = 4c(z''(x))^2 + \frac{K}{2}(z(x) - z_0)^2,$$

and Equation 3.22 becomes

$$4cz^{(4)}(x) + K(z(x) - z_0) = 0.$$

The shapes of the sheet for various gap widths for both the relaxed and constrained solutions are shown in Figure 3.5.

The height of the flexible sheet at the center of the gap, $z(L/2)$ as a function of gap length is shown in figure 3.6 for both the constrained and relaxed solution. Figure 3.6 shows a very smooth transition from open pore to closed pore as the lateral

54
Figure 3.5: Analytical minimal energy sheet shapes in a harmonic potential. The blue lines correspond to the constrained solution while the red lines correspond to the relaxed solution.

Figure 3.6: Midpoint height of the analytical minimal energy sheet shapes in a harmonic potential. The blue lines correspond to the constrained solution while the red lines correspond to the relaxed solution.
Figure 3.7: Minimal energy sheet shapes for a flexible pore in Steele’s potential.

Figure 3.8: Minimal energy sheet shapes for a flexible pore in Steele’s potential.
dimension of the pore increases. Just past the transition to closed pore for the relaxed case the sheet is allowed to overcome the strong repulsion due to the bulk graphite and “overshoot” the equilibrium position. This is likely due to the overestimation of the interaction potential by treating it as harmonic, and such a solution is not expected for a more realistic potential.

A more realistic interaction potential due to a graphene sheet is the 10-4 form from Steele [70],

\[
V_{\text{Steele}}(z) = 2\pi\varepsilon \sigma^2 \rho_c \left( \left( \frac{\sigma}{z} \right)^{10} - \left( \frac{2}{5} \right) \left( \frac{\sigma}{z} \right)^4 \right). \tag{3.26}
\]

where \( \rho_c \) is the areal density of carbon in a graphene sheet, \( \varepsilon \) and \( \sigma \) are the depth of the potential well and finite distance in which the potential is zero, respectively. For the full Steele potential, the Equation was solved using the method of steepest descent using a line search. Motivated by the analytical solution, the shape of the pore wall \( z(x) \) was approximated with a finite Fourier series of the form:

\[
z(x) = \sum_{m=1}^{N} c_m \sin \left( \frac{m\pi x}{L} \right) + \delta z. \tag{3.27}
\]

This form automatically sets the boundary conditions

\[
z(0) = \delta z,
\]

\[
z(L) = \delta z.
\]
For the constrained case, we require

\[ z'(0) = 0 \text{ and } z'(L) = 0. \]

These boundary conditions are satisfied if

\[ \sum_{m=1,3,5,...}^{N} mC_m = 0, \]
\[ \sum_{m=2,4,6,...}^{N} mC_m = 0. \]

Therefore, Equation 3.27 for the constrained case becomes

\[
z(x) = \left( - \sum_{m=3,5,...}^{N} mC_m' \right) \sin\left(\frac{\pi x}{L}\right) \\
+ \left( - \sum_{m=4,6,...}^{N} mC_m' \right) \sin\left(\frac{2\pi x}{L}\right) \\
+ \sum_{m=3}^{N} C_m \sin\left(\frac{m\pi x}{L}\right) + \delta z.
\] (3.28)

Fourier series coefficients up to \( N = 10 \) were determined to be sufficient to reproduce the harmonic potential results using the numerical minimization procedure. To start the numerical minimization, the initial configuration was set to the analytical solution. The gradient of the energy functional \( E[z(x)] \) with respect to each Fourier coefficient was then calculated and a new trial shape created by stepping the initial configuration in direction opposite of the gradient, i.e. the direction of the largest decrease in energy. The size of the step in that direction was optimized at each step.
using a Newton-Ralphson line search algorithm.

The two end points were fixed at the same height corresponding to the equilibrium height of a sheet directly on top of a stack of \(n\) graphene sheets

\[
\delta z = 3.35\text{Å} \, (n + 1). \tag{3.29}
\]

Figure 3.7 (top) shows a few of the minimal energy sheet shapes for both the relaxed and constrained solutions for various lateral pore lengths as well as the height of the center of the flexible graphene sheet, as was shown in Figure 3.5. For both the relaxed and constrained solutions we see a sharp transition between a shape with minimal bending and one with significant bending into the pore space. This transition indicates a limit in the maximum allowable pore size in the model. The transition for the relaxed case occurs at about 14 Å, while the transition for the constrained solution occurs at about 22 Å.

### 3.3.2 Dynamics at 77K

The sheet shape was also studied using an all-atom Molecular Dynamics method using NAMD. The carbon layers were arranged in three layers: a flat, rigid base graphene layer, two rigid pillar graphene sheets, separated in-plane by an intercalated defect of lateral pore length \(L\), and a flexible graphene layer of identical size and shape as the rigid base graphene layers. The lateral pore length was varied from \(L = 10 - 30\) Å. The system was initially in a configuration in which the flexible sheet had zero curvature.

Figure 3.9 shows the distribution of sheet heights at the center of the gap for
various $L$. When the lateral pore length is 18 Å, the sheet fluctuates from a completely open pore to a completely closed pore. This meta-stable state corresponds to the transition length found with the numerical minimization technique. While there are some thermal fluctuations, the results of the simulations agree well with the numerical solution for the ground state as in Section 3.3.1. Below this length the pore remains open as can be seen by the peaks in the distribution near 6 Å. As the length increases towards the transition, the sheet fluctuations increase and the peak becomes spread out. Above the transition length, the distribution becomes a narrow peak near the carbon-carbon equilibrium distance, and the pore is completely closed. The narrow peaks above the transition length indicate that once the sheet slips into the pore, the potential is strong enough to lock the graphene sheet in place and the thermal fluctuations die down.

As expected, the transition length lies in between that of the relaxed and constrained numerical solutions. Evidently the interaction between graphene sheets is strong enough to significantly pin down the top layer, so the transition length from NAMD is very close to the transition length corresponding to the constrained solution. The top sheet appears to slide across the bottom layers as the sheet enters the gap, however the sliding is limited to approximately a carbon-carbon bond length. That is, the graphene appears to fluctuate between AA stacking, in which carbon atoms in adjacent layers line up, and the graphitic AB stacking, in which half of one layer’s carbons sit at the center of the hexagon formed by the carbon matrix. While the simulations showed significant sliding of graphene sheets, little stretching of the sheet was found, due to the strong carbon-carbon bond. This is consistent with the “constrained” analytical solution discussed above. Since the graphene sheet is unable
Figure 3.9: Distribution of heights at the center of the gap for gap widths $L=10$, 15, 18, 20, 23 and 25 Å (top), and snapshots of the MD simulations. Although $L=10$ Å and $L=25$ Å sheets equilibrated in the open and close pore positions, respectively, the $L=18$ Å continuously switched between the closed ($t_1$) and open ($t_2$) pore position throughout the simulation.
Figure 3.10: Pore wall height distribution of a pore with width below the in vacuo transition width for various loading pressures. (L=15, Case 1)

to stretch itself into the gap, and since the sheet is pinned down by neighboring sheets, the graphene sheet must instead slide into the gap. Each sheet can easily slide across the graphene since, while there is corrugation, the potential due to the graphene is essentially isotropic in the graphene plane and there are no deep potential wells for the carbon to get caught.

3.4 RESULTS: ADSORBATE INTERACTIONS WITH A FLEXIBLE PORE WALL

3.4.1 Molecular Dynamics Simulations

Here we expand the molecular dynamics study from Section 3.3 to include adsorbed hydrogen. Hydrogen molecules were treated using the United Atom(UA) approach
Figure 3.11: Pore wall height distribution of a pore with width above the (vacuo) transition width for various loading pressures. (L=25, Case 1)

with Lennard-Jones parameters $\epsilon = 0.0697$ kcal/mol and $\sigma = 2.96$ Å.

We consider two cases. Case 1, in which the gas is allowed to fill the pore prior to relaxing the flexible sheet of graphene and Case 2 in which the graphene sheet is allowed to relax before the gas is loaded. We start with the case 1. Figure 3.10 shows the height distribution for the pore wall of pore of width $L=15$ Å. In vacuum, we saw that a pore of this size is below the transition width and tends to remain open. Here we see the same behavior. The effect of the gas is to reduce the thermal fluctuations of the pore wall to produce a nearly flat, rigid sheet. Figure 3.11 shows the height distribution for the pore wall of pore of width $L=25$ Å. In vacuum, we saw that a pore of this size is above the transition width and tends to close. The behavior is also seen as the gas is loaded into the sample at low pressures. However, as the pressure increases to 20 bar, the hydrogen fills the pore and the film pressure props the pore.
Figure 3.12: Pore wall height distribution of a pore with width above the (vacuum) transition width for various loading pressures. Here the pore wall was allowed to relax as the gas entered the system. (L=25, Case 2)

For Case 2, in which the pore wall is allowed to relax before the hydrogen is introduced, we see pores with lengths larger than the vacuum transition length able to close. Figure 3.12, shows the height distribution of the $L=25$ Å pore wall for this case. The $L=25$ Å length pore in this case is able to close. However, one important thing to note is the increase in fluctuations as pressure is increased. This indicates that it may be possible for the gas to open up the pore if the pressure is increased past that given here. The fluctuations may also indicate that an expansion of the pores could occur on a longer time-scale. The molecular dynamics simulations show two types of behavior for lateral pore lengths above the transition length of $L = 18$Å for the two cases. The fact that the adsorbed film in the pore in Case 1 is sufficient to keep the pore open suggests either a barrier exists between the open and closed pore states, or that the pore opening mechanism requires a time scale unachievable
through molecular dynamics simulations.

### 3.4.2 Monte Carlo Simulations

Molecular dynamics simulations are useful in the kinetics of the system, however due to limited computational resources, only processes with timescales on the order of microseconds or shorter can be simulated. For processes with longer timescales, the true ground state of the system may be unobtainable without prohibitively long computational times. We can attempt to explore the full state space of the system through the Monte Carlo method [71] (MC).

If we let $S_L(x)$ be the *in vacuo* minimal energy pore wall shape described in Section 3.3.1 and $H$ the height of a completely open pore (i.e., without pore wall bending), then we consider a series of bent pores given by:

$$z_\gamma(x) = H + \gamma (S(x) - H)$$

That is, the pore walls are in their *vacuo* minimal energy shape for $\gamma = 1$ and completely flat for $\gamma = 0$. As $\gamma$ goes from 0 to 1, the completely open pore ($\gamma = 0$) goes to a completely closed pore ($\gamma = 1$). The interactions between the pore walls and the hydrogen adsorbate are the same as defined above. Bennet's method was used to calculate the free energy landscape as the pore wall goes from open to closed.

We start with a pore with length which is above but very close to the transition length, $L = 20 \ \text{Å}$. In the MD simulations, a pore of this length remained closed for pressures less than about 5 bar and opened at higher pressures. The relative free energy, $\Delta A$, for this system as a function of $\gamma$ is shown in Figure 3.13.
Figure 3.13: Free energy as a function of $\gamma$ for a 20 Å pore.

Figure 3.14: Free energy and $\gamma = 1$ and $\gamma = 0.5$ for an $L = 20$ Å pore. The values of free energy roughly overlap between $P = 2$ bar and $P = 40$ bar.
The free energy plot at 0 bar reproduces the interaction energy between the two pore walls. At low pressure (0.001bar), we see very little difference, with the slight change owed to the entropy change as a small amount of gas is adsorbed on the pore wall surfaces.

As pressure increases, we see two local minima emerge at $\gamma = 1$ and $\gamma = 0.5$. The minimum at $\gamma = 1$ rises in energy while the minimum at $\gamma = 0.5$ decreases in energy until eventually the minimum at $\gamma = 0.5$ becomes the global minimum on the range $\gamma = [0,1]$. At $\gamma = 0.5$, we can say that the ground state of the system is at a point between completely open and completely closed pore. Figure 3.14 shows how the depth of these two minima varies as a function of pressure. While a precise transition pressure from ground state at $\gamma = 1$ to $\gamma = 0.5$ is not clear, we can clearly see that the ground state at 0 bar is with $\gamma = 1$ and for pressures above 5 bar the ground state is with $\gamma = 0.5$. This is consistent with the prediction from MD simulations for the existence of a barrier between open and closed pore states.

As pore length increases, we see the same features in the free energy landscape as for the $L = 20$ Å case (see e.g. Figure ??), however larger pressures are required for the minimum at $\gamma = 0.5$ to become lower in energy than the minimum at $\gamma = 1$. The uncertainty in precise transition pressure also increases, as can be seen in Figure 3.16.

For each lateral pore length $L$, there exist a range of pressures in which the energy at the $\gamma = 1$ minimum is at the same energy of the minimum at $\gamma = 0.5$ (see Figures 3.14 and 3.16). For pressures in which the minimum at $\gamma = 1$ is clearly lower in energy, the ground state of the system is the closed pore state. For pressures in which the minimum at $\gamma = 0.5$ is clearly lower in energy, the ground state of the
system is the open pore state. We therefore develop the phase diagram in Figure 3.17. The blue points indicate the pressures, for each lateral pore length, in which the minimum at $\gamma = 1$ and the $\gamma = 0.5$ clearly overlap. The red points indicate the pressures in which the energies of the two minima begin to diverge. Below the blue points the ground state of the system is the closed pore state, which above the red points the ground state of the system is the open pore state. Between the red and blue points, the two states are metastable.

To determine the timescale in which transitions between these two states occur, we can model the transition using the Arrhenius Equation,

$$k = Ae^{-E_a/K_bT}$$  \hspace{1cm} (3.31)

where $k$ is the rate constant, $A$ is the frequency factor related to thermal fluctuations of the pore wall and $E_a$ is the activation energy. We can obtain and estimate for
Figure 3.16: Free energy and $\gamma = 1$ and $\gamma = 0.5$ for an $L = 28$ Å pore. The values of free energy roughly overlap between $P = 40$ bar and $P = 60$ bar.

Figure 3.17: Transition pressures as a function of pore length $L$. The blue curve shows the lowest pressures for which the free energy at $\lambda = 1$ is close to the free energy at $\lambda = 0.5$. The red curve shows the highest pressure for which the free energy values are close. Below the blue curve the pores are closed, while above the red curve the pores are open. In between the two curves the system exists in a state of meta-stability.
A from the MD simulations for the $L = 18$ Å pore, since the height of the barrier is negligible, and estimate for $E_a(L)$ from the MC simulations for each $L$ above the transition length. Figure 3.18 shows the height of the carbon atoms in the center of the gap as a function of time from MC simulations. The period of oscillations, determined through inspection of Figure 3.18, between a slightly concaved pore and a completely closed pore at 77K is roughly $\tau = 10$ ps, which gives a frequency factor of $\approx 100$ GHz.

The activation energy for an $L = 20$ Å pore is approximately $E_a = 50$ meV. This gives a rate constant on the order of $10^{-10}$ seconds. During any adsorption experiment performed in the lab, typically performed over the course of an hour, we therefore expect enough time to allow the system to jump between the $\gamma = 0.5$ and $\gamma = 1$ states. This is consistent with MD simulations, which were able to see the transition for an $L = 20$ Å pore within the microsecond of simulated time.

For larger pore lengths, the barrier between states increases. Figure 3.19 shows the barrier heights and inverse reaction rates as a function of pore length.

For an adsorption experiment to see expansion of these larger pores, very long equilibration times would be necessary. The inverse reaction rate quickly approaches at the age of the universe ($\approx 10^{17}$ seconds) above $L = 35$ Å. Opening closed pores of this size via adsorption alone is therefore impossible. Typical adsorption experiments take place on the order of hours (indicated by the dashed line in Figure 3.19), so only pores with lengths less than $\approx 25$ Å will be observed to expand. Adsorbent materials for $\text{H}_2$ and $\text{CH}_4$, however, require pores of this size for adequate performance, and pores of this size are observed in many adsorbent materials.
Figure 3.18: Height of the flexible sheet midpoint as a function of time for the L=18Å pore. The frequency of closing "attempts" from the MD simulations corresponds to the Arrhenious coefficient.

Figure 3.19: Reaction barrier and associated inverse reaction rate as a function of pore length L. The dashed line indicates an upper bound on typical adsorption experiment times.
Chapter 4

Neutron Diffraction Studies of Breathing in Graphene Oxide Framework Materials

4.1 INTRODUCTION

Graphene Oxide Framework (GOF) materials provide an ideal means of directly measuring the effect of adsorbate on slit-shaped or slit-like pores. The graphene oxide (GO) material consists of very loosely bound layers of oxidized graphene, with a layer separation around 6.5 Å (see Figure 4.5). The layer separation is increased by linking the oxide groups of adjacent layers together with benzene 1-4 diboronic acid (B14DBA). An idealized cartoon of a GOF is shown in Figure 4.1. With the linker integrated into the GO framework, the pore size is determined by the competition between the attraction of the GO layers and the bond angle bending energy between the layer and the linker. At low concentrations of diboronic acid, the interaction be-
Figure 4.1: Graphene oxide framework (GOF) material, with Carbon atoms in gray, Oxygen atoms in blue, Boron atoms in red and Hydrogen atoms in white. Shown is an idealized structure. In a real material, the linker molecules are distributed along the pore space randomly. Further, QENS measurements (Chapter 5) suggest significant linker rotation at 300 K. The structure shown is with $\theta_{\text{Link}} = 90^\circ$. At low linker concentrations, the GO-GO interaction causes the linker molecules to orient at an angle $\theta_{\text{Link}} < 90^\circ$ with respect to the GO plane.

to the GO layers overcomes the bond angle energy and the linkers lay at an angle $\theta_{\text{Link}}$ with respect to the GO plane. At higher concentrations, the interaction between the GO layers is not sufficient to overcome the bond-angle energies from the linkers, and the pore expands up to a point in which the linker pillars are perpendicular to the GO plane. The GOF materials show H$_2$ isotherm (Figure 4.2 at 80 K which is similar to sample HS:0B and the GCMC calculated isotherms for a sample with a pressure-variant pore size (Figure 3.1). That is, the adsorption isotherm shows no peak at pressures up to 100 bar and a linear rise in excess adsorption at pressures above.

Further evidence for the adsorbate-induced expansion of pores in GOF materials comes from the low-pressure, sub-critical N$_2$ isotherms (Figure 4.3, top). The adsorp-
Figure 4.2: $\text{H}_2$ adsorption isotherm at 80 K for a GOF material. The adsorption isotherm is qualitatively similar to the adsorption isotherms for the HS;0B sample and the calculated adsorption isotherm for a structure with a pressure-variant pore size.

Adsorption isotherms show a hysteresis in the desorption which extends to very low pressures. Although small hysteresis loops in adsorbent materials observed in experiments have been explained by capillary condensation, the finite surface tension of the adsorbate causes hysteresis loops caused by capillary condensation to close at $\approx P/P_0 = 0.5$, where $P_0$ is the saturation pressure of the adsorbate. Hysteresis loops which extend to very low pressures have been observed in the breathing metal organic framework (MOF) material MIL-53 [56]. The GOF structure consists of many slit-shaped pores of similar size and composition to those found in the much more disordered activated carbon samples. The benefit of using the GOF structure as a substrate for measuring adsorption-induced structural changes is that, unlike typical activated carbon samples which are too disordered to give a Bragg peak, pore changes can be directly
Figure 4.3: Subcritical $N_2$ adsorption isotherm on the GOF material (top). The hysteresis loop observed in the GOF material which extends to very low pressures has been observed in two forms of the breathing MOF Mil-53 [56] (bottom).
measured via diffraction (see Section 4.2.1). In this chapter diffraction measurements of the GOF structure as the sample is loaded with H_2O, N_2 and CH_4 are presented.

4.2 EXPERIMENTAL METHOD

4.2.1 Diffraction

Scattering measurements detect changes in a scatterer’s (e.g. neutron, electron or x-ray) change in energy and momentum as they interact with a material. For a massive scatterer, the incident and final energies are given by

\[ E_i = \frac{\hbar^2 k_i^2}{2m}, \text{ and} \]
\[ E_f = \frac{\hbar^2 k_f^2}{2m}, \]  

(4.1)

where \( k_i \) and \( k_f \) are the scatterer’s wave vector before and after interacting with the sample, and \( m \) is the mass of the scatterer. The change in energy is then

\[ E = \hbar \omega = \frac{\hbar^2}{2m}(k_f^2 - k_i^2). \]

(4.2)

The change in momentum is given by

\[ Q = \hbar (k_f - k_i). \]

(4.3)

A diagram of the scattering vectors is shown in Figure 4.4. From the diagram, we
Figure 4.4: Scattering vectors defining the change in momentum and change in energy during a scattering experiment. The change in momentum is indicated by a change in direction of the incident and scattered wave vectors and the change in energy is indicated by a change in magnitude between the incident and scattered wave vectors.
see that the magnitude of the change in momentum is

\[ Q^2 = \hbar (k_i^2 + k_f^2 - 2k_i k_f \cos(2\theta)), \]  

(4.4)

where \( \theta \) is the scattering angle. Diffraction is an elastic technique; the energy of the scatterer, as far as the resolution of instrument can detect, does not change during the interaction. In this case,

\[ k = k_i = k_f, \]  

(4.5)

and Equation 4.4 becomes

\[
Q^2 = k^2 + k^2 - 2k^2 \cos(2\theta) \\
= 2k^2 (1 - \cos(2\theta)) \\
= 4k^2 \sin^2(\theta) \\
\implies Q = 2k \sin(\theta). 
\]  

(4.6)

In terms of the wavelength of the scatterer, the magnitude of the wavevector is given by

\[ k = \frac{2\pi}{\lambda}. \]  

(4.7)

The magnitude of the momentum transfer \( Q \) is related to the lattice spacing, \( d_{hkl} \) where \( hkl \) refer to the Miller indices of the lattice, in the sample material by

\[ Q = \frac{2\pi}{d_{hkl}}. \]  

(4.8)
Finally, Equation 4.6 then becomes

\[ \lambda = 2d_{HKL} \sin(\theta), \]  

(4.9)

which is Bragg’s law. Bragg’s law gives the condition for strong constructive interference of the scattered neutron waves, giving rise to areas of increased neutron intensity ("Bragg peaks") at the detector. For neutron diffraction experiments at steady-state sources such as the University of Missouri Research Reactor (MURR), measurements of \( d_{hkl} \) are done by scanning a detector over \( 2\theta \). Time-of-flight measurements can be done at pulsed neutron sources, where the measurements are done by scanning over incident wavelength \( \lambda \) and by scattering angles determined by the size of the detector bank.

### 4.2.2 The Two-axis Diffractometer at the University of Missouri Research Reactor Facility

Neutron diffraction experiments of Graphene-Oxide Framework materials loaded with supercritical gases were conducted on the two-axis diffractometer located at the C-port of MURR, referred to henceforth as 2X-C. The 2X-C consists of optionally three Soller collimators, a focusing Pyrolytic Graphite (PG004) monochromator, a Beryllium filter, a monitor, a sample stage and a five-detector data acquisition system. The neutron beam follows the following path: 1) neutron source, 2) first Soller collimator, 3) monochromator, 4) Beryllium filter, 5) monitor, 6) sample, and finally 7) detector box, which holds a third Soller collimator before the detector. The neutron wavelength is selected by the PG002 monochromator to be \( \lambda = 4.3590 \text{ Å} \) (see Appendix
B). To limit higher-order (ie. neutrons with wavelength $\lambda/2$, $\lambda/3$ etc.) and fast neutron contamination, the Beryllium filter is used to scatter neutrons with wavelengths less than about 4 Å away from the beam. The beryllium filter is cooled with liquid nitrogen, which increases the transmission of $\lambda = 4.3590$ Å neutrons by a factor of approximately two compared to room temperature beryllium. The five detector boxes allow for neutron detection at five scattering angles, separated by approximately $15^\circ$, at one time.

The (001) Bragg peak for the GOF structures, which corresponds to the inter-layer spacing between each graphene oxide sheet in the GOF material, was measured as a function of gas loading pressure. The scattered intensity was measured in steps of $\Delta(2\theta) = 0.2^\circ$ for two million monitor counts per point, or roughly 700-900 seconds per point.

4.2.3 Moderate Gas-Pressure Sample Cell

The pressure cell was manufactured in the University of Missouri Physics Machine Shop. It was made of the aluminum alloy T6-6061. This alloy uses magnesium and silicon as its major alloying elements. T6-6061 was chosen over other aluminum alloys as it is commonly used for such neutron scattering experiments. T6-6061 has a yield strength of 2,750 bar. To hold an adequate amount of sample for the experiment, the inner diameter was $2r_1 = 0.71$ cm. To determine the necessary thickness of the sample cell wall, the cell was treated as an infinitely long cylinder, a case studied by
The non-zero stresses are given by

\[
\begin{align*}
\sigma_r &= \frac{r_1^2 r_2^2 (p_2 - p_1)}{r_2^2 - r_1^2} \frac{1}{r^2} + \frac{r_1^2 p_1 - r_2^2 p_2}{r_2^2 - r_1^2} \\
\sigma_\theta &= -\frac{r_1^2 r_2^2 (p_2 - p_1)}{r_2^2 - r_1^2} \frac{1}{r^2} + \frac{r_1^2 p_1 - r_2^2 p_2}{r_2^2 - r_1^2} \\
\sigma_z &= \nu(\sigma_r + \sigma_\theta),
\end{align*}
\] (4.10)

where \( \nu = 0.33 \) is Poisson’s ratio for aluminum T6-6061, \( p_1 \) and \( p_2 \) are the inner and outer pressures, respectively, and \( r_1 \) and \( r_2 \) are the inner and outer radius of the cylinder, respectively.

These stresses were added in quadrature, and a safety factor of 8 was included according to

\[
\frac{\text{YieldStrength}}{\text{SafetyFactor}} = \sqrt{\sigma_r^2 + \sigma_\theta^2 + \sigma_z^2}.
\] (4.11)

With the outer pressure \( p_2 \) set to zero, the solution to Equation 4.11 leads to an outer diameter of \( 2r_2 = 1.89 \) cm, giving a wall thickness of 0.592 cm. A cell of this thickness could theoretically hold pressures up to 1600 bar before rupturing. The cell has been tested to hydrostatic pressures up to 400 bar without leak or rupture (see Appendix A).

4.2.4 Sample Preparation

The synthesis of the GOFs begins with a graphene oxide precursor. The graphene oxide was produced via Hummer’s method [73]. 65 mL of sulfuric acid was placed in a 500 mL Erlenmeyer flask with a stir bar. The flask was placed in an ice bath and stirred until the temperature reached 0°C. 3 grams of graphite powder and 1.5
grams of sodium nitrate were stirred into the sulfuric acid for 10 minutes to allow for complete mixing. Next, 8.5 grams of potassium permanganate was then added to the slurry. This step was highly exothermic, and therefore done in 1 gram aliquots to prevent the temperature of the slurry from getting above 20°C. Once the final aliquot was added and the effervescence reduced, the stir plate was turned off and the slurry was heated to 40°C. The temperature was maintained for 30 minutes. 130 mL of distilled water was very slowly added to the slurry. During this step, the flask was placed in a water bath, and the rate in which the water was added was adjusted to keep the slurry below 90°C. Once all of the water was added, the temperature of the slurry was maintained at 90°C for 15 minutes. Next, distilled water was added to bring the solution up to 400 mL, and the solution was kept at 40°C using the heater. 100 mL of 30% hydrogen peroxide solution was added until the solution turned a bright yellow. The solution was then left over night in order for the graphene oxide to precipitate out. The liquid was then decanted off the top, leaving graphene oxide behind. More water was added and the solution was allowed to settle again. This step was repeated until the pH was neutral. The graphene oxide was then freeze dried and stored in a refrigerator to slow decomposition. Three samples of GOF were produced

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_{BDBA}$ (g)</th>
<th>$M_{GO}$ (g)</th>
<th>$V_{meOH}$ (mL)</th>
<th>d-spacing (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO Control</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>6.38</td>
</tr>
<tr>
<td>GOF 1:2</td>
<td>0.508</td>
<td>1.01</td>
<td>15</td>
<td>7.58</td>
</tr>
<tr>
<td>GOF 1:1</td>
<td>0.998</td>
<td>1.01</td>
<td>15</td>
<td>8.08</td>
</tr>
</tbody>
</table>

Table 4.1: GOF synthesis data, d-spacing determined from XRD measurements according to Table 4.1. The GOFs were synthesized by mixing the given amounts of GO and B14DBA in 10 mL of methanol. The solutions were placed in a high-pressure
acid digestion vessel from Parr Instruments. This solution was then kept in an oven at 80°Celsius for 72-96 hours. The samples were allowed to cool and the excess methanol was removed with a syringe. The sample was then rinsed repeatedly with more methanol to remove unreacted B14DBA. The resulting GOFs were tested by x-ray diffraction (XRD) in Dr. Paul Micili’s lab in the University of Missouri’s Physics Department or by neutron diffraction on the diffraction instruments at MURR. The neutron diffraction data for the GO precursor as well as a typical GOF material is shown in Figure 4.5. The GOF d-spacing corresponding to the XRD measurements are also given in Table 4.1. It is clear that with larger amounts of B14DBA the d-spacing increases. The sample GOF1:2 provides an ideal sample in which to study adsorbate-induced pore expansion and contraction, as the relatively low concentration will not block the pores with B14DBA.

4.2.5 Data Analysis

The d-spacing as a function of loading pressure was determined using Equation 4.9. The scattering angle 2θ was determined by fitting each Bragg peak to a Gaussian function.

\[
I_{\text{fit}} = I_0 + \frac{A}{w\sqrt{\pi}/2} \exp\left(-2\frac{(x - x_c)^2}{w^2}\right)
\]  

(4.12)

where \(I_{\text{fit}}\) is the intensity at an angle \(x\), \(I_0\) is the background intensity, \(x_c\) is the center of the peak, \(A\) is the height of the diffraction peak, and \(w\) is a parameter related to
the full width at half maximum (FWHM) of the peak by

$$FWHM = \sqrt{2\ln 2} w.$$  \hfill (4.13)

The error in the intensity at each angle in which the detector was scanned through is given by

$$\sigma_{\text{Int.}}(2\theta) = \sqrt{N},$$  \hfill (4.14)

where N is the number of detector counts. The fit is performed by minimizing

$$\chi^2 = \sum_{2\theta} \left[ \frac{1}{\sigma_{\text{Int.}}(2\theta)} (I_{\text{fit}}(2\theta) - I_{\text{meas.}}(2\theta))^2 \right].$$  \hfill (4.15)

The fits were performed by the OriginLab software, and the standard error $\sigma_{2\theta}$ calculated. The error in the calculated d-spacing is determined through propagation of errors method,

$$\sigma_d^2 = \sigma_{2\theta}^2 \left( \frac{d}{d(2\theta)} \right)^2.$$  \hfill (4.16)

From Eq. 4.9,

$$d = \frac{\lambda}{2 \sin\left(\frac{2\theta}{2}\right)}.$$  \hfill (4.17)

Taking the derivative we have,

$$\left( \frac{d}{d(2\theta)} \right)^2 = \frac{1}{8} \sin(2\theta) \csc^3\left(\frac{2\theta}{2}\right),$$  \hfill (4.18)
Figure 4.5: Neutron diffraction pattern for the GO precursor as well as a “dry” (outgassed) GOF sample. The three Bragg peaks, in order of increasing $Q$, correspond to the GO/GOF (001), graphite (010) and graphite (120) reflections.

and Eq. 4.16 becomes

$$\sigma^2_d = \sigma^2_{2\theta} \frac{\lambda^2}{64} \sin^2(2\theta) \csc^6\left(\frac{2\theta}{2}\right)$$

(4.19)

### 4.3 DIFFRACTION RESULTS

A typical neutron diffraction pattern for a GOF sample is shown in Figure 4.5. Three Bragg peaks are observed in the pattern. At the lowest $Q$ is the (001) Bragg peak corresponding to the interlayer distance between GO planes. The next two Bragg peaks are graphite (010) and (120) reflections, corresponding to reflections from the in-plane GO structure. These peaks were found to match well with the in-plane graphene Bragg peaks, suggesting the oxygen group concentration on the GO surfaces
is low enough to limit the distortion of the graphene lattice.

After the synthesis of each GOF sample, XRD measurements of the (001) Bragg peak were performed to determine the quality of the synthesis and the d-spacing according to the given linker concentration. Prior to each measurement, the samples were outgassed by heating to 80°C while a millitorr level vacuum was pulled. After an initial XRD measurement, a GOF sample was exposed to the atmosphere for over two months, allowing the GOF to adsorb H₂O from the atmosphere. Figure 4.6 shows the (001) Bragg peak for the GOF just after synthesis, after the exposure to the humid atmosphere and after subsequent outgassing. After exposure to atmosphere, the shift in Bragg peak toward lower Q indicates the GOF sample expanded from an interlayer spacing of 8.08 Å to 8.68 Å, an increase of ≈ 7.4%.

The fitted Bragg peaks for each N₂ loading pressure are shown in Figure 4.7. Figure 4.8 shows the dependence of the GOF d-spacing on bulk N₂ loading pressure. The curve presented in the graph is the predicted d-spacing from the calculations outlined in Section 4.4.1. From P = 0 bar to P = 80 bar the d-spacing was observed to increase from 7.62 Å to 7.75 Å, an increase of 1.7%.

The fitted Bragg peaks for each CH₄ loading pressure are shown in Figure 4.9. Figure 4.10 shows the dependence of the GOF d-spacing on bulk CH₄ loading pressure. The curve presented in the graph is the predicted d-spacing from the calculations outlined in Section 4.4.1. From P = 0 bar to P = 80 bar the d-spacing was observed to increase from ≈ 7.62 Å to ≈ 7.80 Å, an increase of ≈ 2.4%.

The small increase in d-spacings provide an important proof-of-concept for pore expansion work on GOF materials. Due to present limitations to the experimental setup at MURR, the amount of gas loaded into the sample is limited to the amount
Figure 4.6: Measured (via XRD) (001) Bragg peaks for the GOF sample after synthesis (red squares), after exposure to humid atmosphere (blue diamonds) and subsequently outgassed (green triangles). The shift of the Bragg peak toward lower $Q$ after exposure to humidity indicates an expansion of the GOF pores due to H$_2$O uptake.
Figure 4.7: Measured (via neutron diffraction) (001) Bragg peaks for the GOF sample and fits to Gaussian peak shapes for N\textsubscript{2} loaded at room temperature.

Figure 4.8: D-spacings (red circles) for GOF loaded with N\textsubscript{2} extracted from the fits to gaussian peak shapes (Figure 4.7). The blue solid line is the predicted d-spacing from the calculations outlined in Section 4.4.1.
Figure 4.9: Measured (via neutron diffraction) (001) Bragg peaks for the GOF sample and fits to Gaussian peak shapes for CH$_4$ loaded at room temperature.

of gas driven to the sample by room temperature adsorption. In order to provide a means for gas loading while the sample is at cold temperatures, at the beamline, a gas handling system has been designed. The design schematics and safety analysis are provided in appendix C.
4.4 COMPARISON OF DIFFRACTION RESULTS WITH THEORY

4.4.1 Adsorbate-induced pressure

We will consider an adsorbent gas in a slit-shaped pore. Here, the pore will be assumed to be rigid in the sense that no bending will occur. The potential due to each pore wall is given by Steele’s potential (Equation 3.26). The pressure on the pore wall due to the adsorbed film is given by:

\[ P_{\text{Wall}} = - \int \rho_{\text{Film}}(z) \left( \frac{\partial V_{\text{Steele}}}{\partial z} \right) dz. \]  

(4.20)

Since \( \frac{\partial V_{\text{Steele}}}{\partial z} \) is the force on a graphene wall due to one adsorbate molecule, the kernel of the integration can be understood to be the pressure density inside the
Figure 4.11: Angle-bending energy of a B14DBA linker, as calculated at the MP2/6-31g(d,p) level of theory.

pore. This follows from the fact that each adsorbate molecule will provide a force on the pore wall equal in magnitude to the force the pore wall provides on the adsorbed molecule. The integral is taken over the volume occupied by the film.

In GOF materials, the slit-shaped pore walls are propped up by B14DBA linker molecules. The linker molecules are covalently bonded to the oxygen molecules in the GO layer, and minimize their angle-bending energy when perpendicular to the GO plane. We model the angle-bending energy as

\[ U_\theta = K_\theta(\theta_{\text{link}} - \theta_0)^2. \]  

(4.21)

where \( \theta_{\text{link}} \) is the angle between the B14DBA linker and the GO plane and \( \theta_0 = 90^\circ \).

The interaction coefficient, \( K_\theta \), was determined through MP2 calculations modeling the GOF structure as a coronene molecule with a B14DBA linker attached. The potential energy surface as a function of \( \theta_{\text{link}} \) is shown in Figure 4.11. Due to this angle-bending interaction energy, each B14DBA linker molecules provides a force on
the GO layer, given by:

\[ F_{\text{Linker}} = \frac{-2K_\theta(\theta_{\text{link}} - \theta_0)}{L_{B14DBA}(1 + \tan^2(\theta_{\text{link}}) \cos(\theta_{\text{link}}))}, \quad (4.22) \]

where \( L_{B14DBA} \) is the length of a B14DBA molecule. With \( \rho_{\text{Linker}} \) as the areal concentration of linker molecules, the pressure on the pore wall due to the linker molecules is then given by

\[ P_{\text{Linker}} = \rho_{\text{Linker}} F_{\text{Linker}}. \quad (4.23) \]

From the measurements detailed in Chapter 5, we determined an approximate linker concentration of one linker per 75 carbon atoms, corresponding to an areal linker density of \( \rho_{\text{Linker}} = 0.005 \) B14DBA/\( \text{Å}^2 \).

The pressure due to the interaction of a pore wall with the other pore wall in a pore of width \( H \) is given by

\[ P_{\text{gr}} = \frac{8\pi \epsilon \sigma \rho_c^2}{c} \left( \left( \frac{\sigma}{H} \right)^{11} - \left( \frac{\sigma}{H} \right)^5 \right). \quad (4.24) \]

With the areal linker density, there is a point of mechanical equilibrium at \( P = 0 \) bar at \( H = 7.55 \) Å, consistent with the d-spacing given by the “dry” GOF.

The total pressure on the pore wall is then due to the bulk gas pressure (loading pressure) \( P_{\text{Bulk}} \) and the interaction between pore walls.

\[ P_{\text{Wall}} = P_{\text{Film}} + P_{\text{gr}} + P_{\text{Linker}} - P_{\text{Bulk}}. \quad (4.25) \]

The deep potential well in the narrowest of pores means the density of the film
\( \rho_{\text{Film}} \) in the pore can reach very high values, on the order of liquid adsorbate. Here we assume a density which depends on the depth of the potential well, the temperature and bulk gas pressure, but converges to the critical density of the adsorbate:

\[
\rho_{\text{Film}}(z) = \frac{\rho_{\text{Bulk}} e^{-\beta V_{\text{Pore}}}}{1 + \left(\frac{\rho_{\text{Bulk}}}{\rho_{\text{Crit}}}\right) e^{-\beta V_{\text{Pore}}}}.
\]  

(4.26)

It is important to note that the dependence of the film density on the temperature, pore width, and bulk loading pressure from Equation 4.26 is an ansatz. The form of the ansatz gives reasonable values for the bulk loading pressure dependence of the total adsorbate uptake. For \( \text{N}_2 \), the calculated isotherm, assuming a density function given by 4.26, for a 600 m\(^2\)/g GOF sample is shown in Figure 4.12.

Figure 4.13 shows the net pressure on a pore wall, from Equation 4.25 for a GOF sample loaded with \( \text{N}_2 \) at bulk loading pressures from \( P_{\text{Bulk}} = 0 \) to \( P_{\text{Bulk}} = 120 \) bar at 300 K and 135 K. Here, positive pressures tend to increase the pore width,
while negative pressures (tensions) tend to decrease the pore width. For very small pore widths no adsorbate can enter the pore, and the pressure is due purely to the interactions between the pore walls and the angle-bending interaction of the linker molecules. Once the pore is wide enough to allow an adsorbate in, a large spike in total pressure due to the adsorbate gas is observed. The location of the peak in the total pressure corresponds to the pore width in which the potential overlap from each pore wall gives the deepest potential well, giving rise to a large density.

We observe two points in which the total pressure is zero and the pore structure is in equilibrium. The first, at $H \approx 5.5$ Å is unstable, as deviations toward smaller pore width will tend to push out all of the adsorbate and collapse the pore completely. Deviations toward larger pores will allow more adsorbate into the pore and the large pressure due to the adsorbate will cause the pore to expand. A stable equilibrium is seen at the next x-intercept. To close a pore of this width would require overcoming the large pressure due the adsorbed film, while any deviations toward larger pore widths will be opposed by the tension of the adsorbed film. This point of stable equilibrium is dependant on the bulk pressure. As the bulk pressure increases, the equilibrium point shifts toward larger pores.
Tracking this equilibrium point as a function of bulk gas pressure allows us to predict the d-spacing corresponding to each bulk gas pressure. As one can see from both the predicted and experimental values, the expansion at pressures up to 120 bar for adsorbates loaded at room temperature are small compared to the expansions predicted for low temperature adsorption. This is due to the relatively low amount of adsorbed gas driven to the sample at room temperature. With a new gas handling system (see Appendix C), further experiments will be carried out which allow for low-temperature expansion measurements.
Chapter 5

QuasiElastic Neutron Scattering Studies of Hydrogen in Graphene Oxide Framework Materials

5.1 INTRODUCTION

The diffusion of an adsorbate gas in a flexible material as a function of coverage may lead to insights into the expansion mechanism. In static adsorbents, diffusion rates tend to decrease as a function of pressure as the high density of the gas confines each individual molecule [74, 75]. Computational studies have been done to explore the influence of pore flexibility on molecular diffusion in adsorbent materials. Calculations of methane in the MOF known as ZIF-8 suggest that flexibility can significantly enhance molecular diffusion relative to a rigid framework [76]. A rigid framework with narrow pores exhibits very slow diffusion, while a framework which expands as a function of loading pressure has shown enhancement of the diffusion coefficient for
CH$_4$ by a factor of $10^4$ at room temperature and a factor of $10^{14}$ at liquid nitrogen temperature (77 K). Less drastic enhancements of the diffusion coefficient as a function of pressure have been predicted computationally in the MOF Zn(tbip) [77]. Experimentally, a rise in diffusion coefficient as a function of CH$_4$ pressure has been observed via QENS in MIL-53[Cr(III)] [78] as well as for CO$_2$ and N$_2$ in zeolites [79].

In this chapter, we present quasielastic neutron scattering (QENS) spectra from molecular hydrogen adsorbed in GOF. The measurements probed the motion of adsorbed hydrogen as a function of pressure, in order to understand the relationship between the motion of adsorbed molecules and the mechanism of pore expansion. Evidence of an increase in diffusion rates as a function of pressure are consistent with diffraction measurements of pore expansion in GOF materials. The quasielastic measurements were also able to detect rotational motions of the linker molecules in the solid GOF structure. A measurement of the rotational diffusion coefficient was made, as well as an estimate of the linker concentration.

5.2 EXPERIMENTAL METHOD

5.2.1 Quasielastic Neutron Scattering

The measured scattering intensity can arise from both the coherent scattering, the sum of interactions with the average scattering center, as well as incoherent scattering, the sum of interactions of the neutron wave with individual nuclei. Incoherent scattering intensity is dependent on the deviation from the average scattering, and can arise from disorder in a sample (ie., no single well-defined lattice), thermal vibra-
tions (displacement from lattice positions), isotopic variance in a sample and, because the neutron interacts with the spin state of a nucleus, spin variance.

Hydrogen has a very large incoherent scattering cross section of 80 barn, due to the fact that the scattering lengths for its singlet and triplet states are opposite sign as well as greatly different in magnitude. The large incoherent scattering cross section of hydrogen makes incoherent scattering an attractive measurement tool for the study of hydrogen, because the signal-to-background ratio is optimal. Further, because incoherent scattering represents scattering from individual nuclei, incoherent scattering techniques can measure the motions of individual hydrogen atoms, allowing for the measurement of the self-diffusion.

Quasielastic neutron scattering from a strong incoherent scatterer such as hydrogen measures the dynamic incoherent structure factor

\[ S_{\text{inc}}(Q, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} I_{\text{inc}}(Q, t) \exp(-i\omega t) dt, \]  

(5.1)

where

\[ I_{\text{inc}}(Q, t) = \frac{1}{N} \sum_{i=1}^{N} \exp(-iQ \cdot (\mathbf{R}_i(t) - \mathbf{R}_i(0))) \]  

(5.2)

is the intermediate scattering function. The intermediate scattering function \( I_{\text{inc}}(Q, t) \) is the space Fourier transform of the van Hove function, \( G(r, t) \), defined by

\[ G(r, t) = \int \langle \rho(r' - r, 0)\rho(r', t) \rangle dr', \]  

(5.3)

such that,

\[ I(Q, t) = \frac{1}{N} \int G(r, t) \exp[-iQ \cdot r] dr \]  

(5.4)
where $\rho(r, t)$ is the density of particles at $r$ and time $t$. That is, performing a neutron scattering measurement is equivalent to performing a space- and time-Fourier transformation on the particle density-density correlation function of the system. Thus, to calculate the scattering from a given system, one takes a real-space and time description of the system and Fourier transforms the particle density-density correlation function. MD simulations are often useful for calculating the real-space and time particle density for a given system in motion. Armed with a particular model of a physical system, we can determine the motion through MD simulations and use equations 5.1-5.4 to determine the scattering. Inelastic neutron scattering and MD simulations are complementary techniques to determine the motion of a system.

### 5.2.2 BASIS

The Backscattering Silicon Spectrometer (BASIS) at Oak Ridge National Laboratory [80] was utilized for the QENS measurements described in this chapter. The silicon portion of the instrument name refers to the fact that a silicon analyzer crystal is used to determine the energy of the scattered neutrons. Backscattering refers to the geometry of the scattering and the method in which the high energy resolution ($3.5 \mu$eV) is achieved. The energy resolution is achieved through optimizing the monochromation of the scattered neutrons via Equation 4.9. The uncertainty in the wavelength can be found through implicit differentiation of Equation 4.9,

$$\frac{\delta \lambda}{\lambda} = \frac{\delta d}{d} + \frac{\delta \theta}{\tan \theta}.$$  \hspace{1cm} (5.5)
The term on the left-hand side is the relative uncertainty in the wavelength, which gives the energy resolution. The first term on the right-hand side represents the spread in $d$-spacings in the silicon crystal analyzer, and the second term is the relative uncertainty in the scattering angle $\theta$.

Equation 5.5 can be minimized by maximizing $\tan \theta$, which occurs at $\tan \theta = 90^\circ$, which corresponds to $2\theta = 180^\circ$. From Figure 4.4, we can see that this scattering angle refers to scattering in which the neutron retraces its path after interacting with the sample, i.e, “backscattering”.

5.2.3 Sample Preparation

The 200 bar aluminum pressure cell described in Chapter 4 was filled with $\approx 0.73$ grams of GOF. The sample was periodically compacted while filling. A $\approx 0.5$ gram wad of glass wool was then placed in the sample cell. A $0.61''$ diameter indium o-ring was placed in the groove in the cell cap, and the cap was screwed on and the sample was evacuated to a pressure of $10^{-4}$ Torr. The valve was then closed. The sample was then transported to ORNL, where the cap was replaced with a new cap as requested by ORNL sample environment team. The replacement was be done in a glove bag with a helium environment. Following the replacement of the cell cap, the sample cell was evacuated overnight using a turbo pump to $10^{-7}$ Torr.

5.2.4 Data Analysis

The total scattering is the result of convolution of the instrumental resolution function, $R(Q,\omega)$, with a sum of the elastic peak (delta function) and the quasielastic
component. The latter can be approximated by a Lorentzian function, or a sum of Lorentzians, with variable ($Q$-dependent) full-width at half-maximum (FWHM), $\Gamma_l$. A linear background of slope $B$ and intercept $C$ is also be added as a fit parameter so that the resulting model scattering function is

$$S(Q, \omega) = \left[ A_0 \delta(\hbar \omega) + \sum_{l=1}^{l=N_L} A_l \frac{1}{\pi} \frac{\Gamma_l}{\Gamma_l^2 + (\hbar \omega)^2} \right] R(\hbar \omega, Q) + (B \omega + C). \quad (5.6)$$

where $\hbar \omega$ is energy transfer, $Q$ is momentum transfer, $N_L$ is the number of relevant Lorentzian functions and $A_0$ is the fraction of the elastic scattering in the total signal (EISF), and $A_l$ is the fraction of the $l$th quasielastic component in the total signal.

The resolution function was measured at 5.4 K, the lowest temperature achievable by the cryostat. The data was fit with the use of NIST’s DAVE software [81]. The QENS broadening (FWHM) was fit to a model of diffusion parameters as outlined in Section 5.3.2.

## 5.3 QENS RESULTS

### 5.3.1 “Dry” GOF

Because we are primarily interested in the motions of hydrogen molecules adsorbed on the sample, it is important to minimize the contribution to the measured scattering intensity due to motions of the solid GOF structure. The timescale accessible to the instrument is dependent on the energy resolution via the uncertainty principle,

$$\Delta E_{\text{min}} = \frac{\hbar}{t_{\text{max}}}, \quad (5.7)$$
Figure 5.1: Elastic intensity scan at $Q = 1.1 \text{ Å}$. The elastic intensity is proportional to the number of particles in the system which are immobile within the resolution of the instrument.

where $\Delta E_{\text{min}}$ is the smallest energy transfer which can be detected (i.e. the instrument resolution), and $t_{\text{max}}$ is the time scale of the slowest motion that can be detected. For motions on a longer time scale than $t_{\text{max}}$, the scattering contribution appears as elastic ($\omega = 0$). An elastic energy scan measures the $\omega = 0$ intensity as a function of temperature for a given $Q$ value, in this case $Q = 1.1 \text{ Å}$. The elastic intensity scan for the GOF sample, without any hydrogen loaded, is shown in Figure 5.1. As expected, the elastic intensity increases as temperature decreases, indicating hydrogen motions in the GOF are slowing to values inaccessible to BASIS. When the temperature drops low enough such that all motion accessible to BASIS has ceased, one would expect the elastic intensity to level off to a constant value. For the GOF sample, the
elastic intensity continues to increase to the lowest measurable temperature of 5.4 K, indicating motions in the sample which persist to very low temperatures. Motion at these temperatures can only occur for components of the system which reside in very shallow potential wells, such as the diboronic acid linkers, which are nearly free to rotate. However, inspection of the dry GOF QENS spectra at 40 K (Figures D.1 and D.3) indicate that at even at 40 K, this motion presents negligible signal, and is therefore neglected in the analysis of the hydrogen-loaded GOF spectra.

At 300 K, however, a sufficient number of linker molecules are participating in the motion accessible to BASIS and quasielastic scattering is observed in the spectra (Figures D.5 and D.7). The scattering function for an isotropic rotator is derived by Bée [82] and given by

\[
S(Q, \omega) = A_0(Q)\delta(\omega) + \sum_{l=1}^{\infty} A_l(Q) \times \frac{1}{\pi} \times \frac{\tau_l^R}{1 + (\omega \tau_l^R)^2},
\]

where \(\tau_l^R\) is known as the correlation time and is given by

\[
[\tau_l^R]^{-1} = l(l + 1)D_R,
\]

with \(D_R\) the rotational diffusion coefficient, with units rad\(^2\)/sec. \(A_0(Q)\) and \(A_l(Q)\) are the elastic and quasieelastic structure factors, respectively, given by

\[
A_0(Q) = j_0^2(QR) \quad A_l(Q) = (2l + 1)j_l^2(QR),
\]

where \(j_l\) are the \(l^{th}\) order Bessel functions and \(R\) is the radius of the rotational motion.
The measured scattering functions were fit to the function given in equation 5.8. It was determined that two Lorentzians were sufficient to fit the spectra over the $Q$-range. Since $A_3(QR)$ is negligible for $QR < 1$, this indicates that $R > 0.6$. If $R < 0.6$, a non-negligible contribution from $A_3(QR)$ would appear at $Q = 1.7\text{Å}^{-1}$.

The coefficients $A_1(Q)$ and $A_2(Q)$ were then fit to equation 5.10, where the fitting parameters were a normalization constant and $R$. The data and fits are shown in Figure 5.2. The fit procedure determined a value of $R = 2.02 \pm 0.04 \text{Å}$. If we consider the structure of the diboronic acid linker, this radius of rotation is consistent with rotation about the long axis of the molecule (see Figure 5.3). Because the backbone of the linker molecule is a modified benzene molecule, it is reasonable for the hydrogens in the diboronic acid molecule to be separated by a distance similar to the hydrogen-hydrogen distance in benzene. For a benzene molecule, the distance between second-neighbor hydrogen atoms is 4.31 Å [46]. Thus, for the rotation of a benzene molecule along its long axis one would expect a rotation radius of 2.15 Å.

The isotropic rotation model predicts an Elastic Incoherent Structure Factor (EISF), given by

$$EISF(Q) = \frac{A_0(Q)}{\sum_{i=0}^{\infty} A_i(Q)},$$

(5.11)
to go to zero for large $Q$. Physically, the EISF represents the probability that a particle which is in a volume equal to $(2\pi/Q)^3$ at time $t = 0$ is still in that same volume at a later time governed by the energy resolution of the instrument. This is due to the fact that quasielastic broadening occurs when a particle moves out of a volume $(2\pi/Q)^3$ in time $t$. The higher the probability that a particle remains in the volume, the smaller the quasielastic terms in the denominator of equation 5.11 and the closer the EISF is to unity. Likewise, the lower the probability the particle
Figure 5.2: Measured quasielastic structure factors, $A_1(Q)$ and $A_2(Q)$, along with the fitted model functions.
Figure 5.3: Diboronic acid linker molecule. The QENS measured radius of rotation is consistent with rotation about the axis shown, with $R = 2.02 \text{ Å}$. Carbon = grey; Hydrogen = white; Boron = pink; Oxygen = red.

remains in the volume, the larger the denominator in equation 5.11 and the closer the EISF is to zero. Because $Q = 0$ essentially represents an infinite volume, the probability the particle remains in the volume, and therefore the EISF, at $Q = 0$ is unity. For large values of $Q$, the volume becomes very small and the particle must be moving very slowly to remain in the volume. The EISF therefore goes to zero for large values of $Q$. Practically, it is difficult to accurately measure the EISF, due in a large part to motions beyond the measurement capabilities of the instruments. For instruments with high-resolution and small energy windows, such as BASIS, motions which produce quasielastic broadening larger than the energy window contribute to a flat background and are not accounted for in the measurement of the EISF. For instruments with lower energy resolution, motions slower than detectable contribute to the elastic peak, and the EISF will not tend to zero at large $Q$.

One method of resolving the latter problem is to measure the elastic contribution
from any components of the system which are too slow to be detected, in the absence of any elastic contribution of those components of the system which do present quasielastic broadening within the instrument window. For example, motions in the graphene oxide lattice in the GOF structure are expected to be either harmonic, which would appear in the spectra as a flat background, or too slow to be detected by even the high-resolution BASIS offers. One would then need to make a measurement of spectra given by the graphene oxide lattice without any linker molecules. The elastic peak from this spectra would then be incorporated in the calculation of the EISF. Unfortunately, this type of measurement would require us to destroy the GOF material (for example, by heating until linkers are removed), which would change the sample in such a way that the measurement would not be of any use.

Instead, we can estimate the fraction of the sample which is participating in the motion detectable by BASIS by inspecting the high-Q limiting value of the measured EISF. In terms of the model EISF, the measured EISF is given by [83]

\[
EISF_{\text{Measured}} = 1 - p_m + p_m EISF_{\text{Model}},
\]

(5.12)

where \(1 - p_m\) is the fraction of the sample involved in the relevant atomic motion. Rather than tending to zero at large \(Q\), equation 5.12 approaches the proportion of sample which remains immobile on the time scale accessible to the instrument. The EISF computed by equation 5.11 using the isotropic rotation model and the rotational radius determined in the fit of equations 5.10 was fit to the measured EISF using \(p_m\) as a fit parameter. Figure 5.4 shows the fit function as well as the measured EISF. The fraction of sample involved in the relevant atomic motion was found to be \(p_m = 3.8 \pm 0.4\%\). If we assume all linker molecules are participating in the motion at
Rather than converging to zero for high $Q$, the EISF for our sample converges to a value near 0.96. This is due to components of the system which remain immobile within the resolution of the instrument.

300 K, this fraction of mobile sample would correspond to a linker concentration of $\approx 1$ linker molecule per 75 carbon. The value is consistent with the pore expansion as a function of linker concentration detailed in Chapter 4.

The measured FWHM is plotted in Figure 5.5. The average FWHM has a value of $22 \mu eV$, corresponding from equation 5.9 to a rotational diffusion coefficient of $D_R = 17 \pm 5 \times 10^9$ rad$^2$/sec.

### 5.3.2 Hydrogen Diffusion in GOF

The quasielastic spectra for hydrogen loaded in the GOF sample at 15 bar, 45 bar, and 75 bar at 35 K are shown in Appendix D.

As hydrogen adsorbs in a GOF, the molecules move into two types of pore spaces:
Figure 5.5: QE FWHM, as a function of $Q$, along with the fitted model function. The FWHM corresponds to a rotational diffusion coefficient of $D_R = 17 \pm 5 \times 10^9$ rad$^2$/sec.

Macropores, where the interaction potential from the solid is weak and the gas behaves like an ideal gas, and micropores, where the interaction potential from the solid is strong. The motion of the hydrogen molecules will differ in each pore space type. In the very small pores, the large film densities and the interactions with the solid structure will slow the motion of the hydrogen molecules. In the macropores the diffusion will be faster, with quasielastic broadening on the order of meV, which is outside of the dynamic window of BASIS. The quasielastic broadening due to the fast molecules will present in the scattering in the form of a nearly flat background within the energy window of the instrument. Figure 5.6 shows the background intensity, as a function of $Q$, for each pressured measured. As pressure increases, the intensity of the background increases.

We can understand the $Q$ dependence of the background intensity as due to the
Figure 5.6: Background intensity for each $Q$ from the fits of the QENS spectra. Hydrogen in macropores behave like ideal gas molecules and diffuse much more quickly than hydrogen in pores. The quasielastic broadening due to these fast hydrogen is larger than the energy window of BASIS, so that their contribution to the scattering comes in the form of a flat background. As pressure is increased, there is a larger amount of fast hydrogen, and the height of the background increases. The curves are fits to Equation 5.18.
limited energy window of the BASIS instrument. The quasielastic broadening is Lorentzian,

\[ L = I_0 \frac{1}{\pi} \frac{\Gamma}{\Gamma^2 + (\hbar \omega)^2}, \quad (5.13) \]

where \( I_0 \) is the intensity of the quasielastic broadening and \( \Gamma \) is the FWHM. For an incoherent scatterer such as hydrogen, \( I_0 \) is independent of \( Q \). The fast hydrogen in the macropores undergo Fickian diffusion, i.e,

\[ \Gamma = DQ^2, \quad (5.14) \]

where \( D \) is the diffusion coefficient. When the entire Lorentzian is within the energy window, the intensity is

\[ I_0 = \int_{-\infty}^{\infty} Ld\omega. \quad (5.15) \]

On BASIS the energy window, \( W \), is much less than \( \Gamma \) of the fast hydrogen quasielastic broadening. The integral in Equation 5.15 is then taken over the energy window of BASIS, and the “truncated intensity” is

\[ I_{\text{Trunc.}} = \int_{-W}^{W} Ld\omega = \frac{2 \arctan \left( \frac{W}{\Gamma} \right)}{\pi} I_0. \quad (5.16) \]

The background intensity in Figure 5.6 is the height, \( B \), of a flat background in the QENS spectra. With the assumption that \( \Gamma \) is much larger than \( W \), we can relate \( B \) to \( I_{\text{Trunc.}} \) by

\[ I_{\text{Trunc.}} = 2WB. \quad (5.17) \]

Equating Equations 5.16 and 5.17 gives the \( Q \) dependence of the background intensity
as
\[ B = \frac{\arctan \left( \frac{W}{DQ^2} \right) I_0}{W\pi}. \]  
(5.18)

The curves in Figure 5.6 are fits of Equation 5.18 to the background intensity data. The fact that Equation 5.18 fits well with the background intensity data indicates the background intensity is primarily due to the motion of fast hydrogen in the macropores.

In addition to the contribution from the fast hydrogen, the QENS spectra present a component of quasielastic broadening within the energy window on BASIS from hydrogen adsorbed in the narrow GOF pores. Figures 5.7-5.9 show the FWHM of the quasielastic component at each pressure. As a function of \( Q \), the FWHM for each pressure exhibits a local maximum, indicative of jump diffusion [82].

Chudley and Elliot [84] developed their jump diffusion model to describe jumps on a lattice, however the model has been used to describe adsorbed hydrogen in narrow carbon pore spaces previously [85]. In the Chudley-Elliot model, a particle moves from nearest-neighbor lattice points, a distance \( L_{\text{Jump}} \), after oscillating about its initial position for its “residence time” \( \tau \). The quasielastic broadening is Lorentzian with \( Q \)-dependent FWHM given by

\[ FWHM_{CE} = \frac{2\hbar}{\tau} \left[ 1 - \frac{\sin(QL_{\text{Jump}})}{QL_{\text{Jump}}} \right]. \]  
(5.19)

The diffusion coefficient is related to \( L_{\text{Jump}} \) and \( \tau \) by

\[ D_{CE} = \frac{L_{\text{Jump}}^2}{6\tau}. \]  
(5.20)
The FWHMs were fit to the Chudley-Elliot model and the fits are included in the figures. In the data, the FWHM at $Q = 0.3$ was neglected. During the fitting procedure, it was found that the Lorentzian which best fit broadening at this $Q$ value had a very high FWHM, on the order of 40-50 $\mu$eV. There are two reasons which justify neglecting the FWHM data at this $Q$ value. First, the high FWHM value is likely due to fast hydrogen in macropores. If we assume the FWHM at $Q = 0.3$ of 50 $\mu$eV is within the regime in which the broadening due to fast hydrogen is proportional to $Q^2$, the broadening suggests diffusion rates on the order of $10^{-4}$ cm$^2$/s. Diffusion rates of this magnitude have been observed in carbon nanohorns [86], in which the pore sizes are tens of nanometers, an order of magnitude larger than for the GOF samples. Because at low $Q$ values the quasielastic broadening is proportional to $Q^2$, this low value of $Q$ is the one measured for which the broadening due to the fast hydrogen is visible within the energy window of BASIS. At higher $Q$, the broadening due to the fast hydrogen will contribute as a flat background to the spectra. Second, upon inspection of the FWHM data, it is clear that the broadening at $Q = 0.3$ due to the motion of the slow, confined hydrogen would give FWHM of $\approx 5\mu$eV or less. This broadening is very close to the instrument resolution, and within the resolution function measured for this particular GOF sample. The contribution to the scattering of the quasielastic broadening at $Q = 0.3$ due to the slow, confined hydrogen will therefore be difficult to resolve from the elastic peak.

Before discussing the fit parameters extracted from the Chudley-Elliot model for hydrogen adsorbed on the GOF structure, it is instructive to consider the expected behavior of the jump length and residence time as a function of pressure for static adsorbents. From kinetic theory, the mean free path length for a particle is inversely
proportional to the pressure. In a confined system, however, the limiting distance of the mean free path length is likely due to the solid structure rather than the mobile adsorbate molecules. Thus, for diffusion of an adsorbate in a static structure, one would expect the jump length to remain relatively unchanged or to decrease as a function of pressure. One would also expect the residence time to increase as a function of pressure, yielding a decreasing diffusion coefficient as a function of pressure. This interpretation is intuitively reasonable, as the increase in the H\textsubscript{2} density in the pores near a given molecule would increase the time spent before the molecule makes each jump. The net effect of the constant (or decreasing) jump length and the increase in residence time would imply that, as a function of pressure, the diffusion coefficient decreases.

The residence time, extracted from the Chudley-Elliot model fits, as a function of pressure is shown in Figure 5.10. The residence time increases as a function of pressure. The jump length, extracted from the Chudley-Elliot model fits, as a function of pressure is shown in Figure 5.11. The jump length also increases as a function of pressure. At $P = 75$ bar, the jump length is 43% larger than the jump length at $P = 15$ bar. In a static solid structure, as a function of pressure, one would expect the jump length to decrease because the increased density will decrease the distance a molecule could travel before colliding with another. Because the measured jump length is less than the mean free path for a gas molecule at 35 K (approximately 75 Å at 15 bar and 20 Å at 75 bar), the limiting dimension is the solid adsorbent structure. A jump length which increases as a function of pressure indicates that the limiting dimension of the solid adsorbent structure is increasing as a function of pressure. From equation 5.20, one can see that the diffusion coefficient is proportional to the
Figure 5.7: FWHM and fit to the Chudley-Elliot jump diffusion model for the 15bar, 35K measurement. For reference, the inset shows the intensity of the Lorentzian fit to the quasielastic contribution to the spectra.
Figure 5.8: FWHM and fit to the Chudley-Elliot jump diffusion model for the 45bar, 35K measurement. For reference, the inset shows the intensity of the Lorentzian fit to the quasielastic contribution to the spectra.
Figure 5.9: FWHM and fit to the Chudley-Elliot jump diffusion model for the 75bar, 35K measurement. For reference, the inset shows the intensity of the Lorentzian fit to the quasielastic contribution to the spectra.
Figure 5.10: Residence time, $\tau$, from the Chudley Elliot jump diffusion model. The residence time increases as a function of pressure, indicating the higher density of adsorbate confines a given molecule for a longer period of time.

Figure 5.11: Jump length, $L_{\text{Jump}}$, from the Chudley Elliot jump diffusion model. Typically as a function of pressure the jump length decreases. The increase in jump length suggests changes in the pore space.
square of the jump length while inversely proportional to the residence time. Thus, the increase in residence time as a function of pressure has the effect of decreasing the diffusion coefficient. The increase in jump length, on the other hand, has the effect of increasing the diffusion coefficient.

The pressure dependence of the diffusion coefficient, extracted from the Chudley-Elliot fits, is shown in Figure 5.12. At $P = 75$ bar, the diffusion coefficient is 43% larger than the diffusion coefficient at $P = 15$ bar.

The increase in $L_{\text{jump}}$ and the increase in $\tau$ as a function of pressure have competing effects on the diffusion coefficient; the former tends to increase the diffusion constant while the latter tends to decrease the diffusion coefficient. One can imagine that the “cage” formed by neighboring hydrogen molecules traps a given hydrogen molecule for a longer period of time due to the larger density of particles, however the distance between each “cage” is separated by larger distances due to expansion.
in the pore volume. From Figure 5.11 we can see that the increase in \( L_{\text{Jump}} \) is linear with pressure, at least over the range of pressures studied here. For this type of mechanism, in which both the residence time and jump length increase, the diffusion coefficient will increase when \( \tau \) grows slower than \( P^2 \).

QENS spectra were also measured during desorption; the FWHMs and fits are shown in Figures 5.13 and 5.14. The residence time, jump length and diffusion coefficients are plotted in Figures 5.15, 5.16 and 5.17, respectively.

During the step from 75 bar to 45 bar the residence time decreases to a value near that of the 45 bar adsorption step, however the jump length has only a very small decrease. The combination of these effects leads to an increase in diffusion coefficient as the pressure was dropped from 75 bar to 45 bar. This may indicate a hysteresis in the structural changes during desorption. From 45 bar and 15 bar both the jump length and residence time drop to a value near their 15 bar adsorption step values, and the diffusion constant is, within error bars, the same as during the adsorption step at 15 bar.

Another possible explanation for the observed increase in diffusion coefficient could be a transition from a two-dimensional system, in which the hydrogen molecules are confined to a single plane, to a three-dimensional system, in which the hydrogen molecules can move in the direction perpendicular to the pore walls in the system. Assuming the jump rate is the same in each dimension, opening up the system from a two-dimensional motion to a three-dimensional motion would increase the diffusion coefficient by a factor of 3/2, roughly the same amount measured via QENS. This explanation still requires an increase in the pore volume as a function of pressure.
Figure 5.13: FWHM and fit to the Chudley-Elliot jump diffusion model for the 15bar, 35K measurement. For reference, the inset shows the intensity of the Lorentzian fit to the quasielastic contribution to the spectra.
Figure 5.14: FWHM and fit to the Chudley-Elliot jump diffusion model for the 45bar, 35K measurement during the desorption cycle. For reference, the inset shows the intensity of the Lorentzian fit to the quasielastic contribution to the spectra.
Figure 5.15: Residence time, $\tau$, from the Chudley Elliot jump diffusion model for the desorption cycle.

Figure 5.16: Jump length, $L_{Jump}$, from the Chudley Elliot jump diffusion model, during the desorption cycle.
Figure 5.17: Diffusion coefficients from the Chudley Elliot jump diffusion model, during the desorption cycle.
Chapter 6

Summary and concluding remarks

In the previous chapters, I discuss calculations and scattering experiments addressing the issues of boron solubility in carbon and adsorbate-induced structural changes.

In Chapter 2, *ab-initio* calculations of $\text{B}_{10}\text{H}_{14}$ adsorption on carbon, adsorption isotherms, and hydrogen interaction energies with boron-doped carbon structures were presented. It was shown that the strong interaction of $\text{B}_{10}\text{H}_{14}$ with carbon allows for high uptake even with doping at the low pressures required to prevent pore clogging due to liquid $\text{B}_{10}\text{H}_{14}$. Our calculations show that $\text{B}_{10}\text{H}_{14}$ is a feasible material for delivering a large amount of boron to a carbon sample. Once adsorbed, however, there are large energy barriers in the reaction replacing a carbon with a boron. A carbon structure with a defect is shown to readily absorb boron. In reactions of boron with intact carbon structures, the only achievable product was shown to be an anionic boron-doped carbon structure.

In Chapter 3, a model is developed for the structural response of a carbon host to $\text{H}_2$ adsorption. The calculations predict closed-pore structures with lengths less
than approximately 25 Å can open during typical adsorption experiments. From the
calculations, an experimental signature of pore expansion or contraction is shown to
occur in the adsorbent isotherms of some ALL-CRAFT activated carbon and graphene
oxide framework adsorption isotherms.

In Chapter 4, I discuss neutron and x-ray diffraction measurements of structural
changes in graphene-oxide framework materials. Small expansions were observed for
samples loaded with N₂ and CH₄. In order to perform these experiments with samples
loaded at room temperature, a gas handling system for use on the beam port floor of
the MU research reactor has been designed (Appendix C).

In Chapter 5, quasielastic neutron scattering measurements of the diffusion of
H₂ in a graphene-oxide framework are discussed. Rotational diffusion of the linker
molecules in the structure was observed at room temperature and an estimate for
linker concentration was derived from the data. At 35 K, the hydrogen diffusion was
observed to be jump-like. An increase in both residence time and jump length were
observed as a function of pressure, yielding an increase in diffusion coefficient as a
function of pressure consistent with pore expansion.
Appendix A

Gas-pressure cell
Figure A.1: Schematic diagram of the gas-pressure cell for neutron diffraction experiments for gas pressures up to 200 bar.
Figure A.2: Schematic diagram of the gas-pressure cell cap for neutron diffraction experiments for gas pressures up to 200 bar.
Appendix B

Calibration of the 2X-C Instrument
To measure the incident neutron wavelength we measured the Bragg peak from the reflection from the silicon (111) planes. Silicon has a cubic diamond crystal structure with lattice parameter \(a = b = c = 5.431020504 \pm 0.0000089\) [87]. Silicon powder is used for calibration of neutron wavelengths due to its well-defined crystal structure which is not susceptible to significant degradation over time.

The d-spacing of the (111) reflection can be determined by:

\[
\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} = \frac{3}{a^2} \Rightarrow d = \frac{a}{\sqrt{3}}
\]  

(B.1)  

(B.2)

The measured Bragg peak was fit to a Gaussian peak shape (see Figure A.1). The center of the peak was determined to be:

\[
2\theta = 88.0560 \pm 0.00242^\circ
\]  

(B.3)

The incident wavelength is then determined from Bragg’s law:

\[
\lambda_{inc} = 2d \sin(\theta)
\]  

\[
= 4.3590 \pm 0.0055\text{Å}
\]  

(B.4)  

(B.5)
Figure B.1: Si (111) Bragg peak used to calibrate the incident neutron wavelength
Appendix C

Gas Handling System for \textit{in situ} Neutron Scattering Measurements at MURR
1. **Project Leader:** Helmut Kaiser
   **Project Co-Leader:** Haskell Taub

2. **MURR Affiliation:** Neutron Scattering and Neutron Materials Science Program

3. **Project Name:** Gas Handling System for *in situ* Adsorption Measurements for 2XC (RL-33), PSD (RL-61) and TRIAX (RL-46)

4. **Description of Radioactive Material/Radiation:**
   Beamport C (upstream 60°, 81°, and 102° beam holes on west side), Beamport D (RUR 248) and Beamport A (RUR 258).

5. **Location Requested:** Room/Area Restricted: **YES (X)  NO ( )
   - Level I  ( )
   - Level II  (X)
   - Level III  ( )
   - Level IV  ( )
   - Other  ( )

   Beamport floor area is a restricted Level II area and only accessible by authorized personnel. The location and monthly survey of the area is adequate for this project.

6. **Purpose and Brief Description of Project:**
   The main purpose of this Gas Handling System (GHS) is to load samples with N₂, CO₂, H₂, CH₄, D₂, CD₄, He and Ar for *in situ* adsorption measurements during experiments using the MURR 2XC (BP “C”), the PSD (BP “D”), and the TRIAX (BP “A”) instruments. The GHS will be used in conjunction with a pressure cell previously approved for off-site loading with flammable and non-flammable gases. **Pressure cell experiments up to 200 bar with non-flammable gases have been approved in RL-77, and for flammable gases in RL-84.** The thermodynamic parameters to control for the GHS measurements are the temperature of the sample and loading pressure of the gas. **Small quantities of gas will be used (See Appendix I).** The GHS will allow the experimenters to perform *in situ* elastic and inelastic neutron scattering measurements to obtain structural and dynamical information as a function of sample...
temperature, loading pressure, and gas species. The GHS schematics can be found in Appendix II. The GHS is comprised of:

- the gas manifold (Appendix II, Figure 1) with pneumatic valves controlled by,
- the solenoid switches (Appendix II, Figure 2), controlled by,
- the electronic components (Appendix II, Figure 3).

Custom LabView software will be designed to control the electronics relay. The software will also be designed to monitor pressure and detect leaks in the GHS. Flammable gas detectors will be installed near the GHS to alert users in the unlikely event of a leak. A leak check will be performed prior to installation of the GHS on the beam port floor, and periodic leak checks using non-flammable gases will be performed periodically. All electronic components will be physically separated from the gas manifold. **Only the gas manifold will be exposed to the gas of interest.**

The components of the GHS are labeled according to Table 1. The components are: a port to the sample, a vacuum pump, a vacuum transducer (LPT), a 245 bar pressure transducer (HPT), a gas inlet port, and a lecture bottle. The 245 bar pressure transducer is OMEGA brand absolute pressure transducer. The vacuum transducer is MKS brand 974 QuadMag™ Cold cathode/MicroPirani™/Piezo Vacuum Transducer, which measures pressures on the range of 10^{-8} Torr to 1500 Torr.

Six normally-closed pneumatic valves (PV1-6) will be used to open/close the ports to each component excluding the pressure transducer which will be exposed to the gas manifold at all times. A normally-open pneumatic valve (PV7) will separate the gas loading section of the manifold to the sample/vacuum pump section of the manifold. The PV7 valve will allow for purging of the sample side without affecting the gas loading side, a procedure which will be utilized for desorption measurements. To prevent damage in the event of an over-pressurization, two high pressure burst disks connected to large expansion volumes are included in the GHS. The burst disks will activate when pressures exceed 243 bar. The expansion volumes are double-ended, with a ¼” NPT fitting on each side. Vacuum fittings will be connected to the ends opposite the GHS so the expansion volumes can be evacuated periodically.

<table>
<thead>
<tr>
<th>Component Abbreviated Name</th>
<th>Component description</th>
</tr>
</thead>
<tbody>
<tr>
<td>LFC#</td>
<td>Low-flow constrictor</td>
</tr>
<tr>
<td>PV#</td>
<td>Pneumatic Valve</td>
</tr>
<tr>
<td>MV#</td>
<td>Manual Valve</td>
</tr>
<tr>
<td>HPT</td>
<td>Pressure Transducer</td>
</tr>
<tr>
<td>LPT</td>
<td>Vacuum Transducer</td>
</tr>
<tr>
<td>BD#</td>
<td>Burst Disk</td>
</tr>
</tbody>
</table>

Table 1: Component abbreviations and their meanings.

The pressure ratings for all other components of the system (stainless steel tubing, valves and pressure transducers) are greater by at least a factor of 1.2. Pressure rating details of the GHS components can be found in Appendix III. The GHS will be connected to a pressure cell which is typically mounted either directly on the sample table or in one of the cryogenic environments (blue dewar cryostat for 2XC, PSD and TRIAX). **The GHS has been designed such that the failure of a single component will not lead to quick release of gas into the beam port floor.**
7. Special Facilities/Utilities/Equipment Required:
The GHS will require use of the house compressed air system to control the pneumatic valves, as well as access to the flammable gas exhaust port located on the beam port floor. Equipment necessary for operation of the PSD and 2XC have been listed in RL-61 and RL-33, respectively. The additional equipment necessary for the cooled experiments on 2XC includes liquid nitrogen for the blue dewar and the Beryllium filter cryostat.

The facilities and utilities are adequate. Equipment is specifically designed for this purpose and is adequate for the work to be performed. The radiation monitors used for dose rate measurements are maintained under the MURR Health Physics Instrument Program.

8. Safety Analysis:
The hazards and accident analysis below outline the possible scenarios that may arise during the normal operation of the GHS.

a) Gas Leak
The gas manifold portion of the GHS will be equipped with flammable gas detectors which will alert users in the unlikely event of a gas leak. The electronic components will be installed inside of a cart in order to minimize the risk of exposure to the gas of interest in the unlikely event of a gas leak. Control of valves near the gas manifold portion of the GHS are all either manually or pneumatically actuated to minimize the risk of sparks occurring near the gas of interest. In the unlikely event of a leak occurring on the beam port floor, the gas will be quickly diluted into the 6371 m$^3$ volume of the beam port floor. For $\text{H}_2$, the maximum volume at STP of gas used is 7.02 L. For $\text{D}_2$, the maximum volume at STP of gas used is 8.26 L. For $\text{CH}_4$ and $\text{CD}_4$, the maximum volume at STP of gas used is 9.39 L (see table in Appendix I). The lower flammability limits for $\text{H}_2$, $\text{CH}_4$, $\text{D}_2$, and $\text{CD}_4$ are 4.0, 4.9, 5.0 and 5.0%, respectively. Once expanded into the large volume of the beam port floor, the gases will be at concentrations of $1.1 \times 10^{-4}$%, $1.3 \times 10^{-4}$%, $2.5 \times 10^{-4}$% and $1.5 \times 10^{-4}$%, respectively. These concentrations are 4 orders of magnitude below their respective lower flammability limits. A passive release of gas into fresh air is expected to rise quickly, with turbulent mixing of gas with the air, pulling the plume apart. This is the dominant means, well above the dissipation due to chemical diffusion, by which gases with densities lower than air released in the room dissipate to concentration levels well below the lower explosive limit.

b) GHS Component Rupture
The GHS has been designed to withstand pressures above intake cylinder pressures available. The GHS system will only be handled by trained individuals. The gas manifold portion will be covered by a ventilated acrylic casing to protect the components. In the unlikely event of a component rupture, the safety considerations in a) will apply.

c) Over-pressurization
The GHS is equipped with three burst disk/expansion volume assemblies. One is placed on the GHS cart (“GHS-side”, BD1), one is connected directly to the blue dewar (“sample-side”, BD2), and the third is placed near the vacuum transducer on the GHS-side (BD3). BD1 and BD2 have been designed to burst when pressure exceeds 243 bar. BD3 has been designed to burst when
Pressure exceeds 3 bar. The GHS will operate both in low-pressure and high-pressure regimes. During low-pressure operation, over-pressurization occurs when the pressure at the vacuum transducer exceeds 2 bar. During high-pressure operation, over-pressurization occurs when the pressure at any section of the GHS exceeds 200 bar.

- Over-pressurization during low-pressure operation
  During low-pressure operation, gas is exposed to all three burst disk assemblies. Software will be designed to monitor the pressure on the vacuum transducer and close PV3 in event the pressure exceeds 2 bar. In the unlikely event of a failure to close PV3, BD3 will activate at 3 bar which will vent the gas to the flammable gas exhaust.

- Over-pressurization during high-pressure operation
  Although the burst pressure is larger than the maximum normal operation pressure, the burst pressure is much less than the pressure ratings for the GHS components. During gas loading, PV3 will be closed and the gas will be exposed to only BD1 and BD2. During neutron scattering measurements, the gas will be exposed to BD2 only.

  During gas loading, over-pressurization is unlikely as commercially available full gas cylinders are typically available at pressures only up to 170 bar. The maximum amount of gas to be used will be 0.390 moles (using CH₄ as worst-case scenario). In the event of an over-pressurization over 243 bar during sample loading, the burst disk assemblies will activate and the gas will expand into the additional 2,000 cc volume, reducing the pressure of the entire system to 7.45 bar.

  During neutron scattering measurements, the gas will be exposed only to the sample-side burst disk assembly (BD2). The maximum amount of sample-side gas is 0.148 moles. In the event of an over-pressurization over 243 bar during the neutron scattering measurements, the sample-side burst disk assemblies (BD2) will activate and the gas will expand into the additional 1,000 cc volume, reducing the pressure of the sample-side to 9.51 bar.

d) Failure of Cryostat
  During neutron scattering measurements, PV2 will be closed and therefore the sample side of the GHS will be isolated from the GHS-side. Therefore, the maximum volume involved in a plausible cryostat failure incident will be limited to the sample cell volume and line connecting to the GHS. In the event of a cryostat failure (such as rapid warm-up), the pressure on the sample-side will raise, potentially above the rated pressure of the GHS. The safety mechanisms in a) will take effect. Assuming that the gas used is loaded at 200 bar, the sample is at 77 Kelvin and that the entire portion of the line enclosed in the cryostat is at 77 Kelvin, there would initially be 2.5 cc at 77 Kelvin in the sample cell, 2.4 cc at 77 Kelvin in the cold line and 4.8 cc in the warm line. This is equivalent to 376 bar at 293 Kelvin. However, once the pressure exceeds 200 bar, the burst disk will activate and allow the gas to expand into the expansion volume. During the expansion, this pressure would quickly drop to 15 bar, well below the maximum pressure of the GHS.

e) Power Outage
The pneumatic valves connecting the GHS to the sample and other auxiliary components are normally-closed. In the event of a power outage to the GHS computer and electronic components, the valves will close to contain any gas within the GHS. As the cooling system relies on liquid coolant, it is not expected for a failure of the cryostat to occur due to power outages. However, in the event of a power-outage related over-pressurization, the safety mechanisms in a) will take effect. In the event of loss of control of the valves, the system will close all valves to components (PV1-6) to isolate the gas. The valve separating the gas manifold (PV-7) is normally open; in the event of a power outage, the valve will open and allow the gas to expand into the extra volume of the gas manifold to reduce the pressure and, in the event of a severe over-pressurization, access to the gas manifold burst disk and 1000 cc expansion volume.

f) **Loss of House Air Pressure**

Loss of house air pressure will result in a loss of control of the pneumatic valves controlling the GHS. The response of the system due to a loss of house air pressure will be identical to that of a power outage. In the unlikely event of a loss of house air pressure, the safety features outlined in e) will take effect.

9. **Handling Procedures for Radiation Safety Purposes:**

The handling procedures for radiation safety purposes of 2XC (RL-33), PSD (RL-61) and TRIAX (RL-46) apply. The GHS will not be exposed to the neutron beam during normal operation. Only the sample cell (RL-78, RL-84) will be exposed to the beam.

(a) The parts of the pressure cell which are exposed to the beam are made of aluminum alloy T6-6061. No long term activation of the pressure cell, powder sample or the gases is expected.

(b) When the pressure cell that has been exposed to the neutron beam is removed from the instrument it should be surveyed for activation. Parts may be surveyed by placing them near the shielded frisker located at the Health Physics work table on the beam port floor or may be surveyed by using an ionization chamber instrument. If there are any concerns or assistance is needed, contact Health Physics or Reactor Operations. **If a sample is to be removed from the beam port floor area, it must be checked and cleared by the Health Physics group.** In general, when a new sample and its associated shielding are placed in the neutron beam, the immediate area around the instrument should be surveyed by the approved worker to insure that a high radiation field has not been created. Note that the area radiation monitor will also be of some assistance in this determination.

(c) Activated samples are stored depending on the level of radioactivity in one of the storage ports or locked away in a designated storage cabinet.

(d) It is the responsibility of the approved worker to ensure they are wearing a whole body dosimeter, EPD, and extremity dosimetry (finger rings) each time they perform experimental manipulations such as sample changes.

(e) No special emergency procedure is required. The general facility procedures apply.

(f) Approval for the project leader and project co-leaders is requested from the MURR Reactor Manager and Health Physics Manager, since these individuals’ training and experience meet the requirements listed below. Authorizations for approved workers will be documented on the attached form.
The method for handling irradiated radioactive materials removed from the neutron beam is specified in the project application. No additional emergency planning should be required beyond that described for general emergency response to a containment isolation. In the event that the local area radiation monitor alarms, personnel will evacuate the local area and contact Health Physics and/or Reactor Operations.

10. **Administrative Controls and Training Requirements:**

   (a) Persons involved in this project are either authorized supervisors (scientists and postdocs who work with that project extensively and are typically involved longer than one year), approved workers (collaborators, visiting experimenters, graduate students and others who work on the project), or visitors (collaborators, students and others who work with that project for a short time and are typically involved for less than one week).

   (b) Due to the potential high radiation levels in the beams, all workers on this project will be trained and their training documented in the following manner.

      1. All workers will complete the MURR Training Program. All individuals who desire unescorted access to the beamport area will need to complete “Beamport Area Radiation Safety” training form.

      2. All workers will complete a MURR Form 150 “Statement of Individual Training,” to document their radiological experience and obtain a Class II level of training. A Class II level of training can be done at MURR. The Project Leader and the Health Physics Manager may approve equivalent training/experience at other facilities.

      3. All workers will have to have completed specialized training on the 2XC, PSD and TRIAX prior to being allowed to work unsupervised on any of these instruments. “2XC diffractometer at Beamport C”, “PSD diffractometer at Beamport D” and “TRIAX at Beamport A” training will be conducted by an authorized supervisor on site and documented on the training form. Training documentation for all approved workers and supervisors will be kept by the project leader.

      (c) Authorized supervisors, as a minimum, will need to complete Class I level of training.

      (d) Approved workers performing any work on this project are required to complete all training listed under 9(b) above.

      (e) Visitors performing any work on this project are required to take a special HP determined training and complete training listed under section 9(b)(3) above.

11. **Anticipated Radiation Doses and Contamination Levels:**

Radioactive materials will be stored in a way to contain contamination and maintain exposure rates in compliance with ALARA (as low as reasonably achievable). In order to obtain exposure rates ALARA, the following recommendations are made: It is recommended that the time spent close to the concrete shielding and the sample stage area be kept at a minimum during the operation of the instrument.

Whole body and extremity doses are expected to be reasonable during operation and set up. The use of gloves and prudent handling should be adequate to control the spread of contamination.

12. **Transfer, Waste Production, and Disposal Requirements:**
Transfer of radioactive samples to other MURR areas shall be done in accordance with procedure RP-HP-105, “Transfer of Radioactive Materials-In Facility” or approved equivalent.

Any transfer of radioactive material from the facility must have prior approval of campus Health Physics and be transferred by the PSO Shipping group.

Sample/components removed from the beamport floor area shall immediately be surveyed by the Health Physics group prior to leaving the building or carried to offices or other non-radiation areas.

Radioactive waste will be minimal in volume and will be processed through routine radioactive waste disposal.

12. **Other Approvals/Authorizations/Interfaces Required:**  
None Required

13. **Revision Analysis:**  
This is a new project for using the GHS on the 2XC, PSD and TRIAX neutron scattering instruments.

14. I have read the MURR Radiation Worker Procedures and recognize its application to my requested project in the utilization of radioactive material/radiation under the MURR Reactor License. I recognize my responsibility as a project leader to inform and provide a safe work environment for individuals at MURR in accordance with University and NRC requirements. I recognize my responsibility to maintain proper and current documentation in regard to utilization of radioactive material/radiation under this project authorization.

Evaluation Conducted and Submitted By:

<table>
<thead>
<tr>
<th>Health Physics: ________________________________</th>
<th>Date: ____________</th>
</tr>
</thead>
<tbody>
<tr>
<td>Project Leader: ________________________________</td>
<td>Date: ____________</td>
</tr>
<tr>
<td>Project Co-Leader: ______________________________</td>
<td>Date: ____________</td>
</tr>
</tbody>
</table>

15. **Approvals:**

<table>
<thead>
<tr>
<th>Reactor Manager: ________________________________</th>
<th>Date: ____________</th>
</tr>
</thead>
<tbody>
<tr>
<td>Health Physics Manager: _________________________</td>
<td>Date: ____________</td>
</tr>
</tbody>
</table>
Appendix I

Estimation of Amount of Gas Used

We can estimate the maximum amount of gas which will be used for each species by considering the GHS volume to be completely full of the gas species at a pressure of 200 bar at 300K and the sample volume to be completely full of the gas species at a pressure of 200 bar and the lowest temperature of interest (77K for H₂/D₂, 190K for CH₄/CD₄). The density of the gas in each portion is determined from NIST tables. Note that due to the presence of the adsorbent material, the actual amount used will be less than stated in the table. Further, the entire sample-side temperature is assumed to be the lowest temperature of interest, however a temperature gradient will exist in the gas line and the true amount of gas in the line will be less than stated.

<table>
<thead>
<tr>
<th>Gas Species</th>
<th>( \rho_{\text{GHS}} ) (200bar,300K) (g/cm(^3))</th>
<th>( \rho_{\text{Sample-side}} ) (200bar,T) (g/cm(^3))</th>
<th>Max. Mass (g)</th>
<th>Max Moles (millimoles)</th>
<th>Volume at STP (liters)</th>
<th>Lower Flammability Limit (V/V) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>0.0114(^1)</td>
<td>0.0497(^1)</td>
<td>0.584</td>
<td>292</td>
<td>7.02</td>
<td>4.0(^3)</td>
</tr>
<tr>
<td>D₂</td>
<td>0.0288(^1)</td>
<td>0.105(^1)</td>
<td>1.37</td>
<td>343</td>
<td>8.26</td>
<td>4.9(^4)</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.155(^1)</td>
<td>0.331(^1)</td>
<td>6.24</td>
<td>390</td>
<td>9.39</td>
<td>5.0(^5)</td>
</tr>
<tr>
<td>CD₄</td>
<td>0.194(^2)</td>
<td>0.414(^2)</td>
<td>7.82</td>
<td>390</td>
<td>9.39</td>
<td>5.0(^6)</td>
</tr>
</tbody>
</table>

References
2. Estimated assuming same molar density as CH₄
Appendix II
Gas Handling System Schematics

Figure 1: Gas Manifold schematics

GHS Volume: 25 cc
“Warm-line” Volume: 4.8 cc
“Cold-line” Volume: 2.4 cc
Sample Cell Volume: 2.5 cc
Figure 2: Pneumatic Manifold schematics
Figure 3: Electronic components schematic.
## Appendix III

### GHS Component Pressure Ratings

<table>
<thead>
<tr>
<th>Manifold System Parts Description</th>
<th>Pressure Rating (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OMEGA 245 bar Pressure Transducer</td>
<td>1034</td>
</tr>
<tr>
<td>MKS 974 QuadMag Cold Cathod/MicroPirini/Piezo Vacuum Transducer</td>
<td>29¹</td>
</tr>
<tr>
<td>SWAGELOK 316 SS Welded VCR Face Seal Fitting, 1/4 in. Rotating Female Union</td>
<td>550</td>
</tr>
<tr>
<td>SWAGELOK 316 SS VCR Face Seal Fitting, 1/4in. Union Tee</td>
<td>690</td>
</tr>
<tr>
<td>SWAGELOK 316 SS VCR Face Seal Fitting, 1/4 in. Double Male Union Body</td>
<td>550</td>
</tr>
<tr>
<td>SWAGELOK 316 SS VCR Face Seal Fitting, 1/4in. Union Elbow Body</td>
<td>350</td>
</tr>
<tr>
<td>SWAGELOK 316L SS Double-Ended TPED-Compliant Cylinder, 1/4 in. FNPT, 1000 cm³, 300 bar (4350 psig)</td>
<td>300</td>
</tr>
<tr>
<td>SWAGELOK Stainless Steel High-Pressure Bellows-Sealed Valve, 1/4 in. Female Swagelok VCR Face Seal Fitting, NC Actuator</td>
<td>723</td>
</tr>
<tr>
<td>SWAGELOK Low flow needle valve (0.004Cv) SS Low-Flow Metering Valve, 1/4 in. Male Swagelok VCR Metal Gasket Face Seal Fitting, Vernier Handle</td>
<td>344</td>
</tr>
<tr>
<td>SWAGELOK SS Bellows-Sealed Valve, Gasketed, Spherical Stem Tip, 1/4 in. Female Swagelok VCR Face Seal Fitting, SC-11 Cleaned</td>
<td>723</td>
</tr>
<tr>
<td>SWAGELOK 316 SS VCR Face Seal Fitting, 1/8 in. Cap</td>
<td>550</td>
</tr>
<tr>
<td>SWAGELOK 316 SS VCR Face Seal Fitting, 1/8 in. Plug</td>
<td>550</td>
</tr>
<tr>
<td>SWAGELOK 316 SS VCR Face Seal Fitting, 1/4 in. Union Cross</td>
<td>690</td>
</tr>
<tr>
<td>SWAGELOK 316 SS VCR Face Seal Fitting, 1/4 in. Union Elbow</td>
<td>550</td>
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</tbody>
</table>

¹ Note MKS 974 is a vacuum transducer and will not be exposed to gas during high pressure operation. A low-pressure burst disk will be installed to prevent over-pressurization and rupture (see Section C).
Appendix D

Quasi-elastic Neutron Scattering Data
D.1 Dry GOF

Figure D.1: $S(Q, \omega)$ for the “dry” GOF sample at 40K for $Q = 0.3 - 0.9$ Å$^{-1}$. 
Figure D.2: Fit parameters for “dry” GOF sample at 40 K for $Q = 0.3 - 0.9 \, \text{Å}^{-1}$. 

(a) $q = 0.3$

(b) $q = 0.5$

(c) $q = 0.7$

(d) $q = 0.9$
Figure D.3: $S(Q,\omega)$ for the "dry" GOF sample at 40K for $Q = 1.1 - 1.7$ Å$^{-1}.$
Figure D.4: Fit parameters for “dry GOF” sample at 40 K for $Q = 1.1 - 1.7 \text{ Å}^{-1}$. 

(a) $q=1.1$

<table>
<thead>
<tr>
<th>Curve 1: DELTA</th>
<th>Curve 2: BACKGROUND</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_0$: area: 5.807e+000 +/- 2.571e-002</td>
<td>$q_2$: offset: 3.554e-005 +/- 1.928e-005</td>
</tr>
<tr>
<td>$q_1$: center: -6.358e-002 +/- 6.412e-003</td>
<td>$q_3$: slope: 0.000e+000 +/- 0.000e+000</td>
</tr>
<tr>
<td>Chi-squared: 0.930</td>
<td>Chi-squared: 0.717</td>
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</table>

(b) $q=1.3$

<table>
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<tr>
<th>Curve 1: DELTA</th>
<th>Curve 2: BACKGROUND</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_0$: area: 5.739e+000 +/- 2.531e-002</td>
<td>$q_2$: offset: 3.302e-005 +/- 0.000e+000</td>
</tr>
<tr>
<td>$q_1$: center: -4.174e-002 +/- 7.005e-003</td>
<td>$q_3$: slope: 0.000e+000 +/- 0.000e+000</td>
</tr>
<tr>
<td>Chi-squared: 0.984</td>
<td></td>
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</table>

(c) $q=1.5$

<table>
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<tr>
<th>Curve 1: DELTA</th>
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<tr>
<td>$q_0$: area: 5.807e+000 +/- 2.571e-002</td>
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<td>$q_3$: slope: 0.000e+000 +/- 0.000e+000</td>
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<tr>
<td>Chi-squared: 0.930</td>
<td>Chi-squared: 0.717</td>
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(d) $q=1.7$

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<tr>
<td>$q_0$: area: 5.739e+000 +/- 2.531e-002</td>
<td>$q_2$: offset: 3.302e-005 +/- 0.000e+000</td>
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<tr>
<td>$q_1$: center: -4.174e-002 +/- 7.005e-003</td>
<td>$q_3$: slope: 0.000e+000 +/- 0.000e+000</td>
</tr>
<tr>
<td>Chi-squared: 0.984</td>
<td></td>
</tr>
</tbody>
</table>
Figure D.5: $S(Q, \omega)$ for the “dry” GOF sample at 300K for $Q = 0.3 - 0.9$ Å$^{-1}$.
Figure D.6: Fit parameters for “dry GOF” sample at 300 K for $Q = 0.3 - 0.9 \text{ Å}^{-1}$. 

(a) $q = 0.3$

(b) $q = 0.5$

(c) $q = 0.7$

(d) $q = 0.9$
Figure D.7: $S(Q, \omega)$ for the “dry” GOF sample at 300K for $Q = 1.1 - 1.7 \, \text{Å}^{-1}$. 

(a) $q=1.1$

(b) $q=1.3$

(c) $q=1.5$

(d) $q=1.7$
Figure D.8: Fit parameters for “dry GOF” sample at 300 K for $Q = 1.1 - 1.7 \text{ Å}^{-1}$.
D.2 Hydrogen-Loaded GOF

D.2.1 15 bar

Figure D.9: QENS spectra, fits and residuals for the 15 bar, 35K measurement for $Q = 0.5 - 1.1 \text{ Å}^{-1}$.
Figure D.10: Fit parameters for the 15 bar, 35 K measurement for \( Q = 0.5 - 0.9 \text{ Å}^{-1} \).
Figure D.11: QENS spectra, fits and residuals for the 15bar, 35K measurements for $Q = 1.3 - 1.7 \, \text{Å}^{-1}$.
Figure D.12: Fit parameters for the 15 bar, 35 K measurement for $Q = 1.1 - 1.7 \text{ Å}^{-1}$.
D.2.2 45 bar

Figure D.13: QENS spectra, fits and residuals for the 45 bar, 35K measurement for $Q = 0.3 - 0.9 \text{ Å}^{-1}$. 

(a) $q=0.3$  
(b) $q=0.5$  
(c) $q=0.7$  
(d) $q=0.9$
Curve 1: Delta
#0: area: 5.631e+000 +/- 8.354e-003
#1: center: -1.176e+000 +/- 4.907e-001

Curve 2: Background
#2: offset: 9.937e-003 +/- 4.905e-005
#3: slope: -3.159e-006 +/- 6.832e-007

Curve 3: Lorentzian
#4: area: 1.234e+001 +/- 9.132e-003
#5: center: -1.176e+000 +/- 0.000e+000
#6: FWHM: 1.217e+001 +/- 1.887e+000

Chi-squared: 1.430

(a) q=0.3

Curve 1: Delta
#0: area: 5.631e+000 +/- 8.354e-003
#1: center: -1.176e+000 +/- 4.907e-001

Curve 2: Background
#2: offset: 9.937e-003 +/- 4.905e-005
#3: slope: -3.159e-006 +/- 6.832e-007

Curve 3: Lorentzian
#4: area: 1.234e+001 +/- 9.132e-003
#5: center: -1.176e+000 +/- 0.000e+000
#6: FWHM: 1.217e+001 +/- 1.887e+000

Chi-squared: 1.430

(b) q=0.5

Curve 1: Delta
#0: area: 3.582e+000 +/- 4.079e-003
#1: center: -9.124e+000 +/- 2.893e-003

Curve 2: Background
#2: offset: 6.976e-003 +/- 1.073e-004
#3: slope: -4.562e-006 +/- 7.538e-007

Curve 3: Lorentzian
#4: area: 1.503e-001 +/- 2.670e-002
#5: center: -9.124e-003 +/- 0.000e+000
#6: FWHM: 4.808e+001 +/- 1.010e+001

Chi-squared: 1.150

(c) q=0.7

Curve 1: Delta
#0: area: 6.692e+000 +/- 7.453e-003
#1: center: -1.204e+000 +/- 1.495e-003

Curve 2: Background
#2: offset: 4.897e-003 +/- 4.293e-005
#3: slope: 2.485e-007 +/- 4.683e-007

Curve 3: Lorentzian
#4: area: 9.807e-002 +/- 8.028e-003
#5: center: -6.678e-003 +/- 0.000e+000
#6: FWHM: 1.702e+001 +/- 2.920e+000

Chi-squared: 1.550

(d) q=0.9

Figure D.14: Fit parameters for the 45 bar, 35 K measurement for $Q = 0.3 - 0.9 \text{ Å}^{-1}$.  

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Figure D.15: QENS spectra, fits and residuals for the 45bar, 35K measurements for $Q = 1.3 - 1.7$ Å$^{-1}$.
Figure D.16: Fit parameters for the 45 bar, 35 K measurement for \( Q = 1.1 - 1.7 \) Å\(^{-1}\).
D.2.3 75 bar

Figure D.17: QENS spectra, fits and residuals for the 75bar, 35K measurements for $Q = 0.5 - 1.1 \text{ Å}^{-1}$. 
Curve 1: **DELTA**
   - #0: area: 5.436e+000 +/- 9.153e-003
   - #1: center: -2.083e-002 +/- 4.252e-001

Curve 2: **BACKGROUND**
   - #2: offset: 1.109e-002 +/- 5.290e-005
   - #3: slope: -2.754e-006 +/- 7.155e-007

Curve 3: **LORENTZIAN**
   - #4: area: 1.385e-001 +/- 4.92e-003
   - #5: center: -2.083e-002 +/- 0.000e+000
   - #6: FWHM: 1.133e+001 +/- 1.658e+000

Chi-squared: 1.572

(a) $q=0.5$

Curve 1: **DELTA**
   - #0: area: 5.345e+000 +/- 7.128e-003
   - #1: center: -9.416e-003 +/- 2.032e-001

Curve 2: **BACKGROUND**
   - #2: offset: 6.722e-003 +/- 4.720e-005
   - #3: slope: 3.005e-007 +/- 5.886e-007

Curve 3: **LORENTZIAN**
   - #4: area: 1.043e-001 +/- 8.279e-003
   - #5: center: -9.416e-003 +/- 0.000e+000
   - #6: FWHM: 1.571e+001 +/- 2.662e+000

Chi-squared: 1.438

(b) $q=0.7$

Curve 1: **DELTA**
   - #0: area: 6.437e+000 +/- 3.886e-002
   - #1: center: -1.353e-002 +/- 6.795e-004

Curve 2: **BACKGROUND**
   - #2: offset: 5.579e-003 +/- 4.184e-005
   - #3: slope: -1.310e-006 +/- 5.273e-007

Curve 3: **LORENTZIAN**
   - #4: area: 1.076e-001 +/- 7.932e-003
   - #5: center: -1.353e-002 +/- 0.000e+000
   - #6: FWHM: 1.432e+001 +/- 2.265e+000

Chi-squared: 1.281

(c) $q=0.9$

Curve 1: **DELTA**
   - #0: area: 4.431e+000 +/- 3.238e-003
   - #1: center: 2.770e-003 +/- 1.842e-001

Curve 2: **BACKGROUND**
   - #2: offset: 4.490e-003 +/- 3.408e-005
   - #3: slope: -5.129e-008 +/- 4.534e-007

Curve 3: **LORENTZIAN**
   - #4: area: 9.958e-002 +/- 6.789e-003
   - #5: center: 2.770e-003 +/- 0.000e+000
   - #6: FWHM: 1.099e+001 +/- 1.719e+000

Chi-squared: 1.323

(d) $q=1.1$

Figure D.18: Fit parameters for the 45 bar, 35 K measurement for $Q = 0.5 - 1.1 \text{\AA}^{-1}$. 

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Figure D.19: QENS spectra, fits and residuals for the 75bar, 35K measurements for \( Q = 1.3 - 1.7 \text{ Å}^{-1} \).
Figure D.20: Fit parameters for the 75 bar, 35 K measurement for $Q = 1.3 - 1.7 \, \text{Å}^{-1}$.
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[56] F. Salles, A. Ghoufi, G. Maurin, R.G. Bell, C. Mellot-Draznieks, and G. Férey. Molecular dynamics simulations of breathing MOFs: Structural transforma-


VITA

Matthew James Connolly was born on May 20, 1986 in Dubuque, Iowa. In 2008 he received a Bachelor of Science degree in Physics from the University of Northern Iowa in Cedar Falls, Iowa. He then moved to Columbia, Missouri to begin graduate work under the supervision of Dr. Carlos Wexler. He graduated with a Ph.D. in Physics in December 2014.

Matthew will begin work under a National Research Council fellowship at the National Institute of Standards and Technology in Boulder, Colorado, in December 2014. There he will study hydrogen-embrittlement and hydrogen-assisted fatigue crack growth in pipeline steels using various neutron scattering techniques.