

**Physical Adsorption of Linear Hydrocarbon Quadrupoles on
Graphite and MgO (100): Effects of the Compatibility of
Surface and Molecular Symmetries**

A Dissertation Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Andrew Jesse Pedersen
August 2021

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This work is dedicated to the memory of my mother, who longed to see this day and would surely have cheered me on as only a mother can do.

Acknowledgements

The completion of my Doctorate in Chemistry is the product of much mentorship, collaboration, and fortuitous opportunities afforded me by countless individuals. Though I cannot list all who have had an impact on me reaching this substantial pursuit, I would first like to thank my family for their support and patience. My mom Debbie, dad Mark, brothers Eric and Brian, sisters-in-law Lee and Chandler, mother-in-law Rhonda, and nieces and nephews George, Thea, and Charles have always provided support and patience and never once made me doubt that I could achieve my goal. A special thanks is further owed to my wife, Alisha, who was always there for me through this process, not only with patience and understanding, but as a source of motivation and inspiration that was truly indispensable to me. Similarly, my closest friends Grant, Scott, and Connor, as well as mentors during my undergraduate and Master's careers including Monica Rabinovich and Drs. Marcus Jones and Michael Murphy, accompanied me before and during this journey. Such a journey would not have been possible without my advisor, Dr. John Z. Lares, who afforded me many opportunities to advance my skillset, learn how to resolve challenging problems, and mature in my self-sufficiency. Other individuals within the University of Tennessee, Knoxville's Department of Chemistry who impacted my ability to achieve a doctorate while also fostering my interest in teaching include Drs. Charles Feigerle (former Department Head), Viktor Nimyken (current Department Head), Shawn Campagna (Associate Department Head), and Nalah Hatab (Lecturer and Director of General Chemistry Laboratories). Lastly, I could not have completed the work presented in this document without the help of my fellow groupmates, past and present, including Nick Strange, Fatema Wahida, Daniele Paradiso, Zach Stroupe, Luther Langston, and Chris Crane.

Abstract

The process of physical adsorption finds a practical role in wide-ranging fields from catalysis, to lubrication, and even optoelectronics. Furthermore, it provides a mechanism to probe the fundamental understanding of intermolecular forces and how symmetries can play a role in the behavior of a system. Linear quadrupoles preferentially adopt square-T configurations when confined in two dimensions. This would lead the system to adopt a four-fold symmetry in the molecular lattice.

Two archetypal surfaces often studied in physisorption research are MgO (100), which has a four-fold symmetry of alternating charges, and the basal plane of graphite, which has a six-fold symmetry to its non-polar, weakly corrugated surface. These differing surface symmetries provide two test cases for comparison. In the case of MgO (100), the molecule-molecule and molecule-surface interaction are synergistic, both driving the film towards the same symmetry; whereas for graphite, the six-fold surface symmetry is incompatible with the preferred four-fold interaction symmetry of the molecules. This presents the opportunity for structurally frustrated systems to arise.

Acetylene and allene are both simple, linear, rigid hydrocarbons with large quadrupole moments of similar strength. The most distinct variations between these two molecules are size and axial rotational symmetry. These molecules, just like the surface, provide two simple, but contrasting symmetry effects. The simple $D_{\infty h}$ point group of truly linear molecules of acetylene allow for them to lie completely flat against a surface. The 90-degree dihedral angle between the hydrogen pairs on opposing sides of allene molecules prevent them from easily being able to lie perfectly flat against the surface, creating another opportunity for broken symmetry in the molecule-surface interactions – this instance in the vertical direction rather than the two dimensional adsorption plane.

This investigation aims to study the behavioral properties of acetylene and allene films through thermodynamic, structural, and phase behavior analyses when adsorbed on both graphite and MgO. To this end, a combination of volumetric adsorption isotherms, elastic neutron diffraction, and computational modeling have been employed.

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Chapter 1 – Introduction and Background

1.1 – Overview

The phenomenon of the physical adsorption of volatile molecules on solid surfaces is a topic that has been researched for centuries. Though often overlooked by laymen, it has found a wide range of uses in applied and fundamental studies. The processes involved are inescapable to notice even in trivial examples in everyday life if one looks closely enough, from the fog on a mirror after a hot shower, to the behavior of one's hair on a humid day. More importantly, many processes and reactions occur at the boundaries between phases and are the basis of heterogeneous catalysis.

1.1.1 – Early History

As far back as 1450, there are records of devices created with the intent to study the process of physical adsorption. Leonardo da Vinci, and several of his contemporaries, were even known to have observed the process using balances loaded with textile fibers to visualize mass changes that resulted from the adsorption of water vapor¹⁻³. Such devices lead to the development of the first simple and reliable hygrometers². In the 1780's, a hygrometer using hair was developed that brought such devices to the masses², and is so reliable that high-end hygrometers today still utilize filaments of human hair.

The first modern and quantitative research began in 1773, when the reversible uptake of air by charcoal was studied by Carl Wilhelm Scheele⁴. These experiments with charcoal eventually lead in 1814 to the proposal by de Saussure that the adsorption capacity and surface area were intrinsically linked. A few decades later, in 1843, this theory was challenged with the conjecture that pores in charcoal played a prominent role in the process³. It would turn out, in time, that both of these viewpoints have validity and were describing two related phenomena: adsorption, the binding of molecules to the surface of a solid material, and absorption, the uptake of gas into a pore network in a solid material. The resolution of this and the importance of the distinction may not have occurred for several more decades, however, as the first recorded use of the term “adsorption” dates to 1883³. The term “adsorption” is now so ubiquitous that it is often used as a malapropism to refer to absorption by pores as well as its correct usage as a surface phenomenon. The true growth of this field into a large area of research interest did not

occur until the 20th century, as the ability to make pristine, high-surface area materials and the improvement and standardization of measurement techniques became a reality^{1-3, 5}.

1.1.2 – Applications

The study of physical adsorption and absorption have been useful in providing great fundamental understanding on the nature of intermolecular interactions. It has provided key incites in the area of surface science and statistical mechanics⁵⁻¹⁰. Beyond this, it also has practical applications in important areas of research such as catalysis¹¹⁻¹³, gas storage^{11, 14}, separation science^{11, 15}, and optical and thin film electronics^{11, 16}. Additionally, it plays a role in applications encountered more commonly, such as adhesion, lubrication, detergency, and corrosion inhibition¹⁶. Charcoal, the substance that initiated widespread interest in these phenomena, is now even used as a cheap and effective water filter due to its high capacity and ability to sorb many contaminants from solution. Furthermore, volumetric adsorption isotherms, used to analyze the thermodynamics of adsorption, are a standard technique in the assessment of specific surface area and porosity of materials^{3, 5, 6, 8, 11, 16}. High-surface area and porous network materials are even finding useful avenues in biomaterials and regenerative medicine in the present day¹⁷⁻²⁴

A more recent area where these studies find potential usefulness is in the study of two-dimensional materials. Since the isolation of graphene less than two decades ago, the search for other two-dimensional systems has proved difficult²⁵. The two-dimensional nature of adsorbed monolayer films provides an alternative method for the fabrication and study of such systems. While these films often lack the stability and permanence of materials like graphene, the number of possible systems that can and have been derived provide many possibilities in the exploration of the world of two-dimensional materials.

1.1.3 – Experimental Methods in Adsorption Science

Investigations on thin films seek to characterize not only the process of adsorption itself, but also the properties of the phases and structures that result. These examinations typically involve the characterization of thermodynamics, phase transitions, film structure, and dynamics (phonons, vibrations, rotations, diffusion, etc.). A large variety of experimental techniques are available to this end, having different purposes, some of which may work well for some systems,

but not others. The following will not be an exhaustive list of possibilities, but will largely touch on techniques directly relevant to the studies in this work.

Perhaps the most widely utilized of these techniques is volumetric adsorption isotherms due to their relative ease of measurements and reliable mathematical models. Isotherms explore the adsorbed amounts and capacities of a film as a function of the equilibrium pressure with the three-dimensional vapor phase. These assist primarily in the analysis of the phase behaviors and thermodynamics of adsorbed systems²⁶. Other methods may be used to analyze the structural ordering or dynamics of molecules within a film. Alternatively, calorimetry is used to examine the enthalpy and specific heats of adsorption and to locate potential phase changes²⁷. These measurements can differ in the direction they pass through the phase diagrams (isotherms are constant temperature; calorimetry is at constant coverage), but ideally yield the same or complementary information.

Surface structure measurements can be either direct (i.e. real space²⁸⁻³⁰) or indirect (i.e. reciprocal space^{29, 31-33}). The most common and viable forms of direct structural imaging of a surface are atomic force microscopy (AFM) and scanning tunneling electron microscopy (STM). Both methods are tip-based scanning techniques that are easily capable of atomic scale resolution²⁹. During imaging, the tip remains in close proximity to the surface and itself will interact with the surface it is measuring. For solid surfaces or strongly adsorbed systems with chemisorbed molecules or large physisorbed molecules (see section 1.2.1), these interactions would not significantly impact the surface structure and reliable real space images can be obtained^{29, 34, 35}. However, in more weakly bound systems, the perturbation of the molecules by the probe tip as it scans may significantly alter the structure it is trying to measure⁵. Additionally, dynamic film structures, those with high equilibrium vapor pressure or high surface mobility of molecules, will always be in flux, preventing direct imaging. Other real space imaging methods include field emission microscopy (FEM) and field ion microscopy (FIM). The best resolution of these techniques is approximately 3 Å, falling short of the required resolution for accurate structural measurements¹⁶. Furthermore, all of these imaging methods ideally require single crystal surfaces, with a comparatively small surface area. This makes it more difficult, though not at all insurmountable, to accurately control the amounts adsorbed.

Indirect structural measurements are those obtained of the reciprocal lattice through elastic diffraction experiments (section 1.5). The three primary types of scattering probes used are x-rays, electrons, and neutrons, which are discussed in the introduction to the aforementioned section. These methods are all easily performed on powders and can measure an ensemble average structure in both time and space. The dynamics of adsorbed films may also be probed through quasielastic and inelastic diffraction experiments. Quasielastic measurements probe small random motions within the film^{36, 37} (e.g. diffusion) and inelastic diffraction probes higher energy motions^{33, 38} (e.g. phonons and vibrations). As a result, diffraction represents the most common structural analysis tool for adsorbed systems.

Computational methods can be used to supplement these experimental methods to hopefully provide a clear picture of microscopic behaviors. These can be used to examine preferred adsorption sites between a single molecule and the surface by employing geometry optimizations, or as an ensemble of an entire adsorbed system using molecule dynamics simulations. In theory, these are capable of providing the clearest and most direct view of the microscopic behavior of a film; thus, these are useful in providing potential explanations of observed experimental behaviors. For example, computational methods may help narrow down structural candidates for refinement of diffraction data or the examination of the mechanism of melting within a film²⁹.

1.1.4 – Competition of Symmetries

The exact characteristics of two-dimensional adsorbed systems are determined by the interplay between the molecule-molecule interactions and the molecule-surface interactions. While the type and relative strength of these interactions are critical to describe such systems, of equal importance are the relative symmetries of these interactions. When the symmetries are compatible (e.g. three-fold and six-fold), along with the relative size scales, synergistic relations between the intermolecular interactions and the molecule-surface interactions can result. Conversely, when the systems are comprised of incompatible symmetries (e.g. four-fold and six-fold), or if the molecular size and surface lattice are too different, competition between the molecule-molecule and molecule-surface interactions can result, in turn resulting in potentially frustrated structures and interesting phase behaviors.

1.2 – Adsorption and Wetting Behavior

Adsorption is the physical process that occurs between a fluid phase (liquid or gas) and a solid phase, in which there is an increase in molecular density or concentration at the interface of these phases³⁹. While adsorption, therefore, is not limited to gas-solid systems^{6, 11}, the work of this dissertation will pertain exclusively to such cases. The process occurs when the forces between free molecules and the substrate surface are sufficiently strong that, when the molecule impinge on the surface, they are trapped in a potential energy well and “stick” to the surface. The nature of the forces involved govern how strongly molecules can bind and, consequently, the properties of the adsorbed film.

1.2.1 – Types of Adsorption

Adsorption processes are divided into two major classifications: physical adsorption (physisorption) and chemical adsorption (chemisorption)⁴⁰. The distinction between these two groups is due to the nature of the molecule-surface interactions. In chemisorption, the binding of molecules to the surface involves the exchanging of electrons, thus forming a chemical bond between molecule and surface. Examples of this are the passive oxidation layers that develop on metals like aluminum upon exposure to air⁴¹ and the adsorption of thiol-based molecules onto metals like copper⁴² and gold⁴³. Alternatively, physisorption, as pertains to this study, arises from the interaction of intermolecular forces (i.e. van der Waal’s and electrostatic interactions)^{5, 6, 11}.

These two processes represent opposing ends on the spectrum of adsorption energies. Since chemisorption involves the formation of chemical bonds, it refers to the higher end of this spectrum, with a typical range of 100 to 500 kJ mol⁻¹. At the opposing end lies physisorption, with 5 to 50 kJ mol⁻¹ being the normal range⁶. Additionally, the average time that a molecule remains in contact with the surface varies with the strength of the interaction. In physisorption, the time scales are approximately on the order of nanoseconds, whereas in chemisorption can be on the scale of seconds to even years⁶. Though some cases fall in the midpoint between these two extremes and may not be considered to be purely physical nor chemical adsorption, this classification is an acceptable general reference for most systems.

1.2.2 – Surface Wetting

Wetting is the term used to describe the way in which a fluid makes and maintains contact with a solid surface. This process is easily observed in relation to bulk phases of matter in the behavior of droplets of water or other liquids on a solid surface. The forces that govern this process for bulk condensed phases are the same as those in physically adsorbed thin films. Therefore, the description of adsorption in terms of wetting is often used.

1.2.2.1 – Wetting in the Bulk Phase

The most easily and commonly observable form of physical adsorption is the bulk condensation of gas phase molecules onto a surface. An everyday example of this is in condensed water vapor onto the surface of a drinking cup. One might also observe in this context that the nature of the droplets formed can vary depending on the materials the cup is made from, whether it be plastic, glass, or metal. As already mentioned, when a condensed phase forms on a surface, it is the relative strength of the molecule-molecule and molecule surface interactions that govern its behavior. In a system of bulk matter, like the droplets on the side of a glass, these forces emerge in the form of surface tensions (γ) at the resulting interfaces between the surface (s), liquid (l), and the interface (or vapor) region (v). The minimization of surface energy from these competing phases leads to the formation of droplets, whose contact angle with the surface is given by:

$$\cos\theta = \frac{\gamma_{s,v} - \gamma_{s,l}}{\gamma_{l,v}} \quad (1.1)$$

where θ is the surface contact angle and $\gamma_{m,n}$ is the surface tension at the interface between the two respective phases of the given indices^{6, 11, 44}.

Based on the behavior of the contact angle, surface wetting can be broadly categorized into three regimes: non-wetting, incomplete wetting, and complete wetting (Figure 1.1). In the non-wetting case, the liquid molecules have no adhesion with the surface, and the liquid forms a spherical droplet with a contact angle of 180°. At the other end of this spectrum, complete wetting is defined at a contact angle of 0°. In this situation, the liquid spreads out evenly on the surface into a flat film of uniform thickness. The intermediate regime between these two extremes is incomplete wetting, which is characterized by drops that are truncated spheres with contact angles between 0° and 180°.

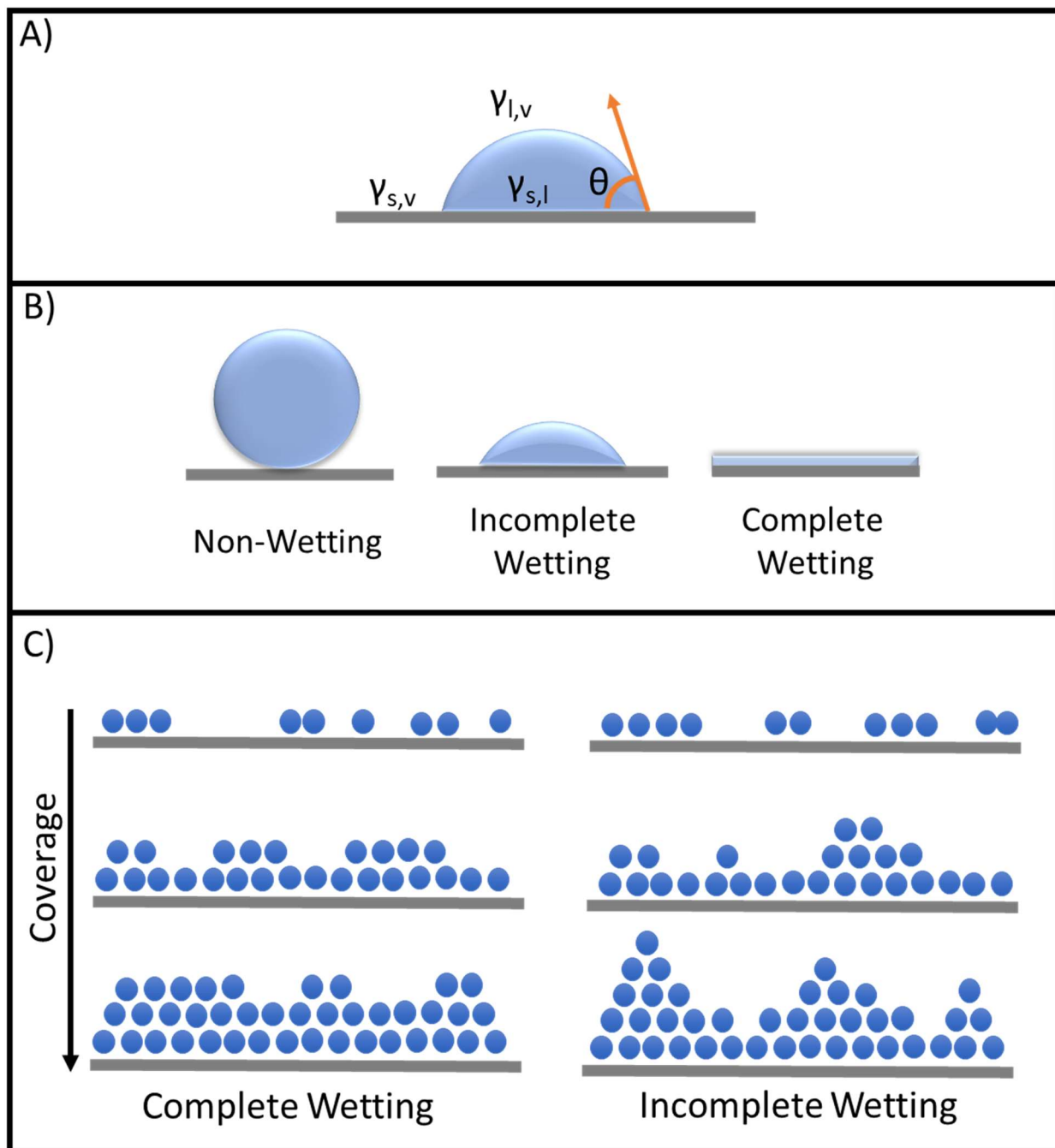


Figure 1.1: Surface Wetting in bulk and adsorbed systems

A) Contact angle of a droplet

B) The three cases for wetting in bulk condensed phases

C) Types of wetting as applied to adsorbed film growth

1.2.2.2 – Wetting in Two Dimensions

The adsorption of gases onto solid surfaces can result in the formation of molecularly thin adfilms with a quasi-two-dimensional nature. The process involves the strength and competition between the molecule-molecule and molecule-surface interactions; thus, adsorbed film growth is analogous to bulk wetting and is often described using the same terminology⁴⁵. For the complete wetting case, the interactions between the molecules and the surface do not strain or overwhelm molecule-molecule interactions, and growth occurs in a layer-by-layer process. With incomplete wetting, the intermolecular forces within the film differ significantly from the molecule-surface interactions, causing a breakdown of the layer formation process. Initially, such systems may begin with layer growth, but as the number of molecules deposited into the film increases, formation of discrete layers is replaced by a continuous transition to the bulk phase. A non-wetting case would refer to a lack of adsorption and might seem to be irrelevant to most discussions of film growth. However, systems of complete wetting may demonstrate regions of non-wetting in between each layering transition. A second possibility that is demonstrated for a system in this dissertation is a non-wetting transition that immediately transitions into bulk condensation without any convergence between the two-dimensional and three-dimensional phases.

1.3 – Forces and Interactions in Physical Adsorption

One way to view physical adsorption is that it is simply a consequence of intermolecular forces. This is a gross over-simplification, as is the case of many emergent phenomena when one tries to explain them through reduction to their basic physical principles. The real behavior of some adsorbed systems would be difficult or impossible to describe before empirical characterization based purely on an examination of these forces, and yet for others, some predictions can be made that are obvious. Whether or not the final state of a system is obvious from an examination of the forces involved, physical adsorption is a phenomenon driven purely by intermolecular forces of attraction and repulsion⁵. These interactions are most generally classified into two types: electrostatic and van der Waals^{5, 16}. Even the latter case here is electrostatic in origin when examined closely, the main difference between the two being one of strength and distance. The molecules to be examined in this dissertation have atypical electron distributions that result in a polarization most commonly described as a molecular quadrupole.

To understand these systems, a formalism of the concept of a quadrupole must be elucidated, as well as a consideration of several different types of van der Waals interactions.

1.3.1 – Electrostatic Forces

For many adsorbed systems, including the ones in this study, the description of charge distribution of the molecule or atom as being either simple monopole or dipole (as is what is generally assumed to be the case for ions and polar molecules), is insufficient to accurately describe their behavior. Higher-order multipoles, such as the quadrupole, octupole, or hexadecapole moments, often must be considered. Electrostatic potentials are described in the context of Coulomb's law. For a fixed point in space, $\vec{r}$, that is located at some location in space near a solitary point charge, the electric field at this point, $\varphi(\vec{r})$, is given by^{46, 47}:

$$\varphi(\vec{r}) = \frac{q}{4\pi\epsilon_0|\vec{r}-\vec{r}'|^2} = \frac{q}{4\pi\epsilon_0r^2} \quad (1.2)$$

where, ϵ_0 is the permittivity of free space, $\vec{r}'$ is the location of the point charge, and $|\vec{r} - \vec{r}'|$, or simply r , is the separation distance from the point charge. If N number of point charges are present, the effective electric field at $\vec{r}$ is simply the cumulative summation of individual point charges⁴⁶:

$$\varphi(\vec{r}) = \frac{1}{4\pi\epsilon_0} \sum_{i=1}^N \frac{q_i}{|\vec{r}-\vec{r}'|^2} \quad (1.3)$$

Though this formalism does not adequately describe the true nature of how charge within a molecule behaves, it does have relevance to molecular dynamics. For molecules, the charges are best described by a continuous charge distribution, $\rho(\vec{r}')$ (Figure 1.2), and replacing the summation above with an integral, the equation becomes:

$$\varphi(\vec{r}) = \frac{1}{4\pi\epsilon_0} \int \frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} d^3\vec{r}' \quad (1.4)$$

While this treatment of charge as a continuous distribution captures the nature of electron density within a polarized molecule, solving this equation must be done separately for every point in space, making it a computationally demanding proposition. For points that are a sufficient distance outside of the region of charge density, an approximation can be arrived at by a Laplace expansion of the $\frac{1}{|\vec{r}-\vec{r}'|}$ term. In spherical coordinates, this yields the solution:

$$\varphi(r, \theta, \phi) = \frac{1}{4\pi\epsilon_0} \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \frac{4\pi}{2l+1} \frac{q_{l,m}}{r^{l+1}} Y_{l,m}(\theta, \phi) \quad (1.5)$$

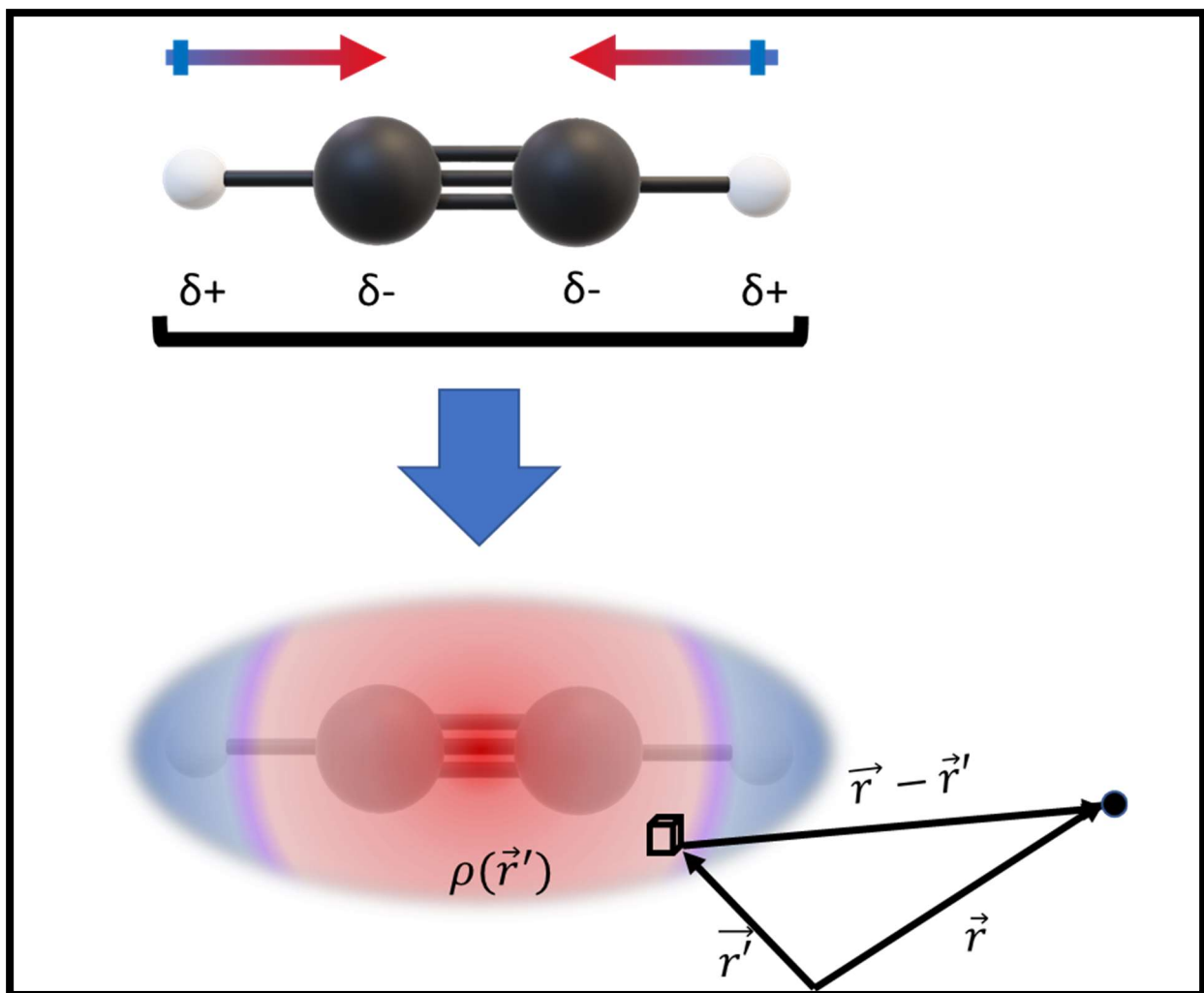


Figure 1.2: Bond polarity of a quadrupole molecule and the resultant continuous charge distribution

(Top): Gradient arrows show the direction of bond polarity for the acetylene molecule. Though the dipole moment is zero due to its symmetry, the pull of electrons towards the central carbon atoms results in an unequal distribution of charge (a linear quadrupole)

(Bottom): More accurate representation of electron density (charge distribution) within the molecule. The vectors shown are a depiction of those used in the derivation as explicated in the text

Figure based on derivation adapted from phys.libretexts.org⁴⁶

where:

$$q_{l,m} = \int \rho(\vec{r}') (r')^l Y_{l,m}^*(\theta', \phi') d^3r' \quad (1.6)$$

The function $Y_{l,m}(\theta, \phi)$ is familiar as the solutions to spherical harmonics⁴⁷ (Figure 1.3). This expansion, in essence, approximates the effects of a charge distribution by successive divisions of the electric field into angular moments with an increasing number of angular poles. The value of the term l refers to particular n-poles for each spherical moment given as powers of 2^l . Hence, the monopole moment is at $l = 0$, the dipole at $l = 1$, the quadrupole at $l = 2$, and so forth. The term m relates different orientational configurations for each n-pole. Equation 1.6 represents the multipole moment of each term in the expansion.

In the cases of molecules like acetylene and allene, the symmetries of the molecules means that the first non-vanishing term in the multipole expansion is the quadrupole moment, $q_{2,m}$ (or commonly also Θ), which is a tensor matrix that separates the moment into its dimensional components such that⁴⁸:

$$\Theta = \begin{pmatrix} \Theta_{xx} & \Theta_{xy} & \Theta_{xz} \\ \Theta_{yx} & \Theta_{yy} & \Theta_{yz} \\ \Theta_{zx} & \Theta_{zy} & \Theta_{zz} \end{pmatrix} \quad (1.7)$$

and with the electric potential being given by:

$$\varphi(\vec{r}) = \frac{1}{4\pi\epsilon_0 r^3} \sum_{ij} \Theta_{ij} \hat{r}_i \hat{r}_j \quad (1.8)$$

where i and j are the dimensional indices of the quadrupole tensor, and $\hat{r}_i$ and $\hat{r}_j$ are the components of the unit vector from $\vec{r}$ to $\vec{r}'$. The symmetry classes of these molecules also result in the charge distributions having no angular dependence on ϕ' , and thus exclude the non-zero values of m . For the $m = 0$ quadrupole, only the diagonal components of the tensor are non-zero. Further simplification also occurs in the symmetry relation of the remaining components such that $\Theta_{xx} = \Theta_{yy} = -2\Theta_{zz}$. The strength of axially symmetric quadrupoles, such as the molecules evaluated in this study, can be referred to solely by the value of Θ_{zz} .⁴⁹

The interaction energy for two linear quadrupolar molecules can be derived by considering a second charge distribution region interactive with the first such that:

$$V(\vec{r}) = \frac{1}{4\pi\epsilon_0} \int \varphi_1(\vec{r}) \rho_2(\vec{r}') d^3r' \quad (1.9)$$

which, when expanded in a Taylor series, results in the potential energy for two interacting linear

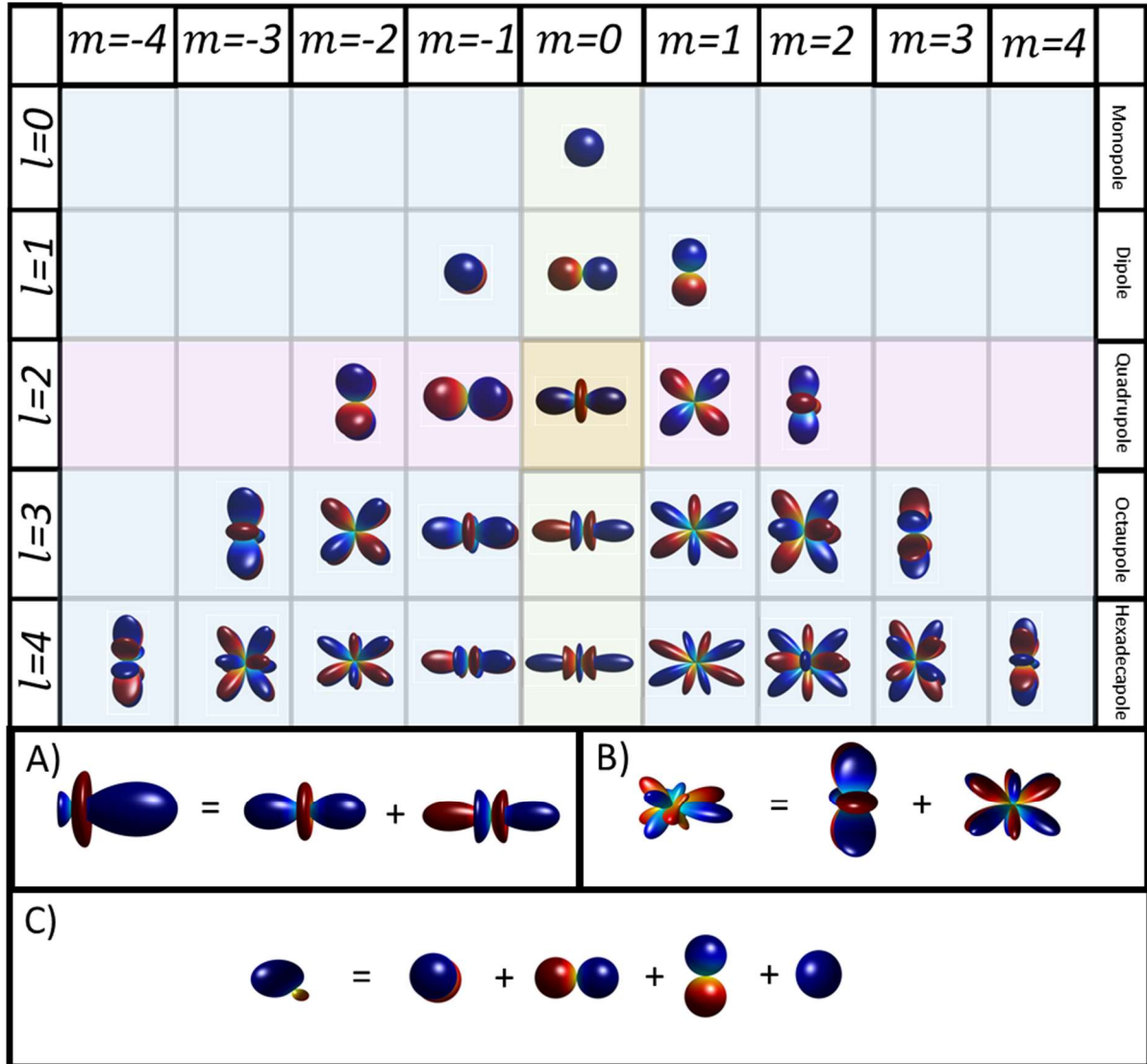


Figure 1.3: Representations of the first five orders of the multipole expansion as spherical harmonics and the decomposition of complex charge distributions

A) Decomposes into a linear quadrupole (2, 0) and linear octupole (3, 0)

B) Decomposes into an octupole (3, -3) and a hexadecapole (4, -2)

C) Decomposes into monopole (0, 0) and three dipoles (1, -1)(1, 0)(1, 1)

Legend for top of figure: green shaded regions are representations of linear multipole moments, purple shaded regions are the various non-linear quadrupole moments, the yellow region is the linear quadrupole moment.

Representations of the spherical harmonics solutions were generated in Matlab using the spherical harmonics community library add-on⁵⁰

quadrupoles being:

$$V(\vec{r}, \theta_1, \theta_2, \phi) = \frac{-3 \theta_1 \theta_2}{16\pi\epsilon_0 r^5} \times \Gamma(\theta_1, \theta_2, \phi) \quad (1.10)$$

This is comprised of two components, the first being a function of the separation distance that decays as r^{-5} , as well as an angular component that defines the relative orientations of the two quadrupoles, shown in Figure 1.4. The angular function, fully expanded, is⁵¹:

$$\begin{aligned} \Gamma(\theta_1, \theta_2, \phi) = & 1 - 5\cos^2(\theta_1) - 5\cos^2(\theta_2) - 15\cos^2(\theta_1)\cos^2(\theta_2) + \\ & 2(4\cos(\theta_1)\cos(\theta_2) - \sin(\theta_1)\sin(\theta_2)\cos(\phi)) \end{aligned} \quad (1.11)$$

As a closing comment, it will be important to remember that this formalism describes a charge distribution as a superposition of increasing multipole moments. It assumes the region of charge is spherical, and that the multipole moments in this model are simply angularly polarized point charges centered at the origin. Therefore, application of this model directly to describe a process like the quadrupole interactions in acetylene will only reasonably be expected to work at large enough distances as it overestimates the interaction energies at close range⁵². Nevertheless, it does provide a good starting point to describe the meaning of a quadrupole moment and provides a basic model to describe how molecules might be expected to interact.

1.3.2 – Van der Waals Forces

Van der Waals forces are weak interactions between molecules comprised of atoms with a typical energy variation of 0.4 to 4 kJ mol⁻¹. These forces include both attractive and repulsive elements that are heavily dependent upon separation distances between interacting species with a normal effective range of 3 to 6 Å. There are several different types of interactions that are combined in the description of van der Waals forces:

- Short range repulsive forces arising from the Pauli exclusion principle⁵³
- London dispersion forces creating transitory electrostatic moments^{5, 6, 53}
- Debye forces where permanent electrostatic moments induce transitory electrostatic moments in non-polar species⁶
- Keesom forces, which are the ensemble average for molecules with orientable electrostatic moments at high enough temperature to cause dynamically varying orientations⁶

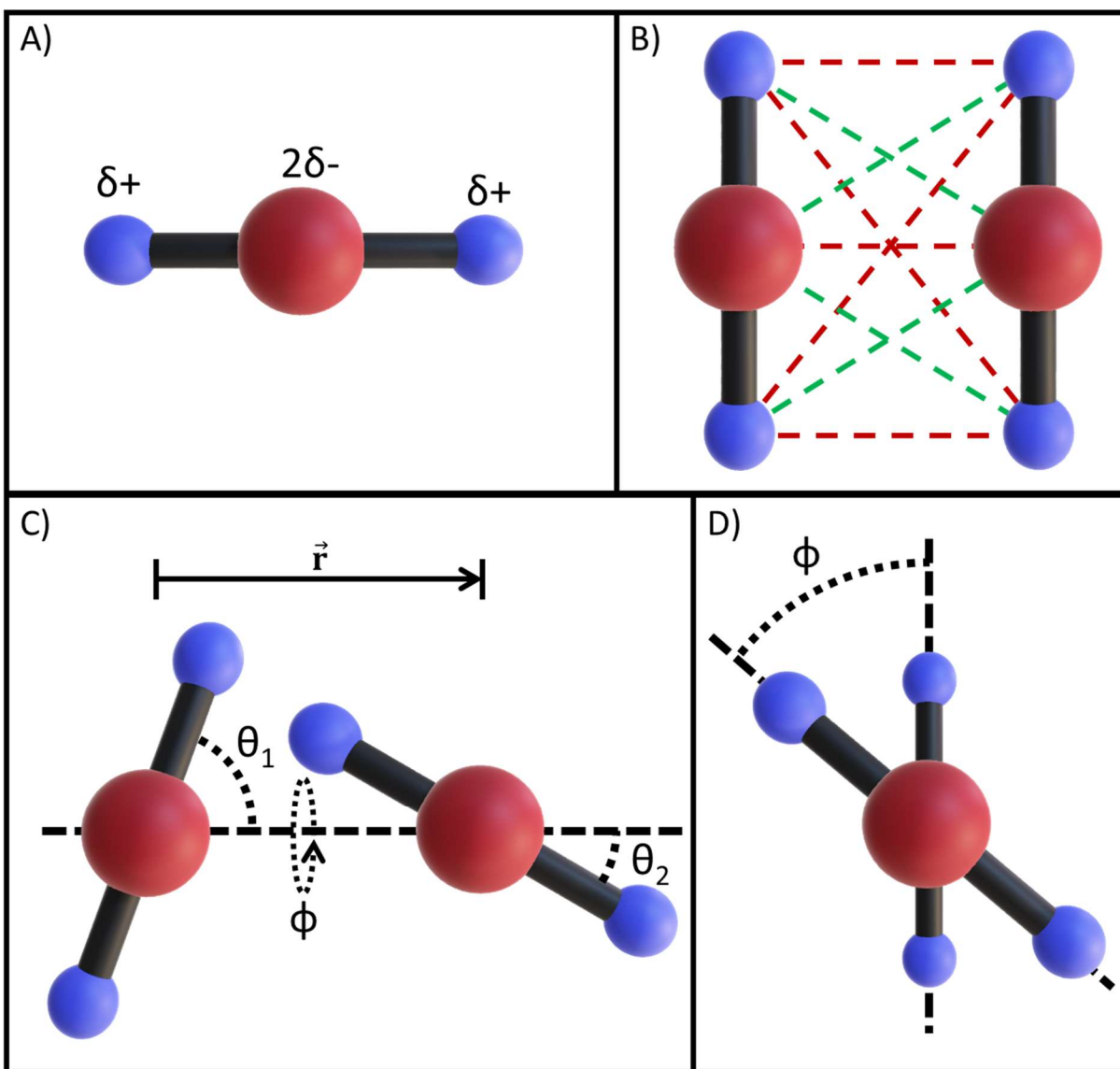


Figure 1.4: The interactions of two linear quadrupoles

A) Approximation of the charge distribution of a simple linear quadrupole⁵⁴ with a positive Θ_{zz} value. For a negative Θ_{zz} , the sign of charges are reversed.

B) Attractive (green dashed line) and repulsive (red dashed line) forces for two interacting linear quadrupoles⁵⁵

C) Diagram of relative coordinate system for governing the interactions of two linear quadrupoles.

D) Newman Projection along $\vec{r}$ demonstrating the dihedral rotation, ϕ , for the relative coordinate system.

Representations of the spherical harmonics solutions were generated in Matlab using the spherical harmonics community library add-on⁵⁰

The Pauli exclusion principle acts on two species when they are at a sufficiently close range for the boundaries of their electron clouds to encroach on each other. The exclusion principle will not allow for overlap of these electron clouds, forcing a reduction in electron density of both species in the region of close contact. This in turn reduces the effective shielding of their nuclear charges, resulting in a repulsive electrostatic interaction between the nuclei⁵³.

London dispersion forces are observable between two non-polar species. Fluctuations in the electron density of one species from the random motion of its electrons result in the creation of a transitory electrostatic moment. The degree of this phenomenon relates to the polarizability of the species. Oftentimes, only the transitory dipole moments need be considered as the dipole polarizability is much higher than for higher order multipoles. Once such an instantaneous dipole is created, the charges act on the electron clouds of the surrounding species, inducing the creation of more instantaneous dipoles. These dipoles then interact either attractively or repulsively due to the anisotropy of the dipole moments⁵³. It is perhaps relevant to mention that, for axially symmetric molecules, the quadrupole and octupole polarizabilities have had to be considered on occasion to explain observations⁵⁶. Since van der Waals forces are weak, they are usually only significant in the absence of permanent electrostatic potentials. As such, they are most often of importance in the behavior of non-polar species, and it is therefore common for the terms “van der Waals forces” and “London dispersion forces” to be used synonymously.

Thirdly, Debye forces occur when a polar species interacts with a non-polar species. The permanent electrostatic moment of the polar species induces the creation of instantaneous electrostatic moments in non-polar species in close proximity, which then interact. This inductive effect is analogous to London dispersion and can be thought of as permanent-dipole-induced-dipole interactions to the latter’s instantaneous-dipole-induced-dipole interactions. Likewise, the dipole term is generally the most important in many systems, but higher order multipoles do contribute as well⁵³.

The last case is that of Keesom forces. These interactions occur for all types of n-pole molecules except the monopole, because they are anisotropic and depend on their relative orientation to one another. In systems with sufficient thermal energy to overwhelm any preferred orientation of the interacting multipoles, the orientations become dynamically varied dependent on temperature. The electrostatic interactions between species when viewed for the

entire system become disordered and are described by ensemble thermal averaging of the electrostatic moments. The anisotropic nature of multipolar moments means this averaging includes both attraction and repulsion. These forces are quite weak and very short range, but they do remain weakly attractive, indicating some degree of preferred orientation remains even in the disordered state. For linear quadrupolar molecules, the potential energy for this type of interaction is given by^{53, 57}:

$$V(r) = \frac{14}{5} \frac{\theta_{zz}^4}{(4\pi\epsilon_0)^2 k_B T r^{10}} \quad (1.12)$$

where k_B is Boltzmann's constant and T is the temperature of the system. Note the extreme short-range nature of this interaction, which decays with distance by r^{-10} . For an isotropic 2-dimensional fluid state that might arise from the adsorption of linear quadrupole molecules, this type of attractive force, though often overlooked, would be a major part of the molecule-molecule interactions within the film.

1.4 – Structures and Surfaces

The idea has previously been introduced that the adsorption behavior of molecules can be heavily influenced by the structure, symmetry, and type of interactions they have with the substrate surface. When a solid lattice in three dimensions terminates in a surface, the arrangement and incomplete coordination of the surface atoms creates electronic structures that are distinct from those of the bulk. Section 1.3 showed that, for physisorption, all forces that govern this process are electrostatic and, therefore, depend heavily on the electronic states that exist within the exposed surface of the substrate. The following discussion will serve to define the formalism with which to discuss surface and film structures, the nature of surface-molecule interactions, and some possible relationships between film and surface structures.

1.4.1 – Crystal Lattices in Two and Three Dimensions

The structural characteristics of ordered solid materials can be described by an infinite tessellation of a fundamental structural unit, referred to as a “unit cell”. In three dimensions, the unit cell can be used to reconstruct the entire lattice using simple translation vectors⁵⁸:

$$\vec{T}_{3D} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3 \quad (1.13)$$

where n_i is any possible integer and $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$ are the lattice vectors. In the case of two dimensions, the above equation only requires two vectors⁵⁹:

$$\vec{T}_{2D} = n_1\vec{a}_1 + n_2\vec{a}_2 \quad (1.14)$$

These translation vectors can be used to reconstruct a properly defined unit cell for any possible lattice system and configuration. In this two-dimensional case, nomenclature replaces the terms “unit cell” and “lattice” with “unit mesh” and “net”, respectively⁵⁹. However, it is far more common in practice that the three-dimensional terminology is directly applied to two-dimensional systems without making such distinctions, which will be the case for this dissertation as well. For the case of three dimensions, there are seven lattice systems that can be further divided into fourteen Bravais lattices, which further expand into 230 total space groups to account for all possible symmetries⁶⁰. With the interest of this study lying in 2D lattices, these numbers can be greatly reduced to give only four lattice systems, five Bravais lattices (Figure 1.5)⁵⁹, and seventeen wallpaper (or plane) groups (two-dimensional equivalent of space groups)⁶¹.

1.4.2 – Lattice Planes, Surfaces, and Miller Indices

In crystallography, definitions of directions within the lattice, planes of diffraction, and surface exposures are all given in terms of Miller indices, $(h \ k \ l)$. These indices can be defined in the real space or reciprocal space lattice. The meaning of “reciprocal space” will be discussed later as it pertains to diffraction. In defining “real space”, the Miller indices correspond to a specific lattice plane of the lattice vectors (equations 1.13 and 1.14). For any given values of h , k , and l , the corresponding lattice plane is that which intercepts the three lattice points: $\vec{a}_1/l$, $\vec{a}_2/k$, and $\vec{a}_3/l$ ^{32, 58, 60}. Figure 1.6 shows the derivation of several planes for a two-dimensional lattice and several families of lattice planes for correspondence to certain Miller indices, which reveals several equivalent planes for each family. As the symmetries of the hexagonal lattice in three dimensions are not apparent, a forth index, i , is often used, corresponding to an axis that is 120° from both the x and y axes, where $i = -(h + k)$, making the index order now $(h \ k \ i \ l)$ ⁶⁰. This helps distinguish the similar planes that are rotated by 120° from each other in the hexagonal system and is why the carbon layer planes of graphite are described by the indices (0001).

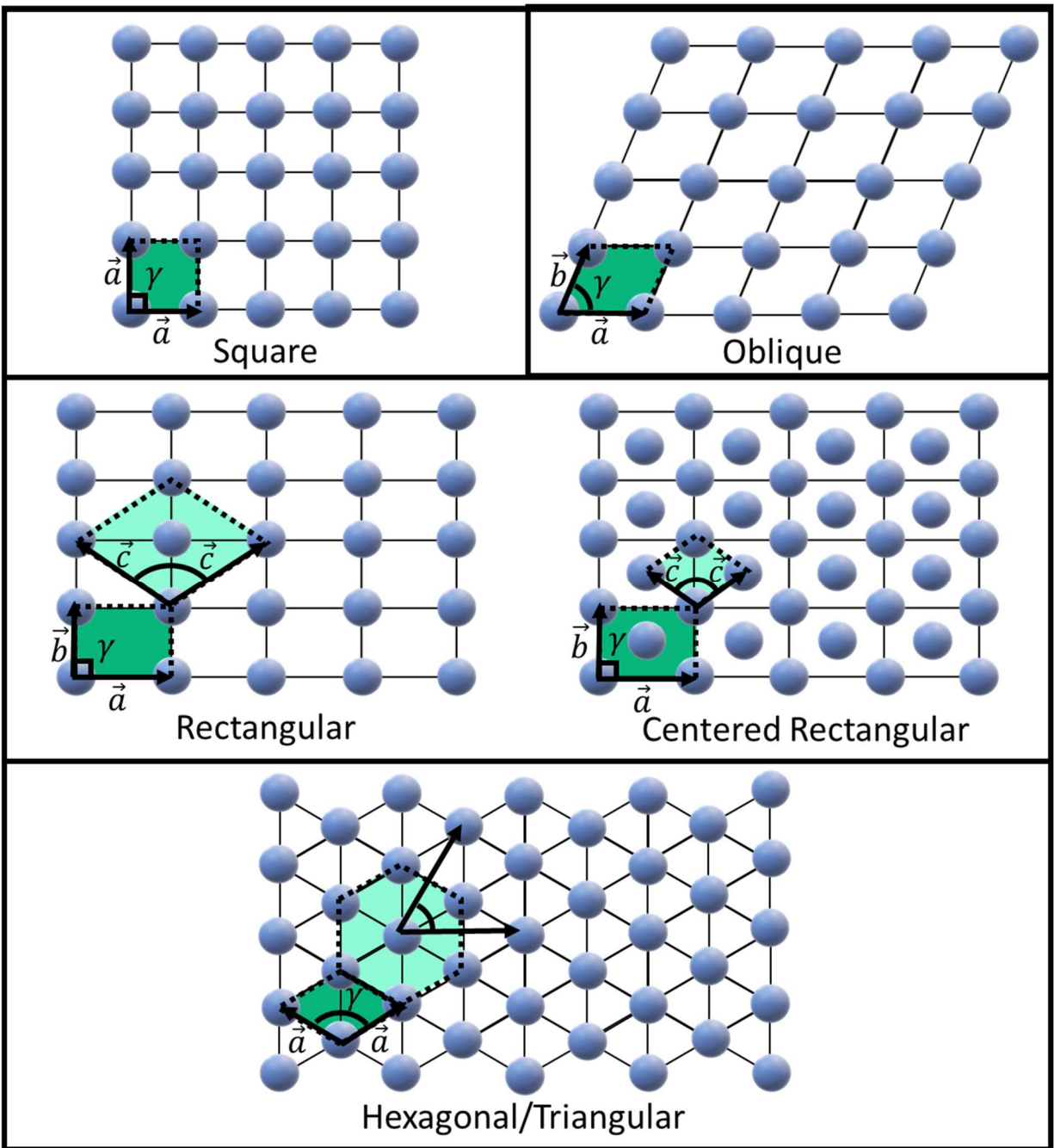


Figure 1.5: The five Bravais lattices of two dimensions⁵⁹

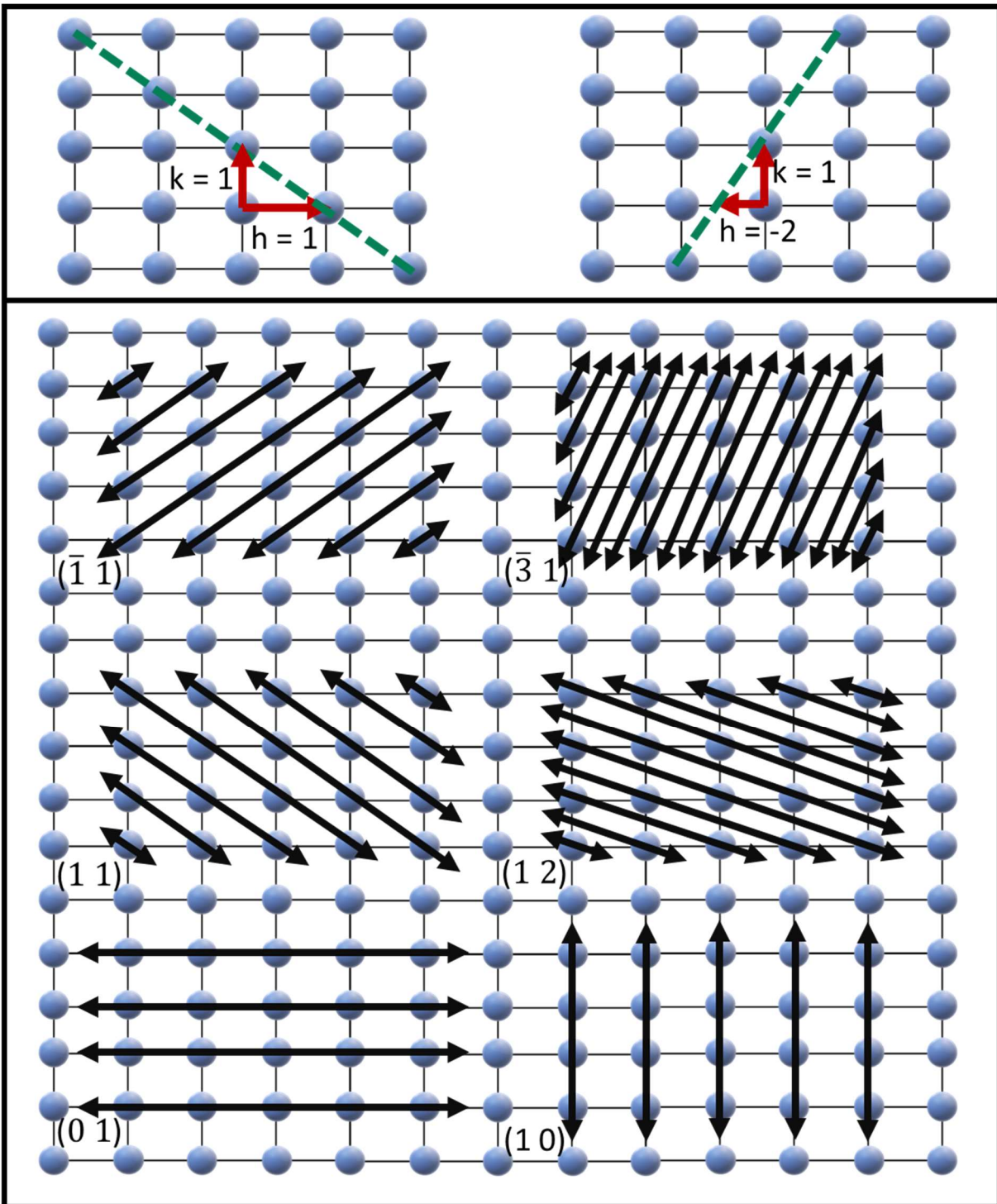


Figure 1.6: Relationship between lattice planes and their respective Miller indices

Surfaces of solids are the result of the termination of a solid lattice and can be described by the plane along which they terminate. Therefore, a surface facet of crystal is defined by the same notation as these lattice planes.

1.4.3 – Surface Corrugation, Defects, and Adsorption Sites

When a molecule approaches a solid surface, it becomes trapped in the mutual potential energy field that exists between the molecule and the surface. This field is a result of the summation of electrostatic and dispersion forces between the entire molecule and the entire surface. Different atoms within the admolecule will have differences in the potential they experience between various locations on the surface. This creates to a location and orientation specific variation in the potential energy field across the surface, which is referred to as the “surface corrugation”⁶². For some substrates, this corrugation is nearly uniform in nature for most of the representative molecules, and the impact that the surface geometry will have on that of the adsorbed film will be mild^{38, 63}. In contrast, the surface of metal oxides like MgO are ionic and can have a large influence on any non-zero charge distribution possessed by the admolecule⁶⁴. These surfaces possess a much larger corrugation and stronger influence on the position and behavior of the molecule. Furthermore, the contour of the corrugation will follow the symmetry of the surface.

The minima in the potential energy corrugation correspond to the adsorption sites for the physisorption process. These are generally located at sites of high symmetry on the surface (i.e. atop surface atoms, the mid points of surface bonds, or center points of hollows between atoms). The adsorbate molecules want to maximize the interactions it has with the surface in order to minimize its potential energy. For graphite and MgO surfaces, these favorable sites are depicted in Figure 1.7.

Defects in the surface can have a significant impact on molecular adsorption. These include terrace (or step) defects in the surface, where the surface is displaced by one or more lattice planes, atom vacancies, and crystal edges and corners^{65, 66}. Such places on a surface have different coordination numbers than other surface atoms, which can significantly alter their polarizabilities or local charge density, changing significantly how they interact with admolecules. In the ideal world, surface scientists would work with materials that are pristine and clear of all defects. Some systems in particular are preferred in this area of research because of their

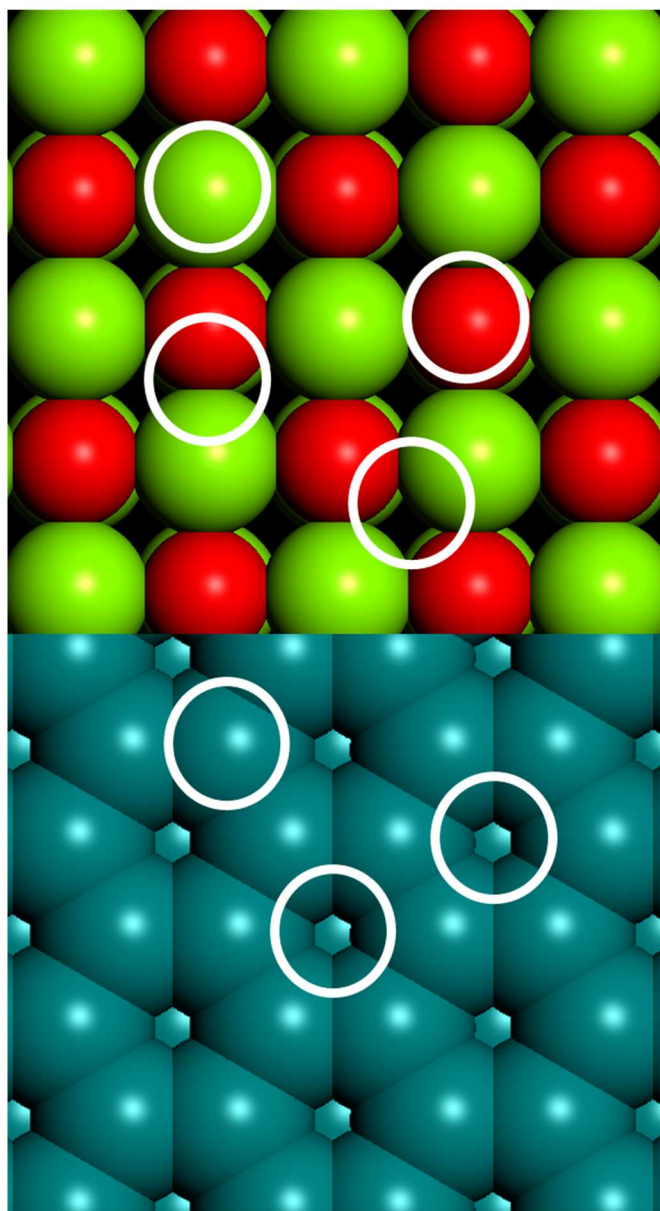


Figure 1.7: High symmetry sites for (top) MgO (100) and (bottom) graphite (0001)

propensity for large, defect-free, single facet surface exposures (like exfoliated graphite and MgO (100)). However, in the trade-off of increased surface area, some degree of edge effects from the finite particle size will always be unavoidable. Exfoliated graphite offers another type of adsorption defect, as the open spaces between lattice planes where the surface exposures are can be narrow, especially when compressed, resulting in pseudo-pores being created by the small spaces. This typically manifests at higher vapor pressures but depends on how compressed the sample is.

1.4.4 – Commensurability

As has been mentioned, the nature of the film that develops as a result of adsorption is the result of synergy or opposition of the molecule-molecule and molecule-surface interactions. If the molecule-molecule forces are sufficiently stronger, they are free to adopt structures that are not subject to the symmetry constraints of the surface. However, when the surface-molecule interactions are the dominant force, or if the symmetry of the molecule-molecule and molecule-surface interactions are the same, then the structure of the film will conform to the influence of the surface corrugation and its structure will lie in registry with that of the substrate^{29, 62, 67}. This commensurate relationship between film and substrate need not be one to one, but for larger molecules, longer range commensurate structures are quite often observed⁵⁹ (see Figure 1.8 for common examples on graphite and MgO).

1.5 – Neutron Diffraction

One of the most useful probes of material structure in two and three dimensions has been diffraction. The three types of radiation most commonly used for this are electrons, x-rays, and neutrons⁶⁸. Electrons have the advantage of being relatively inexpensive, and extremely surface sensitive, but they can cause radiation damage to sensitive systems like adsorbed films and are not always a preferred technique. X-rays are generally quite useful in the studies of films in many cases, with the comparatively large number of synchrotron facilities making them highly accessible. X-rays, however, scatter off of electrons are not a sensitive probe for systems of lighter atoms with lower electron densities, such as hydrocarbons. Neutrons, by contrast, scatter off atomic nuclei and have a fairly uniform scattering intensity that is not strongly correlated to the size of the atoms, with a few notable exceptions of higher scattering cross-sections, such as

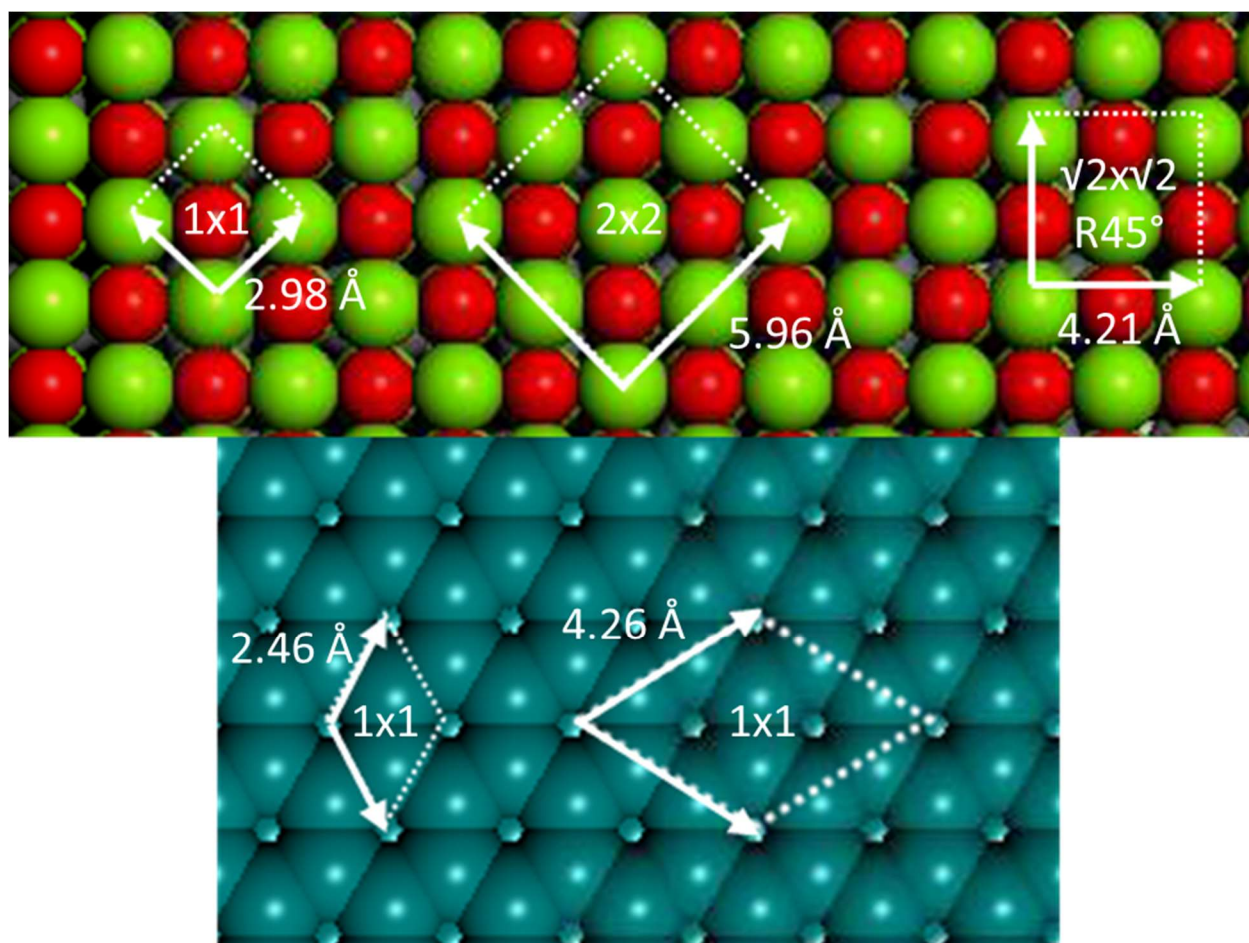


Figure 1.8: Examples of simple commensurate surface registries for MgO and Graphite

hydrogen. This makes neutrons an ideal candidate for structural studies for many adsorbed films^{33, 69, 70}. The reduced interaction and lower energy of neutrons compared to x-rays of comparable wavelength also makes them able to easily probe the dynamics of a system through inelastic scattering experiments. The focus of this dissertation will only be on the analysis of elastic neutron diffraction and structural analysis. As such, the following passages will refer to neutrons as the scattering radiation, however, much of the discussed processes are equally applicable to other types of scatterers.

1.5.1 – Scattering Basics

As mentioned before in section 1.4.2, the long-range ordering of atoms within molecules of a crystal lattice allows for the planes exhibited by the crystal lattice being described by their Miller indices ($h\ k\ l$). These planes all have different spacings (“d-spacings”) between them, which is a result of the angle at which these planes intersect the lattice. When radiation of similar wavelength to these d-spacings impinges on a crystal lattice, the radiations will reflect these planes and can interfere with one another constructively in cases where specific diffraction conditions are met; otherwise the waves will interfere destructively, and no reflections are seen^{68, 71}.

1.5.1.1 – Wave Scattering

For a traveling beam of neutrons, their momentum gives them a characteristic wavelength, λ , defined by the de Broglie equation as⁷²:

$$\lambda = \frac{h}{\vec{p}} \quad (1.15)$$

where $\vec{p}$ is the momentum vector of the particle and h is Planck’s constant; however, a preferred formalism in crystallography is to express the momentum of the incoming wave in terms of its wave-vector, $\vec{k}$ ^{73, 74}:

$$\vec{k} = \frac{\vec{p}}{\hbar} = \frac{2\pi}{\lambda} \quad (1.16)$$

To meet the criteria for a scattering experiment, all of the incoming neutrons (or other scattering probes) must have the same wave vector, and therefore have the same momentum or wavelength. When an incident neutron scatters off a lattice plane of the sample, it leaves with a

new wave vector, $\vec{k}'$ (Figure 1.9). During elastic diffraction, there is no momentum transfer between the neutron and the system, and the magnitude of the wave vectors is conserved⁶⁸:

$$\|\vec{k}\| = \|\vec{k}'\| \quad (1.17)$$

When the diffraction is not elastic (i.e. quasielastic or inelastic), momentum is transferred between the neutrons and the sample and this condition is not met⁶⁸. Quasielastic scattering involves small exchanges of energy between neutrons and the sample corresponding to diffusive motions of atoms or molecules. Inelastic scattering is analogous to the process of Raman scattering and provides information about vibrational and phonon transitions, but without the optical selection rules that prevent some transitions from being visible with other techniques. The change in the wave vector before and after diffraction is described by a new single scattering vector $\vec{Q}$ ⁷³:

$$\vec{Q} = \vec{k}' - \vec{k} \quad (1.18)$$

1.5.1.2 – Scattering Conditions

In a diffraction experiment, the planes of the crystal lattice act analogous to a diffraction grating used in optics. With optical gratings, the angle at which light leaves the surface as it scatters depends on the wavelength of light and the spacing between grooves on the grating. Likewise, the angle at which neutrons are scattered during diffraction off a crystal lattice depends on the wavelength of the neutrons and the spacing between the lattice planes.

The first successful method used to relate the observed diffraction angles to the crystal structure are the Laue equations. Referring back to the definitions established in section 1.4.1, a crystal lattice, L , can be defined by a series of points in space defined by the three lattice vectors $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$ and a translation vector that is an integer linear combination of these vectors. Relating these lattice vectors to the analogy of the optical diffraction grating, the intensity of diffraction at a given angle, $I(\alpha)$, is expressed by the relationship^{71, 75}:

$$I(\alpha) \propto \frac{\sin^2 \left(\frac{N\pi D}{\lambda} \sin \alpha \right)}{\sin^2 \left(\frac{\pi D}{\lambda} \sin \alpha \right)} \quad (1.19)$$

where N is the number of grooves in the grating, D is the spacing distance of those grooves, λ is the wavelength of light, and α is the angle of diffraction from the grating. As the number of

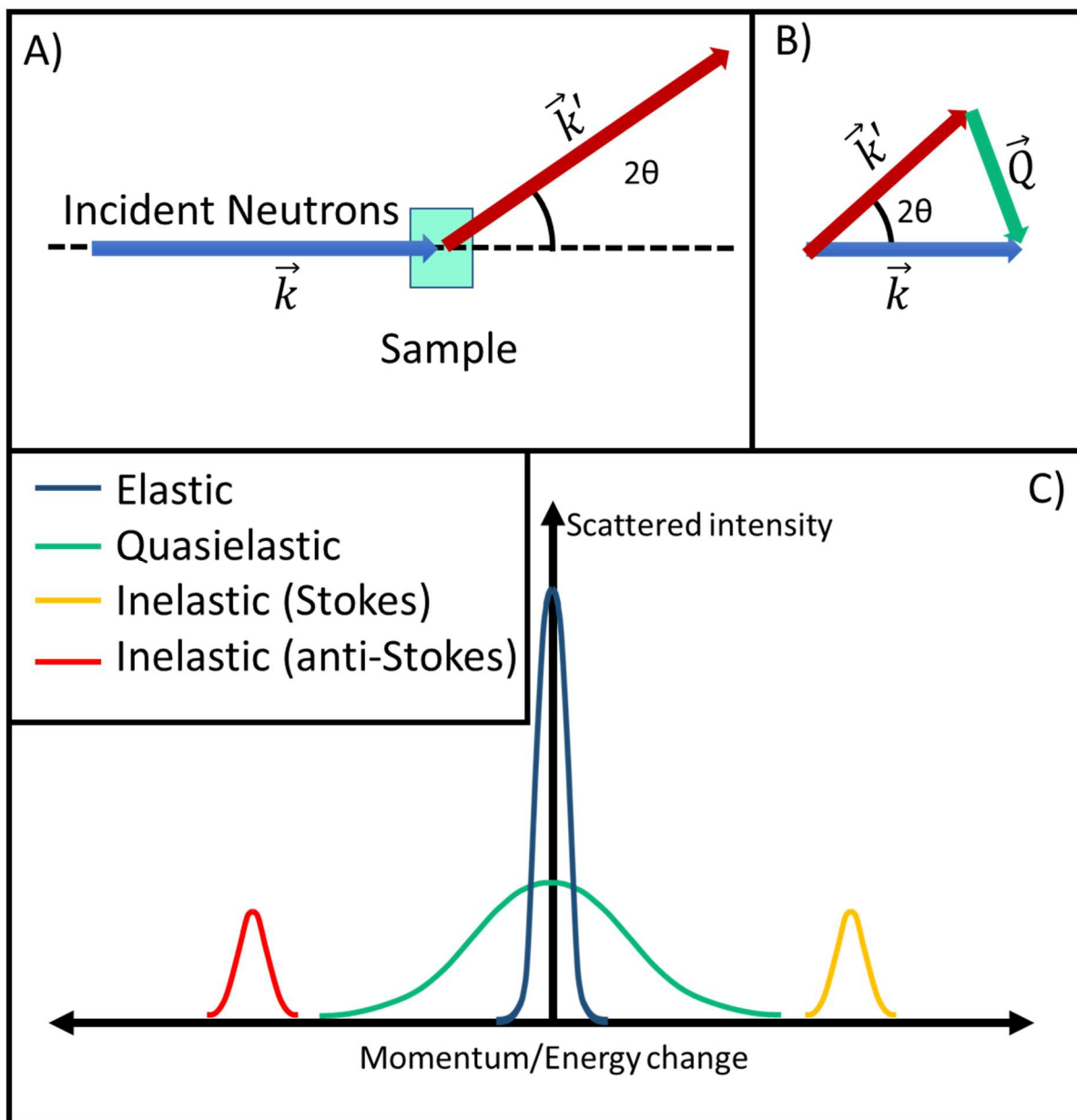


Figure 1.9: Basics of scattering vectors, and elastic, quasielastic, and inelastic neutron scattering

Derived from figure by Maths Karlson⁷⁶

gratings tends towards infinity, the peaks in this function approach delta functions in shape, and are located at⁷⁷:

$$D \cos(\alpha) = n\lambda \quad (1.20)$$

where n is an integer. Expanding on the equations previously established in the previous section, the relationship:

$$\|\vec{Q}\| = \frac{2\pi}{\lambda} \quad (1.21)$$

is used to substitute for λ in equation 1.20. The grating spacing, D , can also be replaced by the lattice constant $\|\vec{a}_i\|$ to yield:

$$\|\vec{a}_i\| \|\vec{Q}\| \cos(\alpha) = 2\pi n \quad (1.22)$$

which is a cross-product of the lattice vector in question and the scattering vector. Doing this for each of the three lattice vectors yields the three Laue equations⁷¹:

$$\vec{a}_1 \cdot \vec{Q} = 2\pi h \quad (1.23)$$

$$\vec{a}_2 \cdot \vec{Q} = 2\pi k \quad (1.24)$$

$$\vec{a}_3 \cdot \vec{Q} = 2\pi l \quad (1.25)$$

where the left side of the expression is satisfied only if they are integer multiples of 2π . These integers h , k , and l are the Miller indices. Non-destructive interference will only occur in the diffraction pattern if all three of these conditions are met simultaneously.

A more intuitive explanation of diffraction is given by Bragg's Law. Section 1.4.2 established that the long-range ordering of atoms or molecules in a crystal lattice allows for the description of lattice planes described by their Miller indices ($h \ k \ l$). These planes all have different spacings ("d-spacings") between them, which is a result of the angle at which these planes intersect the lattice. When radiation of similar wavelength to these d-spacings impinges on a crystal lattice, it will reflect these planes. For the case of any particular set of identical lattice planes, the reflections off consecutive layers will interfere with one another (Figure 1.10). Constructive interference only occurs when exact scattering conditions are met, given by Bragg's Law⁷³:

$$n\lambda = 2d_{hkl} \sin\theta \quad (1.26)$$

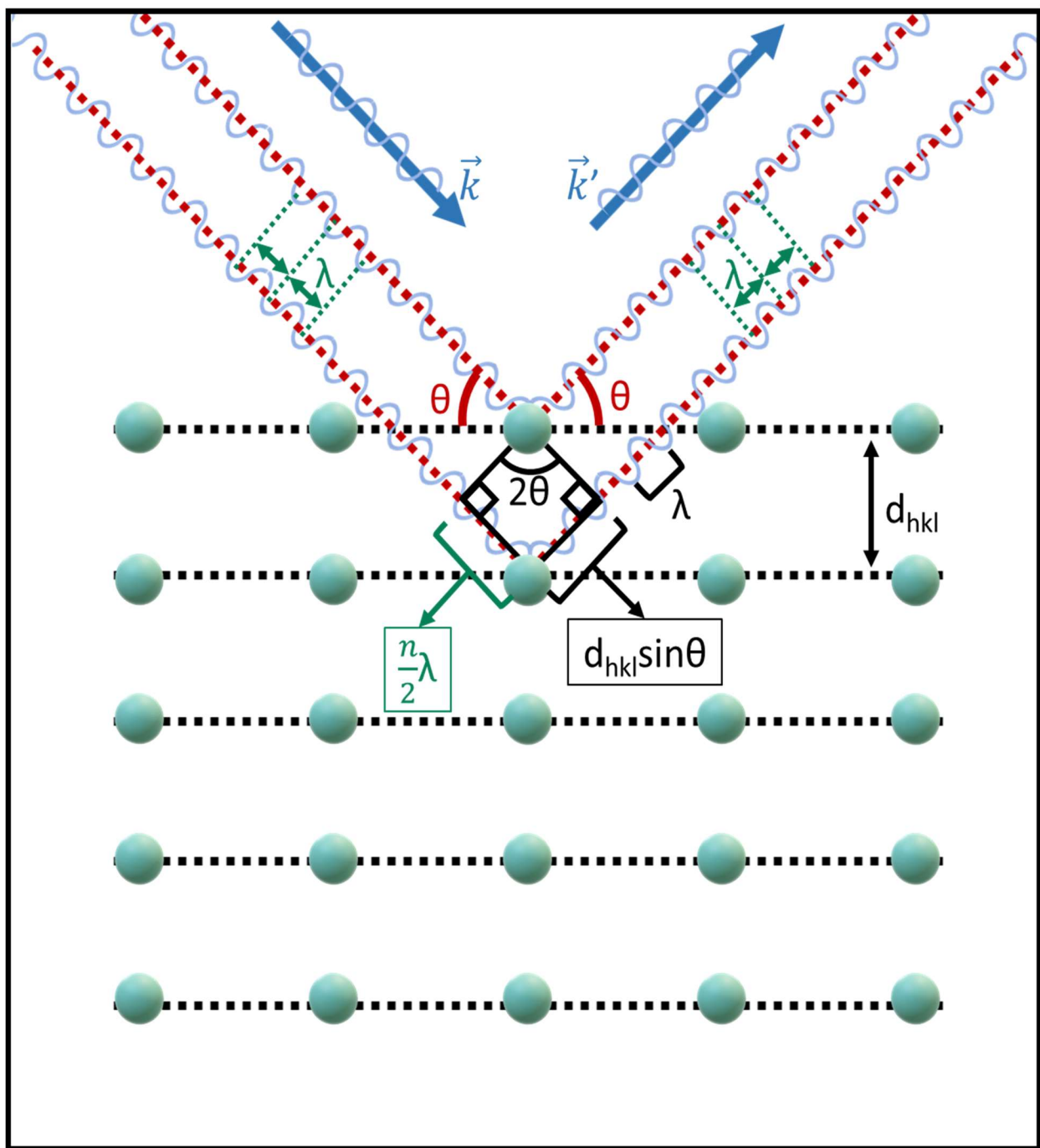


Figure 1.10: Bragg's Law model for the diffraction of radiation off of parallel lattice planes

where d_{hk} is the d-spacing of the family of lattice planes described a specific set of Miller indices and n is an integer. Like with the Laue equations, Bragg's law shows that diffraction only occurs at specific integer multiples of wavelength that depend on the lattice plane spacing in that direction. This can be used to establish relationships between the lattice spacing, diffraction angle, and the scattering vector:

$$d_{hkl} = \frac{\lambda}{2s} = \frac{2\pi}{\|\vec{Q}\|} \quad (1.27)$$

$$\|\vec{Q}\| = \frac{4\pi}{\lambda} \sin(\theta) \quad (1.28)$$

1.5.1.3 – Reciprocal Space

For a given lattice in real space, the diffraction conditions result in a series of points that correspond to specific wave vectors where constructive diffraction interference has occurred. These points make up a lattice in a fictional space with dimensions set by the wave or scattering vector rather and, in accordance with equation 1.27, will have units of inverse length. For this reason, this construct is known as the “reciprocal lattice”, which is the Fourier transformation of the real space lattice. The reciprocal lattice is defined by a set of lattice vectors, $\vec{b}_i$, and a translation vector, $\vec{G}$, given by³²:

$$\vec{G}_{3D} = m_1\vec{b}_1 + m_2\vec{b}_2 + m_3\vec{b}_3 \quad (1.29)$$

or in two-dimensions as:

$$\vec{G}_{2D} = m_1\vec{b}_1 + m_2\vec{b}_2 \quad (1.30)$$

The reciprocal lattice vectors, $\vec{b}_i$, are related to the real space lattice vectors by the following relationships⁵⁸:

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} \quad (1.31)$$

$$\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} \quad (1.32)$$

$$\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} \quad (1.33)$$

From these definitions, some further relationships between the real and reciprocal space lattices can be made. First, the scalar product of a real space and reciprocal space lattice vector is non-zero only if the indices of both vectors are the same, meaning they are orthogonal to one another. If the indices of the vectors are the same, their magnitudes will be related as:

$$\|\vec{b}_i\| = \frac{2\pi}{\|\vec{a}_i\|} \quad (1.34)$$

Second, the vector $\vec{G}$ will be orthogonal to the plane of diffraction in the lattice. Therefore, this derives the reciprocal space definition of the Miller indices. The integer coefficients of the reciprocal lattice vectors in $\vec{G}$ are orthogonal to planes in the real space lattice defined by the same integers. Therefore, equation 1.29 can be rewritten as:

$$\vec{G}_{3D} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3 \quad (1.35)$$

1.5.1.4 – Diffraction Intensity and Structure Factor

The diffraction intensity of observed reflections is a complex variable that depends on multiple factors. For the moment, this discussion will ignore the contributions from instrument response, thermal displacements, coherence length of long-range order, and a few other factors that contribute to what the “peak shape” is and rather focus on the idealized concept of diffraction intensity.

The diffraction from any particular atom in a lattice depends on the type of atom and the type of radiation being diffracted. X-rays scatter more efficiently from atoms with higher electron densities and, therefore, result in more abundant scatter for elements with higher atomic numbers. Neutrons, however, scatter off nuclei and have a more consistent, but random, response to not only atomic number, but also to the specific isotopes present. The intensity to which an atom scatters also depends on the direction of scattering and grows less intense as the scattering angle increases. The scattering intensity for any reflection from a material depends on the type of radiation used, and on the relative positions and orientations of all atoms within the unit cell^{60, 71, 73}.

The scattering intensity, $I(Q)_{hkl}$, is described in terms of the scattering amplitude, F_{hkl} ⁷¹:

$$I(Q)_{hkl} \propto |F_{hkl}|^2 \quad (1.36)$$

where F_{hkl} is the vector sum of the scattering amplitude of all atoms within the unit cell:

$$F_{hkl} = \sum_n f_n \exp [2\pi i(hx'_n + ky'_n + lz'_n)] \quad (1.37)$$

where f_n is the atomic form factor for the n th atom and x'_n , y'_n , and z'_n are the fractional coordinates of the n th atom in the unit cell. The scattering amplitude here is also more commonly referred to as the “structure factor” in crystallography. In disordered systems, a

similar quantity, $S(Q)$, is similarly referred to by this name⁷⁸. In the case of ideal crystals, these two functions can be used equivalently to determine diffraction intensities. However, for the purposes of further discussions present in this dissertation, $S(Q)$ will be the more useful form, and for the sake of convenience will be the one referred to by the name “structure factor”, unless explicitly stated otherwise. Instead of being related to the unit cell explicitly, as with F_{hkl} , it is calculated based on the average of atomic positions within the material. More explicit functional forms of $S(Q)$ will be given in later sections during relevant discussions of the structures of molecular dynamics results and of the structures from two-dimensional liquids.

1.5.2 – Powder Diffraction

Most experiments and analyses of adsorbed thin films require materials of high surface area for a sufficient amount of film to be present to detect. This, by nature, means that solid substrates will generally be powders or foams. As a general approximation, the orientation of particles within the powder should have no preferred orientation, and all orientations will be equally probable⁷⁹ (note: this is not always the case, but it will serve as a starting point for this discussion). For diffraction experiments, this means that the lattice planes of the sample will be randomly oriented with respect to the incoming radiation beam in such a way that a statistically significant number of each lattice plane will have the correct orientation relative to the beam to satisfy scattering requirements. The points of the reciprocal lattice in the diffraction pattern are smeared out into circles, and only the angular separation, 2θ , is conserved. In other words, it simplifies the reciprocal lattice down to a one-dimensional problem dependent on angle, and reflections from symmetrically equivalent lattice planes will overlap as a single peak. (Figure 1.11).

1.5.3 – Rietveld Refinement

The method used to determine structure from powder diffraction is named “Rietveld refinement” in honor of the Hugo Rietveld who developed the original process^{80, 81}. This technique uses a least squares approach to refine a structure to fit experimentally measured powder diffraction patterns. The structure factor, F_{hkl} , regards the diffraction amplitudes as delta functions with precise scattering vectors, i.e. a perfect crystal. In reality, the diffraction intensity profile has width and, furthermore, shape, to which material properties, instrument

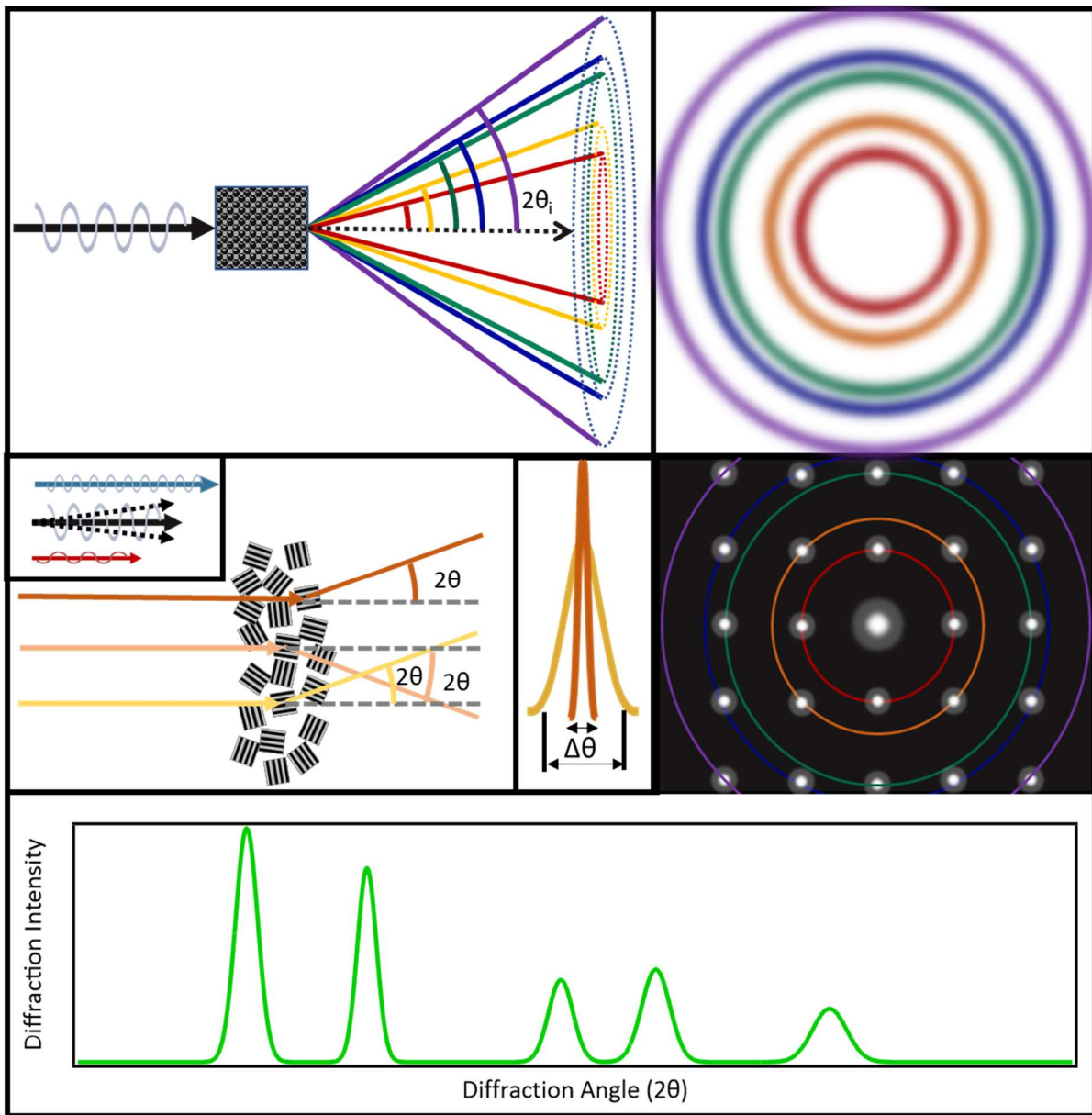


Figure 1.11: Illustration of powder diffraction and its relationship to reciprocal space

configuration, and thermal movements all contribute. The Rietveld method established the formalism for powder diffraction in terms of all of these possible contributing factors. The basic form of this equation looks like⁸¹:

$$I(2\theta_i) = s \sum_{hkl} [L_{hkl} \times m_{hkl} \times |F_{hkl}|^2 \times \Phi(2\theta_i - 2\theta_{hkl}) \times P_{hkl} \times C_{hkl}] + b_i \quad (1.38)$$

where $I(2\theta_i)$ is the calculated diffraction intensity as a function of 2θ , s is a scaling factor to match experimental intensities, $\Phi(2\theta_i - 2\theta_{hkl})$ is the peak shape function, b_i is the background⁸², and, over the appropriate Miller indices of each reflection, L is a Lorentz polarization factor, m is the peak multiplicity, F is the structure factor, P is the preferred orientation correction, and C refers to other fit parameters such as the crystallite size and thermal effects. It is possible to extend this process to refine systems with multiple phases by using⁸¹:

$$I(2\theta_i) = \sum_j [s_j y_j] + b_i \quad (1.39)$$

where the index j corresponds to a given phase, s_j is the scaling factor of the phase, and y_j follows the form expressed in equation 1.38 excluding the background term, which is treated separately from the individual phases if multiple are present. Though refinement of multiple phase systems means the total number of fit parameters increases rapidly and leads to the increased likelihood of false solutions, this issue can be mitigated if prior knowledge of both phases is already known by focusing the refinement on a narrow subset of fit parameters.

More details about specifics of the refinement process that was developed for two dimensional systems as part of this dissertation can be found in appendix B

1.5.5 – Diffraction from Two-Dimensional Systems

The formalism covered above described the relationship of structure and diffraction for systems of three dimensions. The basic logical underpinning is the same for diffraction in two-dimensional systems, however, the simplification of the lattice due to this dimensional reduction results in important practical differences that need to be addressed in diffraction analysis. The definition of the real space two-dimensional lattice is given in equation 1.14 and discussed in section 1.4.1. The important detail is that these systems only require two lattice vectors and, as a result, two Miller indices (h and k) need to be defined. The translation of this reciprocal space

lattice is given in equation 1.30, with the vector coefficients m being replaced with the Miller indices:

$$\vec{G}_{2D} = h\vec{b}_1 + k\vec{b}_2 \quad (1.40)$$

The reciprocal lattice vectors, $\vec{b}_i$, can be related to the real space lattice vectors, $\vec{a}_i$, via a Fourier transformation, just as in three dimensions. This transformation establishes the following relations between the vectors of the two lattices:

$$\vec{b}_1 = 2\pi \frac{\hat{R}_{90^\circ} \vec{a}_2}{\vec{a}_1 \cdot \hat{R}_{90^\circ} \vec{a}_2} \quad (1.41)$$

$$\vec{b}_2 = 2\pi \frac{\hat{R}_{90^\circ} \vec{a}_1}{\vec{a}_2 \cdot \hat{R}_{90^\circ} \vec{a}_1} \quad (1.42)$$

where $\hat{R}_{90^\circ}$ is a 90° rotation operator. Similar to three dimensions, it can be seen that these relationships in two dimensions establish the same orthogonality.

The d-spacings of reflections from lattice planes of the two-dimensional lattice can be calculated as:

$$d_{hk} = \frac{2\pi}{Q_{hk}} \quad (1.43)$$

In reference to the real space lattice vectors in two dimensions, the d-spacings formulation depends on the family of two-dimensional lattice systems⁶¹:

- Square ($\|\vec{a}_1\| = \|\vec{a}_2\| = a, \gamma = 90^\circ$)

$$\frac{1}{d_{hk}^2} = \frac{h^2 + k^2}{a^2} \quad (1.44)$$

- Rectangular ($\|\vec{a}_1\| \neq \|\vec{a}_2\|, \|\vec{a}_1\| = a, \|\vec{a}_2\| = b, \gamma = 90^\circ$)

$$\frac{1}{d_{hk}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} \quad (1.45)$$

- Hexagonal ($\|\vec{a}_1\| = \|\vec{a}_2\| = a, \gamma = 120^\circ$)

$$\frac{1}{d_{hk}^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) \quad (1.46)$$

- Oblique ($\|\vec{a}_1\| \neq \|\vec{a}_2\|, \|\vec{a}_1\| = a, \|\vec{a}_2\| = b, \gamma \neq 90^\circ$)

$$\frac{1}{d_{hk}^2} = \frac{h^2}{a^2 \sin^2 \gamma} + \frac{k^2}{b^2 \sin^2 \gamma} - \frac{2hk \cos \gamma}{ab \sin^2 \gamma} \quad (1.47)$$

It is imperative to make some notes regarding symmetry multiplicity for the different lattice types. In the square lattice, h and k are interchangeable and planes such as the (0 1) and (1 0) are equivalent. In the rectangular case, the lattice vectors are different magnitudes, the symmetry is reduced, and permutations where $|h| \neq |k|$, such as (0 1) and (1 0) or (1 2) and the

(2 1), are no longer equivalent, but when $|h| = |k|$, such as (1 1) and (1 $\bar{1}$), the symmetry still holds and these planes are equivalent. The oblique lattice breaks the symmetry yet further, such that even planes where $|h| = |k|$, like the (1 1) and (1 $\bar{1}$), will not be equivalent. The symmetry of the hexagonal family is different as a result of its rhomboidal Bravais lattice vectors. Reflections such as (0 1) and (1 0) are symmetrically equivalent, yet reflections like (1 1) and (1 $\bar{1}$) are not.

In the case of diffraction studies of systems with two-dimensional ordering, an important distinction exists with regards to the scattering requirement. To consider these requirements more closely, it helps to refer to the Laue equations (equations 1.31 to 1.33). With only two lattice vectors, only two of these equations should need to be satisfied in order to meet the requirements for diffraction. But the incoming wave vector, $\vec{k}$, is still a vector existing in three-dimensional space, and for multiple relative orientations of the wave vector relative to the reflection plane, this means that part of this three-dimensional wave vector can be projected into two dimensions, with less intensity as the z component perpendicular to this plane becomes more dominant. In other words, the third Laue equation may still be satisfied by a continuum of l values instead of discrete quantities and reciprocal space is comprised of parallel rods instead of points^{32, 83}.

The phenomena of two-dimensional diffraction was first realized by B.E. Warren in the study of randomized planes of graphite³². The covalent network of the individual layers still held long-range order within the plane, but the c-axis of the graphite crystals were no longer ordered. The observed diffraction pattern followed a “saw-tooth” like appearance with a sharp rise on the low $\vec{Q}$, followed by a more exponential-like decay towards higher $\vec{Q}$ values after the peak (Figure 1.12). He derived a formulation for the structure factor, F_{hk} , that accounted for the angular dependence on diffraction of this continuum of l ³²:

$$F_{hk} = \sum_n f_n \exp \left[2\pi i (hx'_n + ky'_n + \frac{2lz}{\lambda} (\sin^2 2\theta - \sin^2 2\theta_o)) \right] \quad (1.48)$$

where θ_o is the minimum angle required for diffraction (diffraction angle when $l = 0$). Warren assumed long-range order of the two-dimensional lattice in this formulation, and while this form has been used to analyze diffraction from adsorbed systems before, the assumption of long-range order in such two-dimensional systems is not generally valid⁸⁴. As a consequence of thermodynamic fluctuations, it is not possible under normal circumstances for long-range order to develop⁸⁵. An exception is for highly synergistic commensurate relationships with a substrate

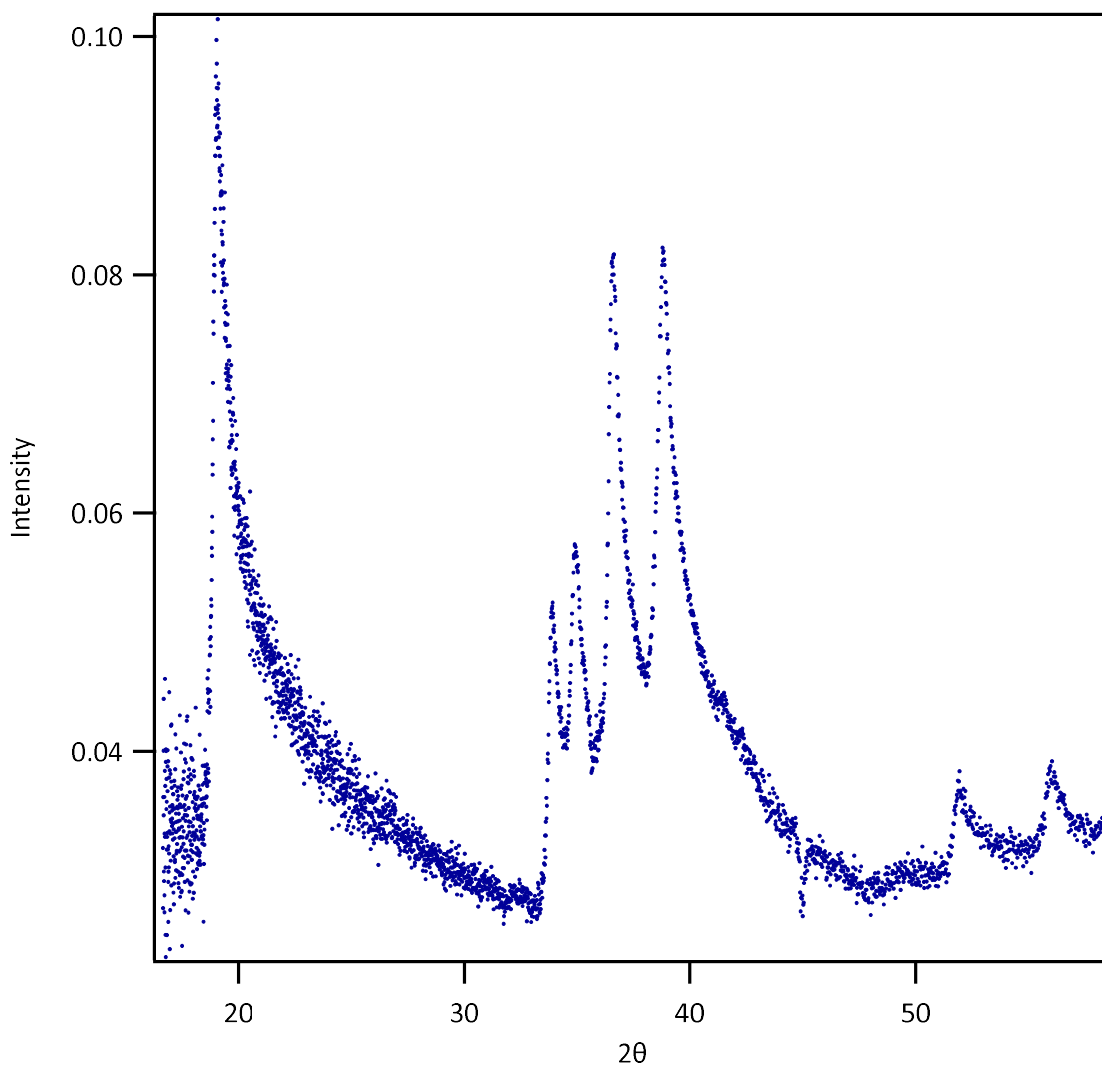


Figure 1.12: Diffraction pattern of butane film on MgO showing lineshapes characteristic of two-dimensional systems

*Taken from Structure of an *n*-butane monolayer adsorbed on magnesium oxide (100)⁸⁶*

that can protect the system against these divergent fluctuations. Alternatively, in some cases, the system is better treated as being partially disordered and described using the other definition for structure factor, $S(Q)$. Several line shapes have been used to describe the form of $S(Q)$ in adsorbed systems, such as convolutions of Gaussian, Lorentzian, Lorentzian squares, and power-law distributions^{83, 84, 87}.

1.6 – Molecular Dynamics

While diffraction is a useful tool to probe the structure and dynamics of adsorbed systems, there is no experimental technique that can provide an actual, high quality, real space picture of a dynamic physisorbed film's behavior at the molecular level. Computational simulations help to fill in this gap with the prospect of providing an intuitive picture to complement other experimental data⁸⁸. Unfortunately, computations that can accurately account for the full quantum mechanical effects and *ab initio* molecular dynamics are computationally demanding and calculation times increase rapidly with the number of atoms in the system, quickly becoming unfeasible. With desktop computers, this scope might be limited to less than 100 atoms and 10 picoseconds⁸⁹.

A more feasible approach is to employ simpler molecular dynamics computations, which have been made possible through the development of generalized, but highly accurate, force fields that can describe systems using simple Newtonian mechanics with low computational demand⁷. This greatly expands the size of systems and the length of time scales that can be examined. Inevitably, though, these force fields are only approximate representations of the intermolecular potentials of real systems and are not always an accurate representation. Despite this, the generalized form of most forcefields enable modification of the potentials used and allow refinement of force fields to be in better agreement with experimentally observed results.

1.6.1 – Calculations of Force

The basic premise of molecular dynamics is the numerical iteration of the Newtonian equations of motion:

$$F_i(t) = m_i a_i(t) \tag{1.49}$$

In order to calculate the forces present in the system at each time step, the potential energy interactions between all objects in the simulation box are calculated using atomic potentials that

are usually assigned through the use of generalized force fields, but when more specific accuracy is required, custom, system-specific potentials are also used.

1.6.1.1 – Force Field Parameterization and Intermolecular Potentials

The non-bonding energies in molecular dynamics simulations are comprised of van der Waals and electrostatic terms. The classic functional form of the latter case is the 12-6 Lennard-Jones potential:

$$V_{LJ}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (1.50)$$

where r is the separation distance between the two atoms, ε is the depth of the potential energy well, and σ is the distance at which the potential energy is zero. The minimum of this function is found at $r_{min} = 2^{1/6}\sigma$. Though rarely applied in most force fields due to the extra calculations required, a possible extra term can be added to the van der Waals interactions to account for higher order relations, such as 3-body interactions.

Electrostatic interactions are often calculated by the placement of point charges on atoms, and the potential energy is calculated through Coulomb's Law:

$$V_{ES}(r) = \kappa \frac{q_i q_j}{r} \quad (1.51)$$

where r is the distance between two atoms, κ is Coulomb's constant, and q_i is the charge value assigned to the point charge. Dipoles and higher order multipoles are approximated by the placement of point charges that ideally correspond to the charge distributions and various multipole moments of the molecule.

While not exclusively true, most modern generalized force fields use "atom type" assignments^{90, 91}. An example of how this process works is for water molecules. The force field would assign the hydrogen in the molecules to the atom type of a "polar H", and sometimes more specifically "polar H bonded to O" or "O/F". The oxygen molecule might receive the atom type assignment of "O sp³ generic", or if the forcefield has a specific consideration for water, it might be "O sp³ water." Each atom type characterized by a force field will have specific parameterizations for each type of interaction and the atom type of the species the interaction takes place with through a combination formula. The Lennard-Jones parameter, σ , for an interaction between a hydrogen of one molecule of water with an oxygen of an adjacent molecule of water, for example, might be calculated:

$$\sigma_{H-O} = \sqrt[6]{\left(\frac{\hat{\sigma}_H + \hat{\sigma}_O}{2}\right)} \quad (1.52)$$

The point charge values are usually assigned through a “bond-increment” method, in which each bond in the molecule receives a partial charge that relates to the atom types of both atoms that comprise the bond^{90, 92}. The point charge value assigned to each atom is the sum of the partial charge values of each bond. Returning to the example of water, the point charge assigned to oxygen would be calculated by examining the H-O bond. The atom type of each atom would be considered as “polar H bonded to O” and “O sp³ water” for a particular force field. This bond type would receive a partial charge value from the forcefield. For a simple example, -0.2 e⁻, done for each bond in water, results in the total point charge for oxygen being assigned as 0.4 e⁻.

Hydrogen bonding, though primarily an electrostatic force, is an interaction type that is not handled well by the electrostatic bond-increment method utilized by some force fields. As a result, some force fields have an explicit hydrogen bond potential function on top of the van der Waals and electrostatic functions to account for the effect. Other force fields use special adjustments in their van der Waals parameters to act as a correction to the electrostatic potentials instead of using a third intermolecular calculation.

The parameterization of a force field is a trade-off between generality and specificity. It is not practical to program an atom type for every specific molecule possible, so the parameters need to be minimal enough to keep the design simple and generalized, while still containing sufficient specificity to maintain accuracy. In a well-developed force field, this compromise should still result in good accuracy for most systems. However, there will inevitably be some molecules or interactions that will not be well-accounted for by such generalization. In the topic of this dissertation, acetylene is an example of one such molecule where standard potentials, and even bespoke potentials, have fallen short of matching empirical data.

There are not only other potentials that can be used to alter a force field to match a specific system’s behavior, but also different functional forms for the potential energy calculations. The van der Waals terms might be described by a 10-4 or a 9-6 or other variants, corresponding to different exponent values in the equation to modify the strength of the attractive or repulsive forces⁹³. Other functions include the Buckingham potential⁶²:

$$V_{LJ}(r) = Aexp(-Br) - \frac{C}{r^6} \quad (1.53)$$

which modifies the repulsive term of the Lennard-Jones potential with an exponential term, serving to “soften” the repulsive forces of the potential while keeping the same r^6 attractive dispersion term. The A, B, and C terms are interaction-specific constants. Another possibility is a damped Morse potential⁹⁴:

$$V_{LJ}(r) = A([1 - \exp(-B(r_m - r))]^2 - 1) - f_6 \frac{C}{r^6} \quad (1.54)$$

where A, B, C, and r_m are the interaction specific constants and f_6 is an interaction specific damping function. Morse potentials generally have significant attractive and repulsive terms that are much too strong to represent intermolecular van der Waals forces, and so the damping serves to correct this imbalance while providing more degrees of freedom in fitting the potential terms to empirical data.

Electrostatic interactions are also often improved upon by higher-order approximations than those of simple point charges⁹⁵. Such considerations might include the addition of further point charges located throughout the molecule, such as between bonds or at the center of mass. Higher-order multipole expansions might also be used at each atom position, replacing the use of singular point charges with combinations of point charges, point dipoles, quadrupoles, or other n-pole moments. Expansion of the force field with customized van der Waals functions or the addition of large numbers of multipoles is costly, however, as these usually involve a significant increase in the computational demands required. As such, these types of modifications should be considered carefully and attempts to keep the model as simple as possible while maintaining accuracy should be made.

1.6.1.2 – Intramolecular Potentials

To account for different internal degrees of freedom within molecules, force fields also must parameterize these bonding energy terms as well. These include bond stretching, angle bending, torsions, and inversions. Furthermore, class II forcefields also account for the interactions of these internal modes with cross terms, such as a torsion-stretch coupling. For force fields that make use of the atom type assignment method described above, the same method is employed for the determination of these intramolecular components. The functional form of such components may vary from one forcefield to another, but a common form of these

is a harmonic approximation where the molecular bond is treated as a network of springs connecting the different atoms⁹⁰:

$$E_{bonding} = \frac{K_0}{2} (\theta - \theta_0)^2 \quad (1.55)$$

where $E_{bonding}$ is the energy associated with a bonding type interaction, K_0 is the force field assigned force constant, and θ and θ_0 are the current and equilibrium angle, respectively. Inversion motions are more complex as they involve the relative angles of three bonds about a central atom; however, these are often approximated the same way by using the average value of the three bond angles in what is referred to as the “Mean Wilson approximation”.

1.6.1.3 – Constraints and Restraints

To save computational expense and create a more idealized system to examine for interactions, constraints can be placed on parts of the system. In the case of adsorption studies, for example, the internal movements of the substrate material itself do not have a significant impact on film behavior but calculating their movements will add significantly to the computational expense of the endeavor. Displacement of the surface in small simulation spaces may also cause significant alterations to the overall surface corrugation, limiting the total accuracy of the simulations. By applying constraints, it is possible to “freeze” the surface atoms into geometrically optimized positions. These constraints mean that the forces acting on these atoms no longer need to be included in the calculations. Forces they induce on unconstrained particles are still considered, however, so this will not alter the substrate effects on molecules in the system.

A tool similar to a constraint is a restraint. This allows for the addition of parameters not explicitly included in the force field. For example, the Compass forcefield lacks a parameter to control torsions along the axis of a molecule when more than four atoms are involved in the torsion plane. In the case of allene and its family of cumulene molecules, this means that the torsion angle of the two perpendicular bond planes at opposite ends of the molecular axes (refer to section 1.9.2 for structure of allene) are not considered in the potential energy calculations, and the torsion angle is free to rotate with respect to the force field. A constraint cannot be used as a viable solution here utilizing software like Materials Studio, as only absolute atomic coordinates may be constrained, not relative coordinates within a molecule. If a constraint were

applied, it would lock this parameter entirely, creating a situation that may not be any more realistic than the system without the constraint. A restraint is treated like a potential energy term within the force field that is assigned directly by the user. In the case of allene, a harmonic torsion restraint may be defined for the axial torsion angle and assigned a force constant that can be obtained through empirical data or other computational methods. This will allow for a potentially more accurate representation than that seen in the uncorrected or constrained molecule.

1.6.1.4 – Temperature and Thermostats

In thermodynamics, temperature is defined by its association with the average kinetic energy of a system^{96, 97}. Molecular dynamics simulations use this definition to calculate the temperature by averaging the kinetic energy of all the particles in the system:⁹⁷

$$T = \frac{1}{Nk_B} \langle \sum_{i=1}^N m_i \|\vec{v}_i\|^2 \rangle \quad (1.56)$$

where T is temperature, N is the number of particles, k_B is Boltzmann's constant, m_i is the mass of particle i , and $\vec{v}_i$ is the velocity of particle i . The simplest thermostat is called the velocity scale thermostat. In this method, the velocity of all particles in the system are rescaled in order to maintain an exact temperature at each time step:

$$v'_i = v_i^o \sqrt{\frac{T_{set}}{T_{sys}}} \quad (1.57)$$

where v'_i and v_i^o are the rescaled and initially-calculated velocities, respectively, and T_{set} and T_{sys} are likewise the set temperature and calculated temperature of the simulation box. This method is incredibly harsh to the dynamics of the system as the abruptness of the temperature regulation serves to dampen the thermodynamic fluctuations that should be inherent to a system, often resulting in physically unrealistic behaviors. Thermostats with greater accuracy attempt to maintain more realistic thermal dynamics of the system while maintaining temperature. For systems near equilibrium, the Nosé-Hoover-Langevin (NHL) thermostat is a reliable algorithm. This method works by instituting an extra degree of freedom to the system that represents contact of the system to a fictitious heat-bath. The energy of this new total system is held constant, instead of directly regulating only the simulation space, and the expression for this constant total energy, H' , is⁸⁸

$$H' = E_{KE}^{sim} + E_{pot}^{sim} + \frac{Q}{2}\dot{\zeta}^2 + Nk_B T_{set} \ln(S) \quad (1.58)$$

where E_{KE}^{sim} and E_{pot}^{sim} are the kinetic and potential energy of the system as already defined, respectively, Q is a mass term associated with the heat bath, and ζ and $\ln(S)$ are position and velocity terms related to the fictitious degree associated with the thermostat heat bath, respectively. The new associated equations of motion are:

$$\frac{d\ln S}{dt} = \dot{\zeta} \quad (1.59)$$

$$\frac{d\zeta}{dt} = \frac{E_{KE}^{sim} - Nk_B T_{set}}{Q} - \gamma\zeta + \dot{w} \sqrt{\frac{2\gamma k_B T_{set}}{Q}} \quad (1.60)$$

where γ is the decay time constant affiliated with the strength of the stochastic process and w is a Wiener process. This thermostat does not function well for systems far from equilibrium and may cause unphysical results in the initialization of a new simulation space as molecules are packed too closely. A method to circumvent this might be to start a simulation for several picoseconds with a velocity scale thermostat in order to initiate the system in a more realistic position, though a better practice would be to set the initial placement of molecules to avoid this problem if possible.

1.6.1.5 – The Compass Force Field

The force field employed in this study is the COMPASS force field, which is a proprietary force field that is incorporated into the Materials Studio software. COMPASS is an empirically derived class II force field that has been well-validated for many light molecule and hydrocarbon systems⁹⁰. The total energy calculation of COMPASS is the sum of individually calculated bonding and non-bonding parameters:

$$E_{total} = E_{bond-stretch} + E_{bond-angle-bending} + E_{bond-torsio} + E_{bond-invers} + \dots + E_{bond-cross-ter} + E_{electrostatic} + E_{van-der-Waals} \quad (1.61)$$

The use of the 9-6 Lennard-Jones potential serves to “soften” the short-range repulsive interactions but comes with a trade-off of less accuracy for the attractive dispersion forces at long range.

The forces at each time step are calculated by means of analyzing the gradient of the potential energy field:

$$-\frac{\partial V}{\partial r_i} = m_i \frac{\partial^2 r_i}{\partial t^2} \quad (1.62)$$

The forces acting on each atom in the system are calculated for each step, out to a predetermined cut-off distance to limit computational demand, and from that velocities are calculated and the system is moved ahead to the new positions at the next time increment, where the process repeats.

Even with the ability to potentially compute the dynamics of systems with thousands of atoms efficiently, there are still upper limits to simulation size. Furthermore, any finite box will suffer from unrealistic conditions at the boundaries of an open system. To account for the comparatively infinite size of real systems compared to a simulated one, and to prevent issues at the edges of the simulated space, periodic boundary conditions are used to wrap the edges of the simulation space back on itself to create a closed system. If a particle leaves the edges of the simulated environment, it will reenter on the opposite edge of the space⁹⁷.

1.6.2 – Trajectory Analysis

Trajectory documents are generated as the result of molecular dynamics simulations which store the positional and velocity data for all species in the simulation box at some selected interval of simulated time. Generally, storing every calculated time step as a frame in the trajectory is not necessary and would require a significant amount of extra storage capacity. A quick analysis of these trajectories can be made by qualitative observations of the animation of these trajectories into movies. These are extremely useful in providing an image of the microscopic structural and dynamic behavior of a system. However, quantitative information obtained from these is more practical for understanding the time average, long range, and variations in the behavior of the systems over time, as well as in providing a meaningful comparison to empirical results.

1.6.2.1 – Radial Distribution Functions

The radial distribution function, $g(r)$, is a useful tool in examining the structure of a system. This paired correlation function gives the probability of finding a second particle at a given radius centered on a particle. Doing this on an atom by atom basis, while including more information about the orientational relationships of molecules to one another, is difficult to interpret due to the increased number of peaks concomitant with the association of each atom in a molecule to each atom in every molecule around it. In practice, this generates data of such

complexity that it is difficult or impossible to interpret. Alternatively, using the radial distribution function of only the centers of mass for each molecule provides a much clearer picture of the translational order of the system. In two dimensions, the radial distribution function is defined as⁹⁸:

$$g(r)_{2D} = \frac{1}{2\pi r \rho_{2D}} \times \frac{dn_r}{dr} \quad (1.63)$$

where r is the radial distance, ρ_{2D} is the two-dimensional number density (particles per unit area), and $\frac{dn_r}{dr}$ is the rate of change of particle count as a function of radius. In simulations, however, this is calculated by numerically histogramming particle counts as a function of radius:

$$g(r)_{2D} = \frac{1}{2\pi r \rho_{2D}} \times \frac{N(r+\Delta r) - N(r)}{\Delta r} \quad (1.64)$$

where $N(r)$ is the number of particles found between zero and radius r . In other words, it is the expectation value of the number of particles found in a circular shell between radii of r and $r + \Delta r$.

This function provides the ability to examine the time-averaged structural variation and extent to which a system is ordered or disordered. It can also provide a clearer picture of what the preferred structure is in a dynamic, disordered system. As a function of temperature, this can help provide an indication of where phase changes might occur within the simulations by the observed changes in the amount of disorder present.

Since the function represents the probability of finding a particle at a given distance, the integral of this function around each peak represents the coordination number at that distance from the center. The widths of these peaks are an expression of the variation in position expected at each site as it relates to radial axis. Additionally, since this is an average over all particle centers in the system, it provides information about the degree of isotropic translational disorder of the system within the two-dimensional plane. Its relation to the structural elements of the system means it can also be related to the structure factor as⁷⁸:

$$S(Q) = 1 + \rho_{2D} \int e^{-iQr} g(r) dr \quad (1.65)$$

Furthermore, the combined variation in the potential energy variation molecules can be related to $g(r)$ at low surface coverages and film densities (i.e. adsorbed gas phases). As an approximation, this relationship is given by⁷⁸:

$$V(r) = -\frac{\ln[g(r)]}{k_B T} \quad (1.66)$$

1.6.2.2 – Concentration Profiles

The radial distribution function is a useful tool for analyzing the translation structure and order of a simulated film; however, since it only focuses on the centers of mass, and only looks at radial distances within the two-dimensional plane, it does not provide information about the orientation of the molecules perpendicular to the surface plane, nor any information about the distance between the film and substrate surface. To better quantify this information, concentration profiles can be used. Similar to radial distribution function, concentration profiles are linear probability distributions of particles along a pre-defined axis of the simulation box. Performed along an axis that is perpendicular to the film and substrate surface for all atoms of the system, this provides information about the vertical ordering and orientation of molecules in the simulations.

1.6.2 – Geometry Optimization and Energy Minimization

While not themselves molecular dynamics simulations in the truest sense, the force fields applied in dynamics studies can also be used to determine the minimum energy configurations of a system. For a single molecule on a substrate, they can be used to examine possible preferred adsorption sites and their associated binding energies, as well as yield some information about the corrugation of the surface potential.

Several efficient algorithms exist for locating minima that can be utilized in such geometric refinement⁹⁹. Gradient decent algorithms measure the derivative of the phase space around its current location within that space. It will move in the direction of the steepest gradient from its current position to define a new position for the next step in the iteration. This method tends to have slow convergence, but high accuracy. There are modified versions of this algorithm that combine the process with line searches to locate optimized starting positions through a one-dimensional sampling of the phase space. It is also possible to sample multiple points in the direction around the current location to find a mutually shared gradient and move in that direction to improve convergence. Algorithms based on modified forms of the Newton-Raphson method are common as well, which incorporates consideration of the local curvature in addition to the gradient in order to determine what direction to move in.

A difficulty in the process, even with efficient algorithms is the complexity of the potential energy function even for just a single molecule, as is demonstrated in equation 1.61. It is

therefore very easy for such calculations to become stuck in localized minima and not locate the absolute global minimum for the preferred binding sites. The process should be repeated multiple times with varying initial conditions to examine a realistic portion of the total phase space of configuration energies.

1.7 – Adsorption Isotherms

The most recognizable experimental technique in the study of adsorption processes is the adsorption isotherm. The goal of an adsorption isotherm measurement is to determine the amount adsorbed as a function of the equilibrium vapor pressure at a constant temperature. In three dimensions, PVT phase diagrams are often created based on the three thermodynamic quantities pressure, specific volume, and temperature. The normal representation of a phase diagram as a function of temperature and pressure is the projection of the PVT phase diagram along axis of specific volume. In two dimensions, one can envisage a PAT phase diagram, that is a function of pressure, specific area, and temperature.

In an adsorbed system, the surface area for adsorption is a fixed quantity of the substrate sample, and the specific area is proportional to the number of moles adsorbed to the surface. Therefore, a PNT phase diagram of an adsorbed system can also be constructed in terms of pressure, moles adsorbed, and temperature. Adsorption Isotherms therefore are measurements follow lines of constant temperature along the surface of this phase diagram¹⁰⁰.

These experiments can use either volumetric or gravimetric techniques to determine the amount of adsorbed molecules as a function of equilibrium vapor pressure. The method used in this dissertation is volumetric and will be the method discussed herein.

1.7.1 – The Volumetric Isotherm Process

The process of the volumetric adsorption isotherm begins by introducing a specific pressure, p_i , of adsorbate gas into a calibrated manifold volume, V_{ds} . This aliquot of gas is then expanded into a temperature regulated cell containing the substrate sample. As the sample adsorbs onto the surface, the pressure falls until the film reaches equilibrium with the vapor pressure of the bulk gas phase. The equilibrium pressure at this point is recorded as the current vapor pressure, p_f , and the quantity of moles adsorbed is tracked through the difference

between the initial dosing pressure of the aliquot and the final equilibrium pressure for the dose, Δp :

$$\Delta p = p_i - p_f \quad (1.67)$$

This process is then repeated by additional introductions of new aliquots of gas and further monitoring of the equilibrium and changes in pressure. The sample cell is not at the same temperature as the calibrated manifold and has voids which add additional volume, referred to as dead-space volume (V_{ds}). The changes in pressure are not only a result of molecules leaving the bulk gas phase during adsorption but are also the result of the increased volume and decreased temperature. To calculate the moles of gas that adsorbed to the surface, a dead space correction is used to account for these other shifts in pressure:

$$\sum_j n_{ads} = \frac{V_{cal} \sum_j \Delta p}{RT_{cal}} - \frac{V_{ds} p_{fj}}{RT_{cell}} \quad (1.68)$$

where j is the index for each isotherm data point in the dosing sequence, T_{cal} is the temperature of the calibrated volume (which is safely considered to be room temperature), T_{cell} is the temperature of the cell containing the substrate (the isotherm temperature), and R is the gas constant. The first term of this equation calculates the total apparent loss of moles from the gas phase using the running total of Δp employing the ideal gas law, and the second term acts as a correction to this by subtracting the current amount of adsorbate still in the bulk gas phase using the current equilibrium pressure and dead-space volume.

1.7.2 – Isotherm Classification and Models

Following adsorption isotherm research in the first decades of the 20th century, Brunauer *et al.* proposed a classification system of isotherms based on the adsorption (or absorption) behavior they presented. This system has been adopted and updated by the IUPAC (International Union of Pure and Applied Chemistry.)¹⁰¹ (Figure1.13)

Type I isotherms are demonstrated systems that obey the Langmuir model for adsorption isotherms. This model was one of the first serious attempts at explaining the adsorption process. It assumes that there are specific binding sites where adsorption occurs, and the amount adsorbed depends on the number of these binding sites. Once full occupancy is reached, adsorption no longer occurs. Adsorption and desorption processes from these sites are viewed

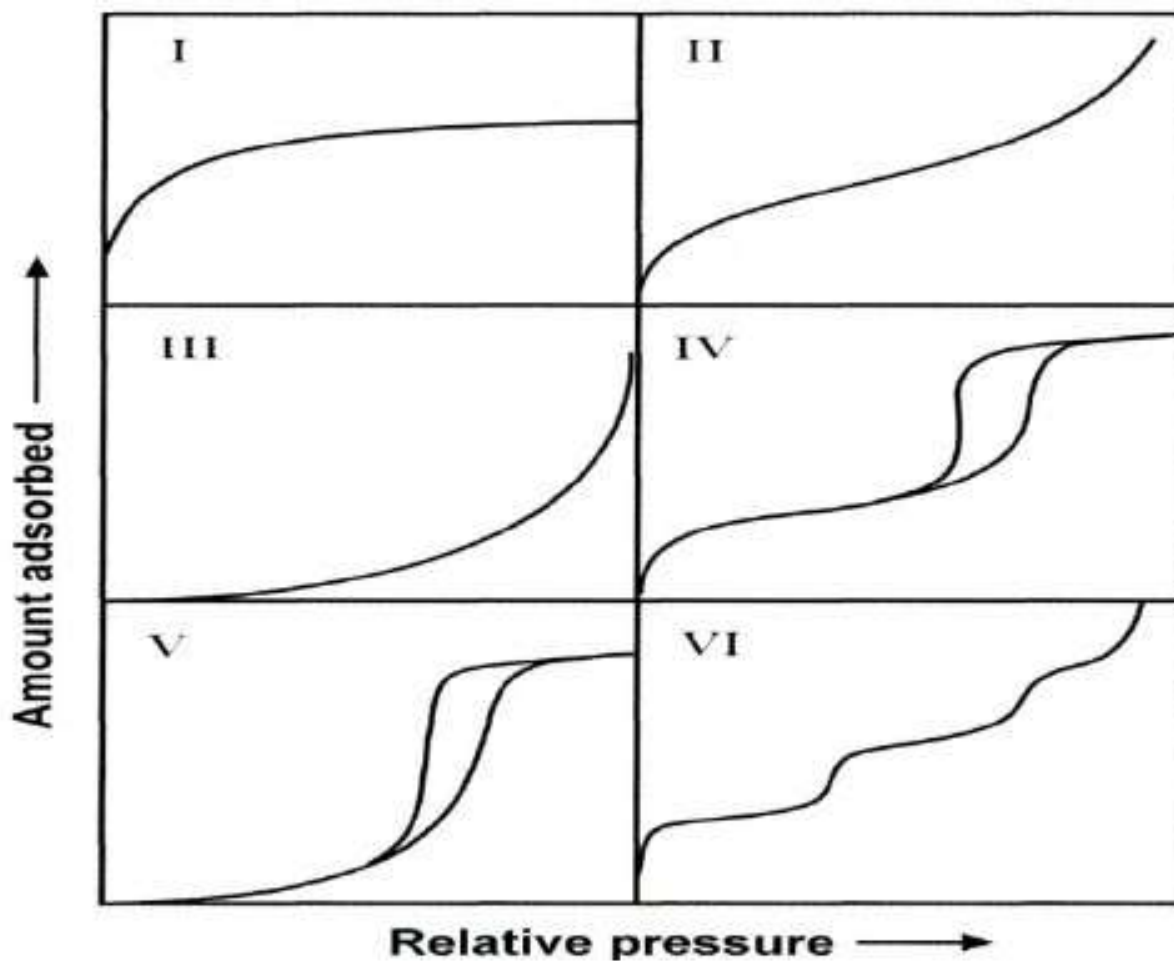


Figure 1.13: IUPAC isotherm classification system

Taken from Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity (Recommendations 1984)¹⁰¹

in terms of the rates of these two processes. The equilibrium condition is set when these two rates are equal, and the fraction of site occupancy, θ is defined by⁶:

$$\theta = \frac{K_{eq}p}{1 + K_{eq}p} \quad (1.69)$$

where p is the pressure and K_{eq} is the equilibrium constant given by:

$$K_{eq} = \frac{k_{adsorption}}{k_{desorption}} \quad (1.70)$$

where k_i is the rate constant of the respective process. The Langmuir model only considers molecule-surface interactions and is not generally quantifiably accurate. There are systems that have or behave like they have discrete binding sites: the first case is in chemisorption, where adsorbates chemically bond to surface atoms, and the second involves systems with micropores that only have the capacity to hold a few adsorbate molecules.

Type II isotherms are demonstrated by adsorption on many non-porous substrates. Originally type II would have included isotherms that display distinct multilayer step features; however, such isotherms now have their own classification type. Type II isotherms under the current definition demonstrate a distinct monolayer formation, followed by multilayering transitions that are not well defined, and the isotherm asymptotically approaches bulk vapor pressure. These isotherm types are often referred to as the BET type after the eponymous model developed by Brunauer, Emmett, and Teller¹⁰². This model is an extension of the Langmuir model, but suffers from many of the same shortcomings. It assumes that the molecule-molecule interactions of the adsorbate molecules only occur between layers, ignoring lateral interactions within the film, and assumes that only the heat of adsorption of the first layer is unique and that of the higher layers is the same as the heat of bulk condensation. The BET equation is generally formulated in terms of fractional coverage relative to a monolayer capacity; however, this model finds use most often in the determination of surface area through the total capacity of the first monolayer. The equation is then more conveniently constructed in a linear form:¹⁶

$$\frac{1}{n_{ads}(p_0/p)} = \frac{c-1}{n_m} \left(\frac{p}{p_0} \right) + \frac{1}{n_m c} \quad (1.71)$$

where p is pressure, p_0 is the saturated vapor pressure of the bulk gas at the isotherm temperature, c is the BET constant related to the heat of adsorption of the first layer and bulk heat of condensation, n_{ads} is the moles of gas adsorbed, and n_m is the monolayer capacity of the

surface. A linear fit of the isotherm data based on this equation can be used to determine the monolayer capacity and, using the specific area of the gas, the surface area of the material.

Type III isotherms display a distinctive convex shape that results from systems where the molecule-molecule interactions are significantly stronger than the molecule-surface interactions. In these systems, no distinct layering transitions can occur, and the pressure will asymptotically approach the bulk saturated vapor pressure.

Type IV and V isotherms both possess a distinct hysteresis between sorption and desorption isotherm branches¹⁰³. This is characteristic of systems that contain mesopores^{104, 105}. The hysteresis is due to capillary forces within the pores and can be used as a method to determine pore size through the use of the Kelvin equation³:

$$\ln \frac{P}{P_o} = \frac{-2\gamma V_L}{RT} \frac{1}{r_m} \quad (1.72)$$

where p/p_o is the reduced vapor pressure, γ is the surface tension, V_L is the molar volume of the absorbate, and r_m is the radius of curvature. The radius of curvature can be related to the pore radius, but the exact relationship between these variables depends on the specific geometry of the pore network. A further subclassification system is defined by IUPAC that relates the appearance of the hysteresis loops to the pore geometry. The distinction between these two types of isotherms is the absence of an adsorption monolayer feature in the type V isotherms. In short, type IV isotherms display both adsorption and desorption, while type V only displays absorption.

Lastly, the type VI isotherms are those that exhibit multiple well-defined layering transitions. These occur on pristine and uniform substrate surfaces of non-porous materials. Systems displaying this type of isotherm are some of the classic examples of isotherm systems, such as xenon adsorbed on graphite and methane adsorbed on MgO.

This classification system represents a generalization of the processes that occur during adsorption and are not an exhaustive list of all possibilities. There are systems that may display characteristics of more than one type of isotherm and those that will not be easily fit into any of these categories. For example, there are adsorbed systems, one such case of which will be a subject of this dissertation, where multiple monolayer sub-steps occur corresponding to probable transitions within the film. Another such example that will also be covered in this

dissertation is a system that displays two distinct monolayer formations before becoming completely non-wetting prior to accomplishment of the bulk saturated vapor pressure.

1.7.3 – Thermodynamics

One of the key utilizations of adsorption isotherms is the determination of the thermodynamics of adsorption. These involve the comparison of the enthalpy and entropy of two-dimensional condensation on the surface over that of condensation to the bulk phases, along with other heats of adsorption quantities such as the isosteric heat of adsorption. These are useful in understanding not only the energetics of the adsorption process, but also help to provide support for potential phase behaviors and transitions.

1.7.3.1 – Henry's Law

During the beginning stages of the adsorption process, the density of molecules is sufficiently low that molecule-molecule interactions should be sparse. This region, corresponding to a low coverage area ideally before the rise of the first monolayer step, is referred to as the Henry's law region. For systems where this assumption holds true and the region has enough data points available, it is possible to isolate and examine the adsorption energy only corresponding to the molecule-surface interactions. This quantity, Q^0 , is the heat of adsorption in the limit of zero coverage, which is related to the slope ($k(T)$) of the isotherm plot within this region^{106, 107}:

$$k(T) = k^* \exp \left(\frac{Q^0}{RT} \right) \quad (1.73)$$

where k^* is a constant of integration. Therefore, on a plot of $\ln(k(T))$ vs $1/RT$, the slope of a linear regression will yield Q^0 . The interpretation of data obtained from the Henry's law region must be done carefully as it is not always an accurate representation for determining Q^0 . The major compounding factors are that the assumptions that molecules will not interact at low coverages may not be valid, and defect sites may result in surface binding in this region and will not reflect the true molecule-substrate interactions.

1.7.3.2 – Differential Enthalpies, Differential Entropies, and Heats of Adsorption

The nature of an adsorbed phase on a surface may be regarded as a condensed phase, just as bulk solids and liquids. These condensed phases exist in equilibrium between the two-

dimensional condensed phase and the bulk three-dimensional gas phase. The equilibrium pressure of this gas phase will then correspond to the vapor pressure of the condensed phase of the adsorbed film. It follows that the layering transitions of adsorbed systems would be expected to obey the Clausius-Clapeyron relationship. This is the basis of the Larher formalism for quantifying the thermodynamics of adsorbed systems^{9, 10}.

The pressure of each layering transition is identified using the location of the maxima in the numerical derivative of an isotherm that corresponds to each transition. Employing a series of isotherms, these data can be plotted using $\ln(p^{(n)})$ vs $1/T$, where n is an index referring to specific layering features observed in the isotherms. The plots of these data can be fit to linear functions using of the following form:

$$\ln(p^{(n)}) = A^{(n)}(1/T) + B^{(n)} \quad (1.74)$$

In accordance with the Clausius-Clapeyron relationship, the coefficients obtained from this linear relationship, $A^{(n)}$ and $B^{(n)}$, are related to the enthalpy and entropy of the adsorption processes, respectively:

$$\ln(p^{(n)}) = \frac{H^{(n)}}{R}(1/T) + \frac{S^{(n)}}{R} \quad (1.75)$$

In order to apply a more relevant basis for interpreting these thermodynamic quantities, a comparison with the bulk saturated vapor pressure serves as a useful standard reference point. It can be assumed if a layering transition occurs below the bulk vapor pressure, the formation of this layer is more thermodynamically favorable than the bulk phase condensation. Expressed in terms of chemical potential $\mu^{(n)}$, this comparison of adsorbed favorability over that of the bulk condensed phase chemical potential, μ^o , is:

$$(\mu^{(n)} - \mu^o) = RT \ln\left(\frac{p}{p_o}\right) \quad (1.76)$$

Therefore, where can use the Clausius-Clapeyron fit parameters of the bulk vapor pressure as a function of temperature, A^∞ and B^∞ (the infinity index is used to refer to “infinite adsorbed layers” which is the bulk phase):

$$\Delta H^{(n)} = -R(A^{(n)} - A^\infty) \quad (1.77)$$

$$\Delta S^{(n)} = -R(B^{(n)} - B^\infty) \quad (1.78)$$

The molar heat of adsorption of each layer can also be quantified as:

$$Q_{ads}^{(n)} = RA^{(n)} \quad (1.79)$$

1.7.3.3 – Isosteric Heats of Adsorption

The isosteric heat of adsorption, Q_{st} , is defined as the amount of energy required for a molecule of the gas phase to adsorb into the surface film at constant coverage, θ . Since this can be applied for the total span of coverages of the isotherm measurements, this quantity is expressed as a function of these ranges of coverage, $Q_{st}(\theta)$. The isosteric heat of adsorption is defined by²⁶:

$$Q_{st}(\theta) = RT^2 \left(\frac{\delta \ln(p)}{\delta T} \right)_{\theta} \quad (1.80)$$

As this quantity involves a partial derivative with respect to temperature, this is not something that can be obtained directly from an isotherm measurement. Instead, it is estimated by the numerical derivative of two isotherms that are closely spaced in temperature ($0.5 \text{ K} \leq \Delta T \leq 1 \text{ K}$):

$$Q_{st}(\theta) \approx R\bar{T}^2 \left(\frac{\Delta \ln(p)}{\Delta T} \right)_{\theta} \quad (1.81)$$

Extending from the definition of isosteric heats, changes in behavior of this function at certain coverages can be used as indicators for sites of potential phase transitions.

1.7.3.4 – Two-Dimensional Isothermal Compressibility

In the calculations of the differential enthalpies and entropies, along with the heats of absorption, the numerical derivative was used to define the locations of layering transitions. Strictly speaking, these locations would be more properly defined by changes in the isothermal compressibility of the system. For two dimensions, this can be calculated from adsorption isotherm data as⁶⁷:

$$K_{2D} = \frac{Ap}{N_A k_B T n^2} \left(\frac{dn}{dp} \right) \quad (1.82)$$

where K_{2D} is the two-dimensional isotherm compressibility, A is the surface area of the substrate, p is pressure, N_A is Avogadro's number, k_B is Boltzmann's constant, and n is the quantity of moles adsorbed. Though convoluted by a factor of p/n^2 , the shape of the isothermal compressibility as a function of the equilibrium pressure is defined primarily by the numerical derivation of the isotherm, dn/dp . The use of numerical derivatives as a representation of the

behavior and location of the compressibility is a reasonable substitution analysis of phase transitions from isotherms.

1.7.4 – Surface Area and Film Density

In three dimensions, the consideration of condensed phases at the saturated vapor pressure is not usually dependent on the number of molecules present, and a solid could theoretically grow indefinitely if more molecules are continually cooled enough for them to freeze. Adsorbed phases, however, are limited by the surface area constraints of the substrate. For a film of a given density, only a certain number of molecules can be adsorbed onto the surface until no additional space is available. The surface area, A , areal number density, ρ , and monolayer capacity, n_m , are linked by the proportional relationship:

$$A = \frac{n_m}{\rho} \quad (1.83)$$

The quantity, $1/\rho$, is the area per molecule of the adsorbate, and is the traditional form in which film densities are reported. It would be possible, therefore, with an accurate determination of surface area, to calculate and the monolayer capacity in order to further calculate the areal density of the film. This can be done by using a gas adsorbate, for which the density is known, on the substrate of study. The amount adsorbed can be determined through an isotherm using this characterization gas, and the surface area can be determined using equation 1.83. This surface area can then be used in conjunction with the monolayer capacity of the primary adsorbate molecule to determine the areal densities of the films.

A consistent definition to delineate at what point the completion of a monolayer occurs and the amount adsorbed at that point is a necessary component for this analysis; however, there have been multiple suggestions on how this point should be defined. The one example already discussed above is through use of the BET equation (1.71). In addition to this model, Brunauer and Emmett proposed a series of other methods referred to by points A through E¹² (Figure 1.14). These all are based on the behavior of the linear region following the monolayer transition. The most favored of these has become the point B method. If the plateau region is fit with a linear function, point B designates the point at the beginning of this linear region, or more observationally, the point at which the linear fit of the plateau region and the isotherm start to diverge. This method has one inconsistency in that this point has some dependence on the

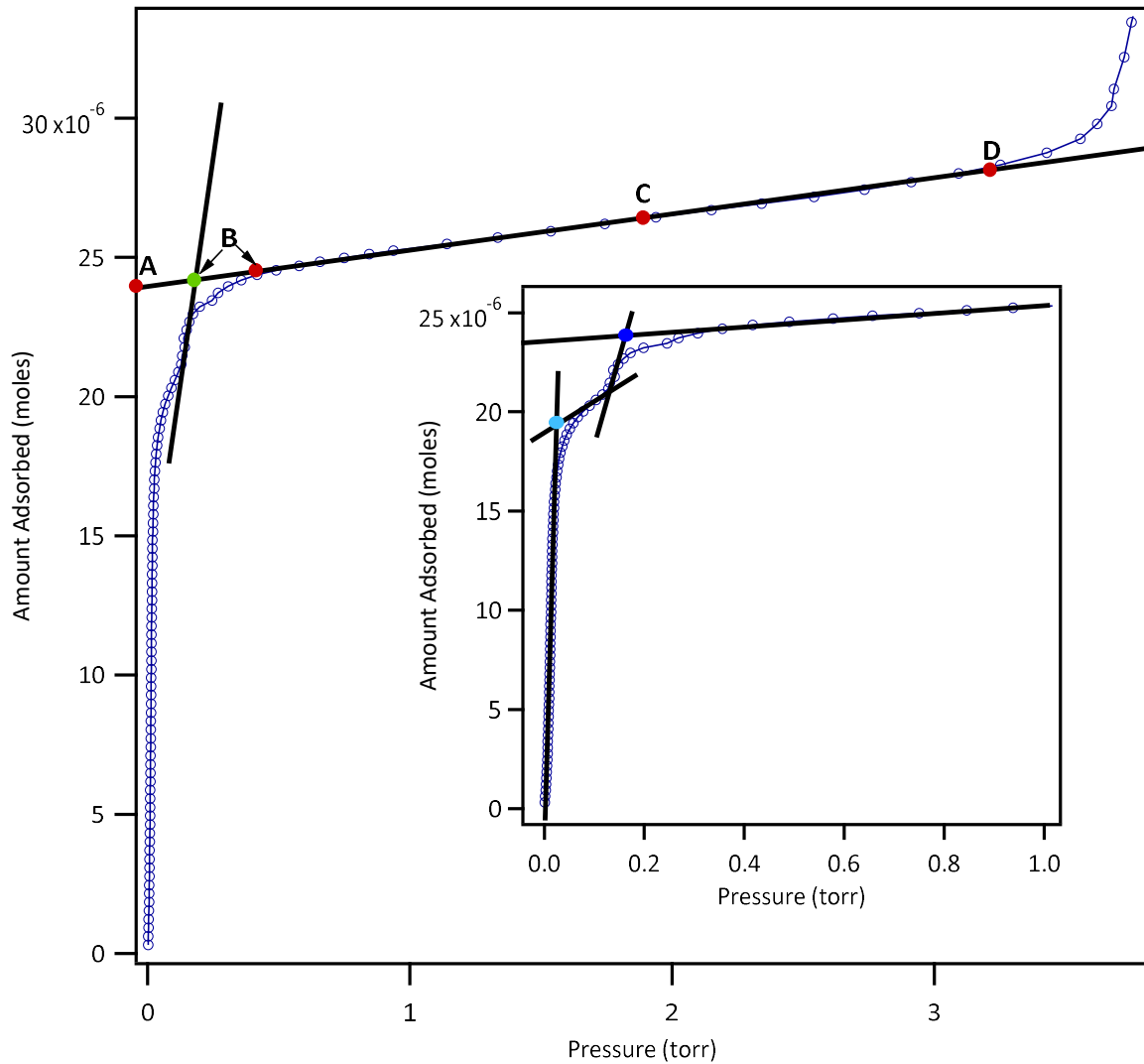


Figure 1.14: Methods for the determination of the amount adsorbed at monolayer completion
Point E is not shown for scaling purposes, but is the point at which the monolayer line intersects a vertical line positioned at the saturated vapor pressure.

qualitative observation of what the linear range is taken to be. A modification to the point B method uses the intersection of a linear fit of the plateau with a linear fit of the vertical region of the monolayer step shown as the green point in Figure 1.14. This modification is what will be used for the determinations of surface area in this dissertation.

1.7.5 – Determination of Phase Transitions

The locations of potential phase transitions can be determined through analysis of the isotherm data. The Clausius-Clapeyron analysis results in a type of pressure-temperature phase diagram where some examination of phase behavior and the temperature where some transitions may occur can be observed. The examination of features in the isosteric heat of adsorption can also be used to suggest qualitatively where phase transitions may occur; however, with this case, the approximations made in the determination of isosteric heats may result in artefacts in the interpolation process necessary to enforce the constraint of constant coverage and noise in the isotherm measurement and can make these data difficult to interpret analytically.

The most common method for the locations of potential phase transitions is through the examination of the two-dimensional compressibility. The compressibility of a phase represents the change in area (or volume in three dimensions) that results from changes in pressure. If a system undergoes a phase transition, there should be a corresponding change in the behavior of the compressibility before and after the transition. By examining the FWHM of the compressibility as a function of the change in chemical potential, temperature of transitions may be extrapolated from a plot of these FWHMs versus temperature as points where the slope of this data appears to change. The compressibility as calculated from isotherms has one significant draw back, though: since it is proportional to p/n^2 , this creates challenges in the limit where p and n both tend towards zero, or if the derivative is too steep, as their relationship means the proportion becomes extremely sensitive to small fluctuations in one or both of these terms. This may result in that for some system, the shape of the compressibility peaks could be distorted and not reliable for use in analysis. Alternatively, the FWHM of the numerical derivatives may be examined since they are a primary component in the definition of the shape of the compressibility function. The derivative function, however, is not convoluted by the ratio p/n^2 , and is not as sensitive to measurement fluctuations near zero.

1.8 – Phase Transitions in Adsorbed Films

The concept of adsorbed systems having phase behavior analogous to three-dimensional systems has already been referenced to in the previous sections of this chapter. These two-dimensional phases bare many analogous relationships to the familiar bulk phases. There are distinct equivalents for solids, liquids, and gases present in monolayer films. There are also unique aspects of these systems that may include phases that have no obvious analog in three dimensions. One peculiar aspect of two-dimensional phases is the melting process, where observations have suggested that the loss of translational ordering of the solid, and the loss of orientational and bond ordering, do not always occur at the same temperature^{85, 87, 108-110}. The following sections will serve as a guide to some aspects of phases and phase transitions in adsorbed systems.

1.8.1 – Two-Dimensional Phase Diagrams

To facilitate better understanding of the behavior of two-dimensional phases, a logical introduction is to examine the phase diagram of a well-behaved adsorbed system (Figure 1.15) This case is of a type referred to as a classical van der Waals film; well-studied examples of systems with this isotherm behavior include noble gases like xenon and krypton. Diagrams of this form are superimposed onto the coverage versus pressure graphs of a series of isotherms, and the isotherms themselves, by definition, correspond to lines of constant temperature within the PN phase diagram. Thus, this is a two-dimensional projection of the full PNT phase diagram, and one can note the similarities with three-dimensional PVT phase diagrams.

The phases are referred to by their analogous behavior to three-dimensional phases. Two-dimensional solids have highly ordered structures. Whereas two-dimensional liquids have less ordered structures and diffusive properties. A two-dimensional vapor or gas phase likewise shares similar properties to its bulk counterpart, i.e. higher compressibilities and diffusion. Also marked in Figure 1.15 are the two-dimensional critical and triple points, that are again analogs of these bulk phenomena. The triple point has a more interesting significance in adsorbed films, however. The phase diagram only shows the thermodynamic relationships of the two-dimensional solid, liquid, and gas, but the system must also be in equilibrium with the three-dimensional vapor phase. Therefore, the triple point with regards to the two-dimensional

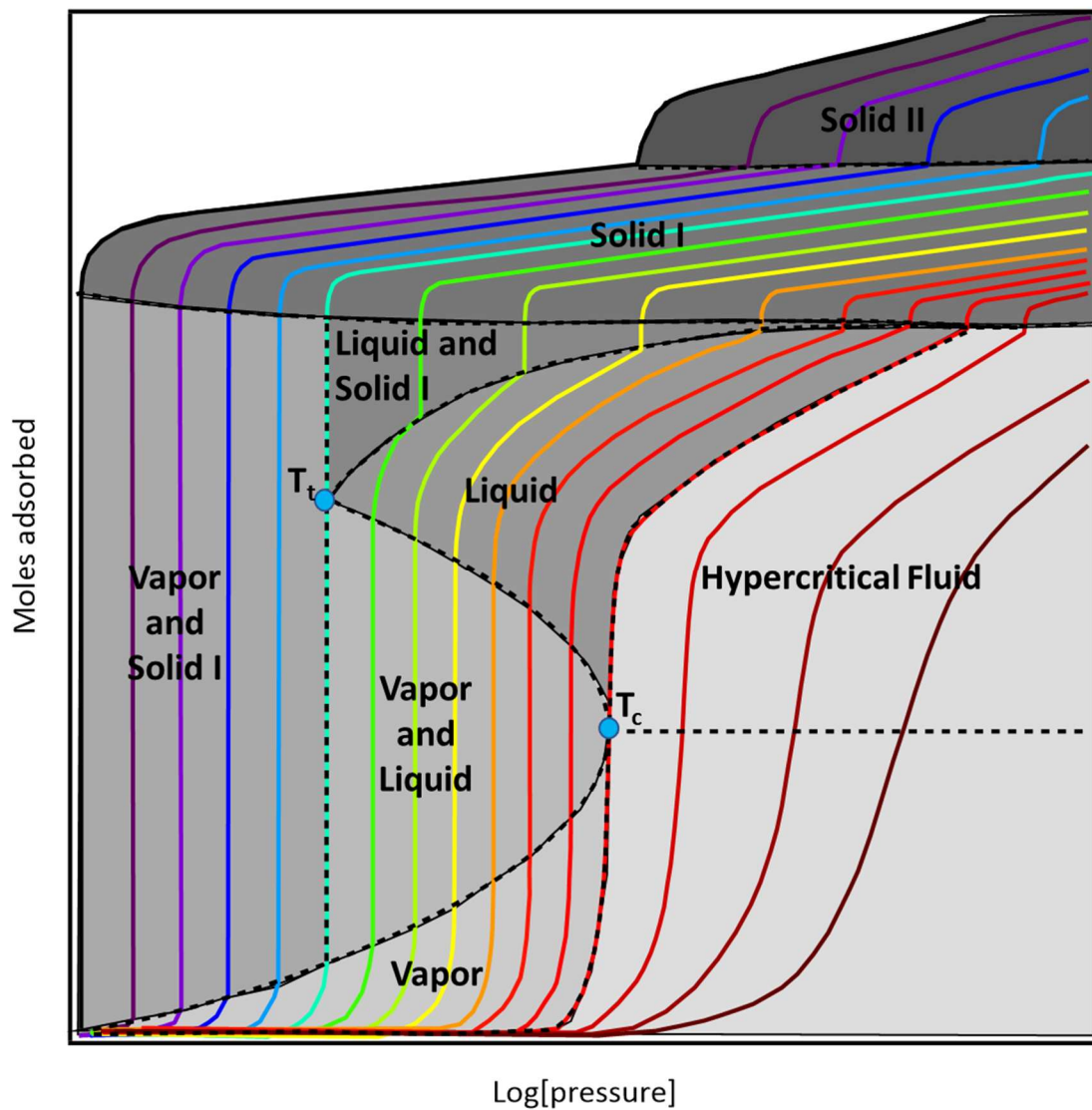


Figure 1.15: Phase diagram of a typical van der Waals adsorbed film
 Based on the phase diagram for xenon on graphite⁶⁷

phases is actually a quadruple point if all components to the system are considered. Figure 1.16 shows a constructure of a Clausius-Clapeyron plot of the system from Figure 1.15.

A quality of adsorbed phases that has no analogy in bulk phases are those arising from substrate effects. A notable manifestation of this is commensurability that was discussed in section 1.4.4. In these phases, the surface corrugation exerts a strong enough influence that directs the interactions of the adsorbed molecules, bringing the overlayer structure of the molecules into registry with the surface corrugation. This would initially seem to suggest that commensurate phases are expected to be two-dimensional solids, since the order is being guided by the long-range order of the substrate^{26, 111, 112}. However, if the driving forces of the molecule-molecule interactions are incompatible with the surfaces, strain between these forces can result. In systems where this is the case, melting would relieve this strain and lead to the possibility of the liquid or disordered phase being commensurate. Likewise, systems may have one or more transitions between commensurate and incommensurate solid states. There are many systems that have such properties, but a common one is that of nitrogen on graphite. This system has an example of two fully commensurate phases: one as a herringbone pattern that is highly ordered, and an orientationally disordered solid that is still in registry with the surface. At higher densities, there are two more solid phases, one of which is uniaxially commensurate with the surface (only has registry along a single lattice vector), and a fully incommensurate solid phase.

Lastly, there are two more types of transitions that are noteworthy here. The first of these is wetting transitions, where a system may switch from incomplete to complete wetting behavior at some specific temperature^{45, 113, 114}. Generally, this is accompanied by a melting of the adsorbed phase, relieving straining forces between the film and surface structure that are preventing complete wetting from occurring. The second is strong substrate interaction in multilayer systems. In some systems, each of these layers may act thermodynamically discrete and show completely different and independent critical points. This also means that, in these systems, different layers of the films may be in different states while at the same temperature.

1.8.2 – Two-Dimensional Melting

Perhaps one of the most unique aspects of two-dimensional phases is the diversity and complexity of melting phase transitions; so much so, that it warrants a much further discussion than was covered above for other phase transitions. First, though, is a brief understanding of the

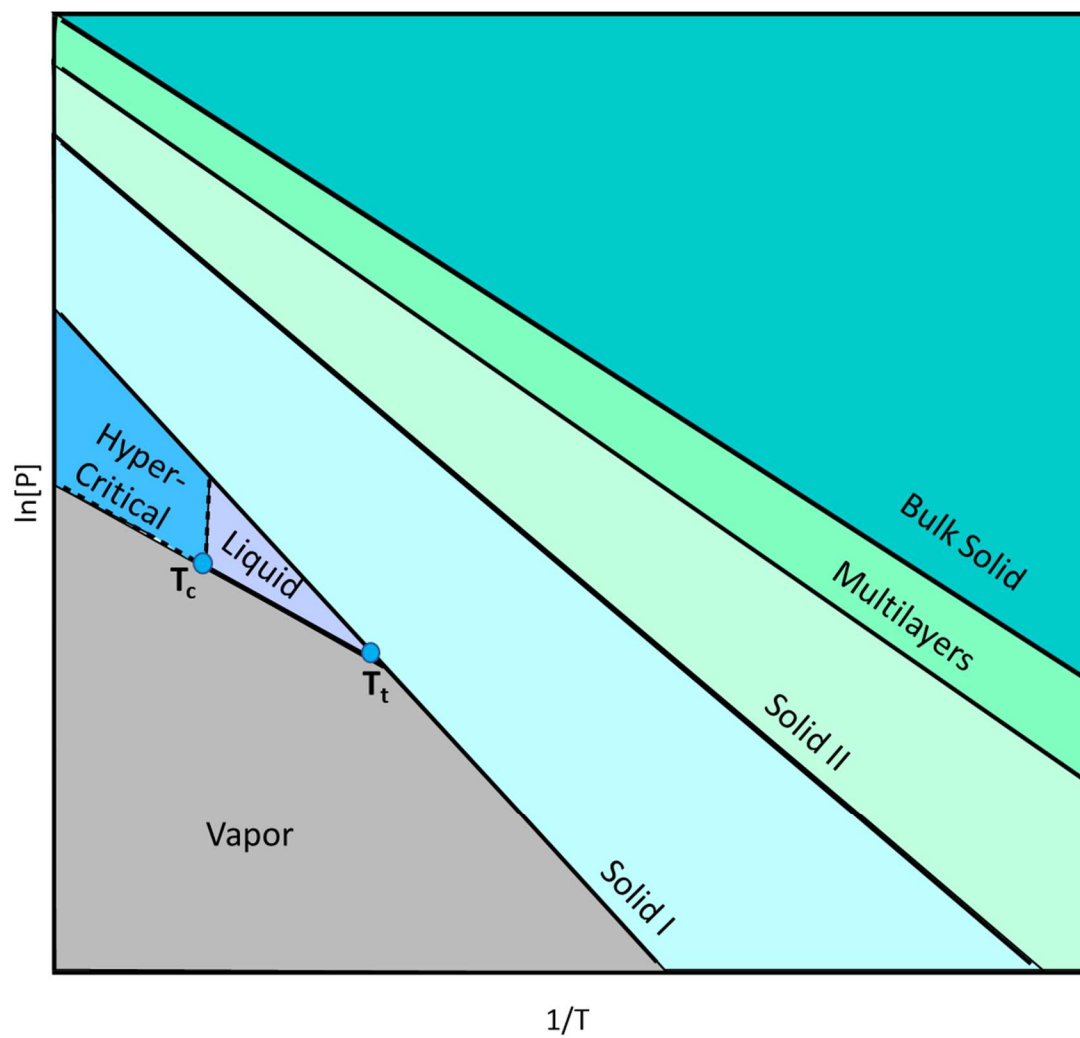


Figure 1.16: Clausius-Clapeyron phase diagram of an adsorbed van der Waals film

nature of two-dimensional solid phases. In three dimensions, solids are generally characterized by the existence of long-range order at low temperature. In a hypothetical one-dimensional case, the opposite is true, and these systems have their ordering destroyed by long wavelength spin wave. Two dimensions is the intermediate between these two cases and displays properties of both the higher and lower dimension. Though originally hypothesized that, in two dimensions, long range ordering would be impossible as phonon's should cause logarithmic deviations in the particle positions, empirical data (e.g. diffraction experiments) have shown that these systems do show distinct patterns of some form of long-range or quasi-long-range order. A caveat to this is a commensurate phase under the effect of a strong molecule-surface interaction, where the corrugation of the surface may serve to "pin" the molecules in their positions and prevent -range order. Also, the theoretical basis of these models is made for two-dimensional solids that lie in a Euclidian plane (i.e. one without any curvature). Most surfaces are planar, and so this assumption makes sense, but it is worth noting that this is not always a reasonable assumption. An example might be made for the case of graphene, which is a two-dimensional crystal with near perfect long-range ordering. This is because not only the in-plane, but fluctuations in height, must be considered as well, for which these early models did not fully account.

1.8.2.1 – Ising Model

An early model of phase transitions in two dimensions is the Ising model. This model consists of particles that have two discrete states that are fixed to a lattice, such as electron spins in a ferromagnetic material. This may also be represented as a lattice of orientable molecules (e.g. molecular dipoles), and thus has a corollary to adsorbed systems. The Ising model has been applied to cases of any dimensionality, however, the square-lattice Ising model in two-dimensions has been shown to be a simple system with an analytical solution that predicts a phase transition. The model predicts a high degree of long-range ordering and a second order phase transition between orientationally ordered and disordered states. Ising-like transitions have been used to describe some transitions observed in adsorbed systems; however, the strict requirement of only two configurational states, which is useful in systems of discrete spin states, like electrons, limits the application of this theory to few specific cases with adsorbed molecules^{85, 115}.

1.8.2.2 – XY Model

The XY model from statistical mechanics describes a lattice of vectors that each possess spin configurations over all 360° . This is similar to the Ising model, but instead of only two states, the system may possibly occupy any possible orientational state. Long-wavelength spin waves can propagate through this system, destroying the long-range order. At low temperatures, moderate long-range order does develop. The decay in the correlation of position depends on the temperature range, where at high temperature, the disorder shows an exponential-like decay in correlation. Around the critical point, this decay becomes algebraic with a decay constant, η , as the system undergoes a type of continuous transition to the solid phase. A difference in the result between this model and the Ising model is that, for the Ising model, such spin waves are not possible since each site on the lattice can only be on one of two states. As a result, long range order persists in the Ising model at low temperatures. However, in the XY model, the extent of long-range order is disrupted by spin waves, and is described in terms of a coherence length due to the gradual decay of the order with distance⁸⁵

1.8.2.3 - Kosterlitz-Thouless Transition

The Kosterlitz-Thouless (KT) model has been a more significant development in the theoretic framework of phase transitions in two dimensions. This model is essentially the same as the XY model but provides a greater context of real systems in two-dimensional superconductors and superfluids. It looks at the effect of topological defects in the lattice structure in the form of spin vortices which can have positive or negative vorticity (vortex and anti-vortex). At low temperatures, formation of isolated vortices is thermodynamically unfavorable, and they exist as bound pair that obey a power-law correlation with quasi-long-range order. At the critical temperature, the formation of vortices is thermodynamically favorable, allowing for the formation of free vortices. This leads to the unbinding of the vortex-antivortex pairs that lead to an exponential decay in the correlation distances⁸⁵.

1.8.2.4 – KTHNY Theory

Kosterlitz-Thouless-Halperin-Nelson-Young (KTHNY) theory is an extension of the KT model that was expanded on in a series of papers by Halperin and Nelson, and then further added to by Young^{87, 109, 110, 116, 117}. It extends the model beyond its original context of superfluids and

superconductors in two dimensions. It generalizes the idea of topological defects as dislocations in the bond ordering of the lattices, which occur in pairs of ± 1 from the normal lattice coordination number (figure 1.17). For a hexagonal system, the dislocations will occur in 5-coordinate/7-coordinate defect pairs, and for a square lattice, the dislocations will be 3-coordinate/5-coordinate pairs. Of these two phases, the hexatic phase is significantly more common in the literature, with most studies of tetratic phases confined to simple model systems¹¹⁸⁻¹²⁵.

The melting transitions predicted follow the same logic as the KT transition, where the dislocations are bound pairs before the transition and undergo a continuous transition as these dislocations unbind, resulting in melting. One key distinction here, however, is that the liquid phase is predicted to be non-isotropic following the unbinding of the dislocation pairs. The translational ordering of the system is lost, leading to a decrease in the coherence length. Bond-orientational ordering is still maintained, resulting in a two-dimensional liquid-crystal-like phase. Halperin and Nelson proposed names for these new phases based on the coordination of the system: in hexagonal systems, it is called a hexatic phase, and for square systems, a tetratic phase. These phases are described in terms of distinct bond-angle correlation functions. In the tetratic phase this correlation function is:

$$g_4(|r - r'|) = \langle \exp(i4[\theta(r) - \theta(r')]) \rangle \quad (1.84)$$

and for the hexatic phase:

$$g_6(|r - r'|) = \langle \exp(i6[\theta(r) - \theta(r')]) \rangle \quad (1.85)$$

A second type of defect, called a “disinclination”, is a disruption of the bond-orientational relationship of the lattice. This will similarly propagate in a fashion similar to the dislocations and eventually destroy the bond-orientational ordering as well (figure 1.17). Though, crucially, this happens at a higher temperature than loss of translational ordering. This is one of the essential aspects of KTHNY theory, where the system melts in two stages: first, the translational ordering is lost, and second, orientational ordering is lost, but at a temperature higher than that of the translational ordering. A stark difference occurs within three dimensions, where these two phenomena happen simultaneously in a first order transition.

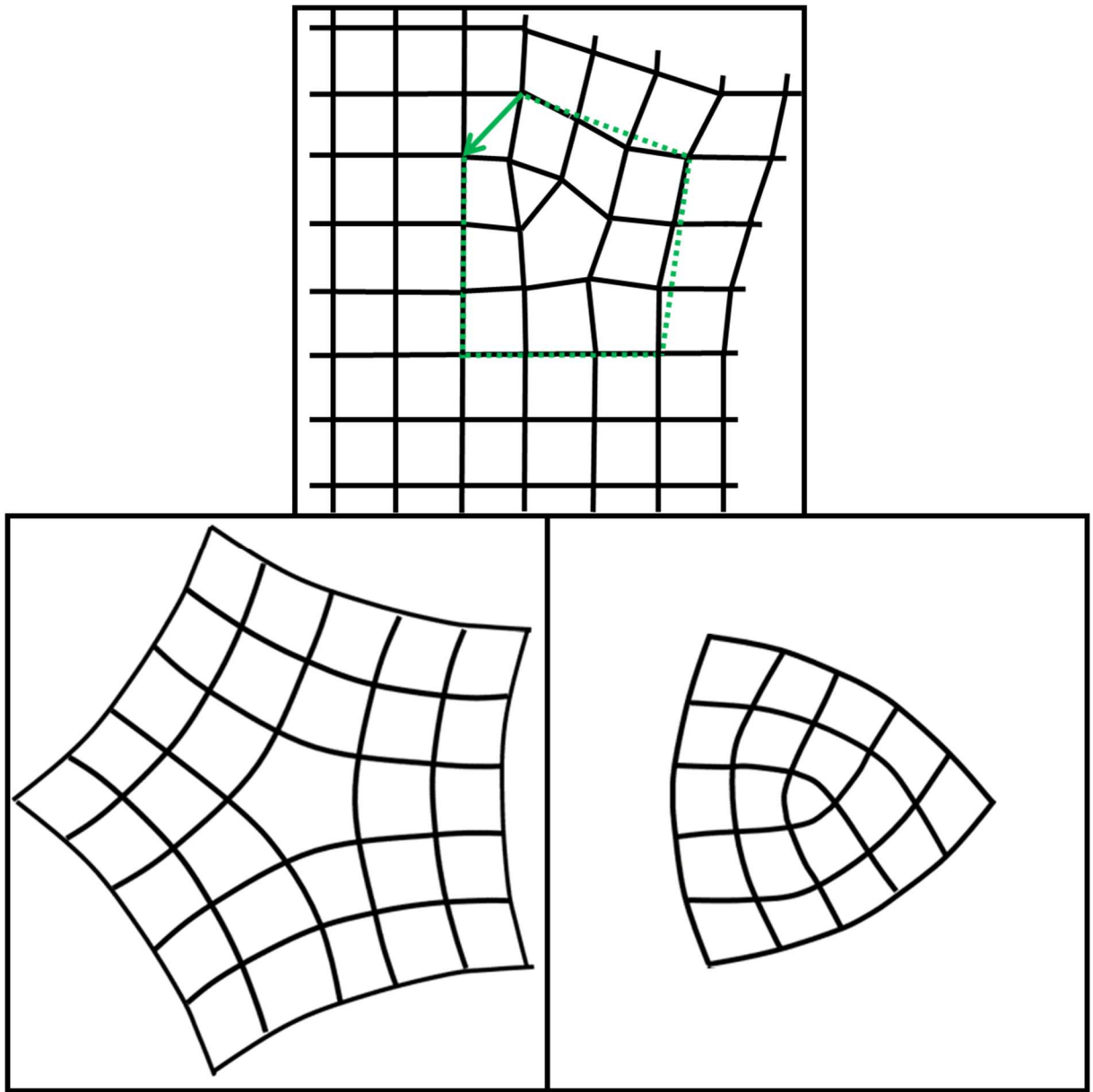


Figure 1.17: (Top) Dislocations and (Bottom) Disinclinations of a square lattice

Based on this model, a behavior of the structure factor of both solid and liquid tetratic/hexatic phases can also be approximated. The original formalism of Warren for two-dimensional lineshapes made assumptions about long-range order that are not valid within the context of this theory, which predicts some amount of disorder in all phases. Instead, the derivation works within the context of $S(Q)$ as the structure factor. For the solid phase, the power-law decay of the translational ordering is represented approximately by the same form of distortion in the diffraction peaks, leading to a power-law structure factor of^{84, 87}:

$$S(Q) \propto \eta(T) \left(\frac{2}{Qa} \right)^{2-\eta(T)} \quad (1.86)$$

where a is the lattice constant and η is related to the elasticity of the solid and is a function of the temperature. The structure factor of the liquid phase was similarly approximated by Halperin and Nelson to be:

$$S(Q) \propto \frac{\xi^2 - \eta^*}{(Q^2 \xi^2 + 1)^{1-\eta^*/2}} \quad (1.87)$$

Here, ξ is the coherence length and η^* is the value of η for the solid at the beginning of the melting region. This structure factor represents a Lorentzian lineshape raised to the power $1 - \eta^*/2$, which of note should always be less than one. In the limit where η^* is small, the lineshape may be represented as a further approximation by a Lorentzian-type lineshape. The coherence lengths obtained through structural refinement of diffraction data can be used to analyze the melting temperature for a system experiencing this type of melting. Two different formulations exist for this prediction, one using information of the solid phase only, and the other expressing properties of the liquid phase from the solid phase data. The solid phase coherence length at the melting temperature can be determined from the coherence lengths of the solid phase during the melting transition:

$$\xi_s(T) = \xi_s^* (T - T_m)^{-\nu} \quad (1.88)$$

where ξ_s is the coherence length in the solid phase during the melting region, ξ_s^* is the coherence length of the solid at the melting point approached from the low temperature side, T_m is the melting point or, more correctly, the temperature at which melting starts, and ν is the power law order as a fit parameter (but does not have significant analytical meaning for this type of analysis). The relationship to the liquid is given by the exponential relationship:

$$\xi_s(T) = \xi_l^* \exp[A(T - T_m)^{-0.3696}] \quad (1.89)$$

where ξ_l^* is the coherence length of the liquid phase as the melting point is approached from the high temperature side, and A is a proportionality constant that also does not have a significant meaning to the analysis herein. These equations establish a formal method for determining a melting temperature where the melting process begins and also provide a predictive indicator as the coherence length of the liquid phase can be derived from the behavior of the coherence length of the solid phase. The ability to analyze data with this method requires performance of two-phase refinement on a series of diffraction patterns over a range of temperatures on two-dimensional lineshapes, that result in consistent high-quality agreement with the data. In the course of writing this dissertation, only a single previous publication demonstrating a proof of concept, could be found that attempted such a data treatment process. Unfortunately, this alone would not be conclusive enough to definitively distinguish the existence of a tetratic/hexatic phase intermediate melting from that of a continuous solid/liquid coexistence region. As of yet, KTHNY theory's application in adsorbed systems remains a beautiful and widely accepted, though unproven, model.

1.9 – Systems of Study

The study herein involves the investigation of the thermodynamic, structural, and phase transition properties of thin films comprised of simple quadrupolar hydrocarbons on surfaces of varying symmetry. The interaction of true linear quadrupoles is primarily a two-dimensional interaction itself with a preferential orientation of molecular pairs to adopt a T-shape configuration. Any angular deflection of either molecule out of the optimal plane of interaction at best weakens the strength of the interaction. However, rotations of molecules about the axis perpendicular to the interaction plane do lead to less optimal configurations, where there is a minimum energy path through a slipped parallel state that can give rise to possible alternative structures when considering multiple interacting quadrupoles, like in molecular films. This makes molecular linear quadrupoles an interesting choice of study in adsorbed films.

1.9.1 Previously Studied Systems

There exists in the literature already many such atoms and molecules whose adsorption properties have been well-studied. Some of the simplest of these are the noble gases, such as

argon¹²⁶⁻¹³⁰ and xenon^{126, 131-138}. The hydrocarbon family has received an equal amount of attention with the focus mainly being on methane^{111, 139-151}, the other linear and cyclic alkanes^{36, 86, 112, 152-158}, and the simple alkene ethylene^{37, 159-161}. None of these systems, involve any notable quadrupole molecules. There are, however, many examples like N₂^{38, 51, 162-172} and O₂^{113, 166, 173-176}, that are small, light molecules which have weak quadrupole moments. Other molecules like CO₂^{51, 166, 177, 178}, N₂O¹⁷⁸, CS₂^{166, 179}, CO^{180, 181}, and in particular C₂N₂^{178, 182} and C₆H₆^{112, 183-188}, have considerably stronger quadrupole moments, but are larger molecules. N₂O and CO, due to their asymmetric nature, are not pure linear quadrupoles, as is the case with the other examples, and possess non-negligible dipole moments. Benzene is another interesting case, as the primary axis of the molecular quadrupole is oriented 90° to the plane of the molecule's ring structure.

1.9.1.1 Behavior of Molecular Quadrupoles

The idealized structure these molecules will adopt in two dimensions depends not only on the strength of their quadrupole and other interactions with one another and the substrate, but also on the size and aspect ratio (axial length/width)^{166, 189}. Figure 1.18 contains a compilation of quadrupole values, aspect ratios, and relative sizes for the example molecules listed above, as well as for acetylene and allene. The interaction energy of 2 linear quadrupoles is a function of only their separation distance and three terms to describe their relative angles (see eq 1.11 and Figure 1.4). The strength of the interaction depends on the fifth power of distance separating the two quadrupoles and an angular function gamma, which will be derived more formally in section 1.4. This angular function has a maximum value when one of the molecules is oriented at 0° to $\vec{r}$, with the other at 90° (θ_i and θ_j), and a dihedral angle (ϕ) of 0°.

Since any deviation in ϕ results in a weakening of the interaction strength, it follows that the interaction of two linear quadrupoles is a two-dimensionally optimized interaction. It is not always the case, however, that in a real system the ideal T-shaped configuration between molecules is not always the most energetically favorable; competing molecule-surface interactions, the van der Waals interactions between the molecules, and, as mentioned before, the molecules, all must be considered. The first two of these are often cooperative in their effects. The packing efficiency in the square-T configuration decreases with increasing aspect ratio, and likewise the van der Waals forces, which would favor a parallel or "slipped" parallel molecule arrangement, also becoming stronger.

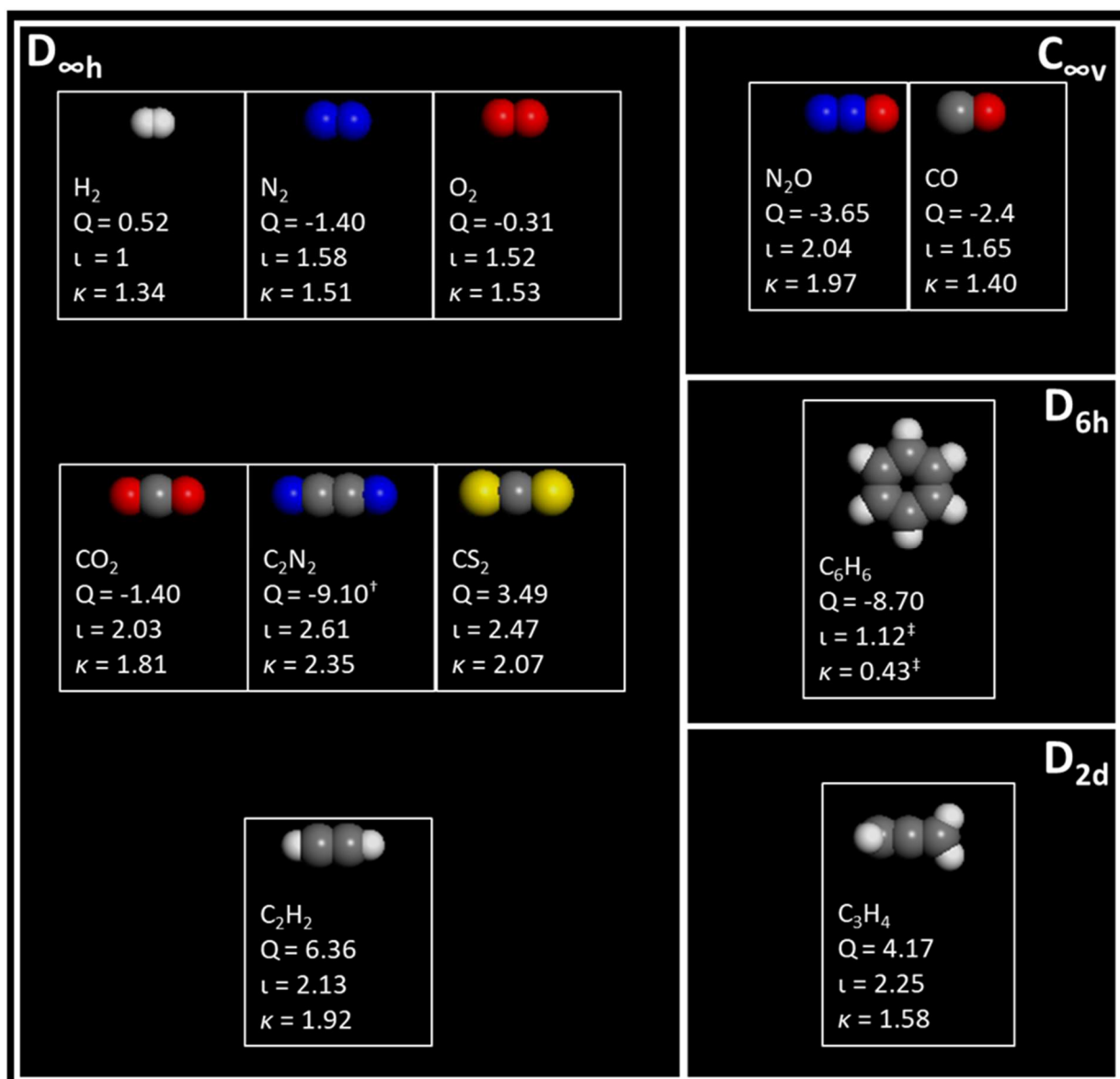


Figure 1.18: Examples of simple quadrupolar molecules organized by symmetry point group. Quadrupole moments, Q ($D \text{ \AA}$), lengths proportional to H_2 ($\iota = L_i / L_H$), and molecular aspect ratio relative to the primary axis of the quadrupole moment ($\kappa = L_i / W_i$).

Quadrupole values given are the respective Q_{zz} value from the molecule's quadrupole tensor, adapted from NIST CCCDBD experimental values¹⁹⁰. Length and width values are estimates based on van der Waals surface calculations in Accelrys' Materials Studio 6.0.

[†]Experimental values not available, value based on average of computational results on the NIST CCCDBD¹⁹⁰

[‡]The quadrupole of benzene is oriented perpendicular to the plane of the molecule. The ratios of ι and κ were calculated relative to the quadrupole axis, not the molecule plane.

A particularly interesting pattern emerges when adsorbed on graphite for the molecules whose film structures have been well studied. The main structural motif of these systems are herringbone patterns, bond (brick-laying) patterns, and occasionally pinwheel structures have been observed^{51, 166}. The minimization of the quadrupole electrostatic potential energy in a perpendicular orientation for these films seems not to be strong enough to overcome the combination of substrate symmetry and the molecule-molecule van der Waals interactions which are stronger when molecules are parallel rather than perpendicular.

1.9.2 – Adsorbate Molecules

The adsorbate molecules examined within this dissertation, acetylene and allene, are the simplest examples of an alkyne and cumulene, respectively. Both of these families of hydrocarbons have a propensity towards strong quadrupolar moments in cases of highly symmetric molecules. The two molecules of this study represent a logical starting point for the examination of a homologous series of quadrupolar hydrocarbons pulled from these families. Though these molecules tend to be much more highly reactive than other hydrocarbons, the problems this may present are not insurmountable.

1.9.2.1 – Acetylene

Acetylene (C_2H_2) is the simplest alkyne molecule that lies in the $D_{\infty h}$ point group. Most commonly, it is encountered as a fuel for industrial welding and the manufacture of some polymers. As a bulk material, it has a critical point 308 K, a triple point at 192.4 K, and a melting point at 191.2 K^{191, 192}. Below the melting point, acetylene exists in a cubic solid phase in the $Pa3$ space group. A solid-solid phase transition to an orthorhombic structure in the $Acam$ space group, which has two reported temperatures in the literature, occurs at either 127 K or 133 K; additionally, 139 K has been reported for deuterated acetylene¹⁹³⁻¹⁹⁸.

Its highly symmetric structure and basic hydrocarbon nature would lead to the conclusion that this molecule is non-polar and has negligible electrostatic interactions. This assumption is inadequate to describe the properties of acetylene, which in fact has a very large quadrupolar moment. The origin of this anomalous quadrupole strength is at least partially a result of the sp -hybridization of the carbon atoms. Normally, the difference in electronegativity of carbon and hydrogen is small enough to avoid unbalanced charge distributions that would be considered a

polar bond. This assumes the carbon is in its common sp^3 hybridized state, for which the electron density is distributed uniformly around the carbon atom. For other hybridizations of carbon (sp^2 and sp), the electrons of the unhybridized p-orbitals are located within π -orbitals. These bonding orbitals move electron density away from the carbon's bonding axis, serving to reduce the electron density from the region of the nucleus. This in turn reduces the effective shielding of the carbon nucleus towards the bonding atom, increasing the ability of carbon to pull electron density away from atoms it is bound to. In carbons with sp^2 and sp hybridization¹⁹⁹, the electronegativity tends to be higher - about 0.2 and 0.4 units higher on the Pauling scale, respectively. This means that the effective electronegativity of carbons in acetylene should be comparable to that of nitrogen¹⁹⁹. There is further evidence of hydrogen bond-like interactions between the carbon and hydrogen of adjacent molecules when in the T-shaped configuration¹⁰⁷.

In the past, considerable efforts made to create accurate atomic potentials to describe the behavior of acetylene in both its bulk and adsorbed phases have been met with varying degrees of success^{52, 95, 107, 200-211}. Some of these have been quite successful in matching empirical evidence for one phase, but not usually the other²¹². At least one forcefield seems to have performed well for both solid phases, but, nonetheless, the values used did not accurately represent the known quadrupole moment for acetylene. In one such case, a model was able to accurately fit most of the data for the cubic phase, but it used a quadrupole moment 60% less than what is generally regarded as its strength, had significant error in the heats of sublimation, and failed entirely to describe the orthorhombic phase⁹⁵. Thus, estimation of atomic potentials is a notoriously difficult proposition to do and is made potentially even more difficult as the quadrupole moment could possibly vary in strength between the solid and fluid phases. While attempts will be made later in this dissertation to explore variations to force-field parameters in the molecular dynamics simulations, the modifications utilized were based on some of the aforementioned works pertaining to the subject and may not be any more accurate than the standard force field parameters used.

Acetylene's abnormal behavior extends into its two-dimensional systems as well. No less than eight previous papers regarding the adsorption of acetylene on graphite have been previously reported^{27, 107, 207, 213-217}. These examples have served to underscore the complexity of the system and how much remains to be known, resulting in more questions being

unanswered rather than answered. More details on this will be shown in Chapters 3 through 5 later in this dissertation.

1.9.2.2 – Allene

Just as acetylene is the simplest example of an alkyne, allene (or propadiene, C_3H_4) is the simplest molecule in a different family of linear hydrocarbons of cumulated double bonds. These are often collectively referred to as cumulenes or allenes, though to avoid confusion in this context, the latter term will only be used to refer to the specific molecule and not to all such molecules with cumulated double bonds. Allene is not as common as acetylene, but manages to find niche applications in polymer production, and is a partial constituent of MAPP gas, which is also a type of welding fuel.

Allene is less chemically stable than acetylene, and without stabilizing agents, exists in equilibrium with its isomer, propyne. It also readily reacts with many types of metal surfaces, as well as some rubbers used in gas handling systems. As such, some reasonable precautions must be taken to avoid these incompatibilities and maintain the purity of the gas during adsorption experiments.

Allene's critical point temperature is at 394 K, triple point temperature at 136.6 K, and normal boiling point at 240.2 K. At its triple point, the vapor pressure is only 130 mtorr, which means that, in two dimensions, the typical place where two-dimensional melting might be expected to occur ($0.8 \cdot T_{\text{triple}} = 108 \text{ K}$, $SVP \approx 1 \text{ mtorr}$) will not be obtainable with the instrumentation available, and the examination will be of the liquid and hypercritical phases only.

Allene's quadrupolar moment is of similar order to, but weaker than, acetylene's, deriving the polarity of its bonds from the same phenomenon. In fact, in terms of not only its quadrupole moment, but also its size and mass, it is close to CO_2 . A distinguishing feature of allene as compared with the previously studied systems mentioned above is the broken rotational symmetry about the bond axis of the molecule. The cumulated nature of double bonds results in the dihedral angle between the hydrogen pairs at opposing ends of the molecules being orientated 90° to one another, placing it in the lower symmetry point group of D_{2d} . The perpendicular nature of the opposing ends of the molecule make it more difficult to lie flat on a surface when adsorbed, resulting in two possibilities: either the molecule will be rotated such that both hydrogen pairs are at 45° to the surface, or one hydrogen pair lies parallel and the other

perpendicular to the surface. This second option would mean the molecule would not actually lie completely flat but would be tilted slightly with respect to the surface.

1.9.2 – Surface Substrates

The preferential geometry of linear quadrupolar molecules will be examined more closely later in this dissertation, but it has already been mentioned that the electrostatically optimized structure should have a four-fold geometry. The two surfaces chosen for this series of studies represent two opposing cases. In the case of MgO (100), the surface geometry and corrugation are a very close match to the charge distribution and preferred lattice spacing of acetylene, representing a system with potentially synergistic interactions. In the case of graphite, the geometry class of the surface is incompatible with the molecule-molecule interactions, creating a system with competing forces.

1.9.2.1 – MgO (001)

Magnesium oxide, MgO, is a common metal oxide with a simple cubic (rock salt) crystal structure ($a = 4.121 \text{ \AA}$). It finds applications in a wide host of industries, ranging from catalyst support materials to food additives. Its largest commercial utility is as a refractory material in high temperature devices, such as stove heating elements. Though it is an electrical insulator with a band gap around 7 eV, it possesses high thermal conductivity and stability, making it well-suited for such applications.

Being an electrical insulator also means that it has little or no optical features from the infrared into the UV and is one of the “true” white standards in diffuse reflectance calibrations. The surface of the material, however, is weakly optically active, with several small absorption and emission bands in the upper visible and lower UV range. These arise from incomplete coordination around varying types of surface defect sites (i.e. vacancies, edges, and corners), and is a possible method to assess the condition of the surface.

The (100) surface of MgO is made of two square sublattices of Mg^{2+} and O^{2-} that form a face-centered square lattice. The alternating charges form a surface highly corrugated with a four-fold symmetric system of charges. The effective charge of each surface ion for MgO has been experimentally measured, being about $\pm 1.2 e^-$ for magnesium/oxygen. This arrangement is compatible with preferred T-shape configurations in quadrupole molecules in a 2×2

commensurate lattice, if the molecule size is sufficiently close to the lattice spacing. In the case of acetylene, the preferred intermolecular distance in the T-configuration is around 4.38 Å, approximately 6% larger than the lattice constant for MgO, 4.21 Å. Despite this, the strong quadrupole moment and surface charge will still play a large role in guiding the system in this direction.

1.9.2.2 – Graphite (0001)

The surface structure of graphite is probably one of the most memetic material structures in all of materials science. It is the most common allotrope of carbon, comprised of stacked two-dimensional layers of carbon atoms, hexagonally arranged as the classic honey-comb lattice. The lattice constant of the surface is 2.46 Å with two atoms per unit cell. It has a wide range of applications itself in industry, but the more everyday uses relevant to most people are its inclusion in pencils and as a lubricant. It is also known for its good conductive properties for both heat and electricity, and so it finds uses in batteries and electronics as well.

The surface being made of only carbon atoms, graphite is completely electrostatically neutral, and adsorption is governed by van der Waals interactions with ad molecules. Hence, the surface corrugation is comparatively shallow and would be expected to have a lesser effect on film structure than in the case of MgO (100). Even still, other systems of small quadrupolar molecules have been shown to prefer adoption of a herringbone lattice that might even further adopt a hexagonal configuration commensurate with the substrate surface. This is likely the effect of several factors that include the surface corrugation, the van der Waals molecule-molecule interactions being better minimized in a parallel configuration, and the quadrupole moment have a saddle point in the molecular orientations in a “slipped-parallel” configuration. This effect should lean to be more in favor of the quadrupole strength for stronger quadrupoles like acetylene and allene; however, the forces will still be in competition and with different preferred symmetries.

Chapter 2 – Materials and Methods

2.1– Purification of Adsorbate Gases

The acetylene used in these studies was atomic absorption grade (99.7% purity) obtained from Airgas. The allene (stabilized) was obtained from SynQuest Labs. Both gases being examined as adsorbates required special considerations to obtain and maintain high purity. Allene is a reactive and unstable molecule and degrades over time, resulting in cumulative impurities. The acetylene gas obtained was dissolved in acetone, which stabilizes it at higher pressures, but results in significant amounts of acetone vapor in the acetylene gas. Careful purification and handling of these gases was used to ensure the quality of the adsorbates for adsorption studies, described in greater detail to follow.

2.1.1 – Purification of Acetylene Gas

The removal of acetone and other common potential impurities (notably hydrogen, oxygen, nitrogen, and phosphine) was performed following the methodology described by Hyman et al²¹⁸. Their process involves first slowly bubbling the gas through concentrated sulfuric acid. This step is extremely effective in destroying both acetone and phosphine contaminants, but in the process, carbon dioxide, sulfur dioxide, and sulfuric acid vapor are introduced to the gas. The gas is then bubbled through a solution of 5 M sodium, which is reported to remove the sulfur dioxide and sulfuric acid vapors. Third, the gas is passed through a column of Drierite and soda lime to remove carbon dioxide and water vapor introduced by the two scrubber baths used. The gas is then collected in a cryogenic trap, where it is subjected to a freeze-pump-thaw process, removing the hydrogen, oxygen, and nitrogen contaminants.

The process used herein followed this procedure, with one significant modification. The use of soda lime following the sodium hydroxide bath was eliminated. Group I metal hydroxides are well understood and utilized as carbon dioxide scrubbers. Furthermore, the quantity and flow rate of gas that was purified for these studies was substantially lower than what was outlined in the original procedure. Therefore, the sodium hydroxide would have already removed the carbon dioxide before the gas reached the soda lime column, making this component redundant. In place of this, a larger volume of Drierite was used to ensure total removal of water vapor from the acetylene. A diagram of the purification manifold can be seen in Figure 2.1.

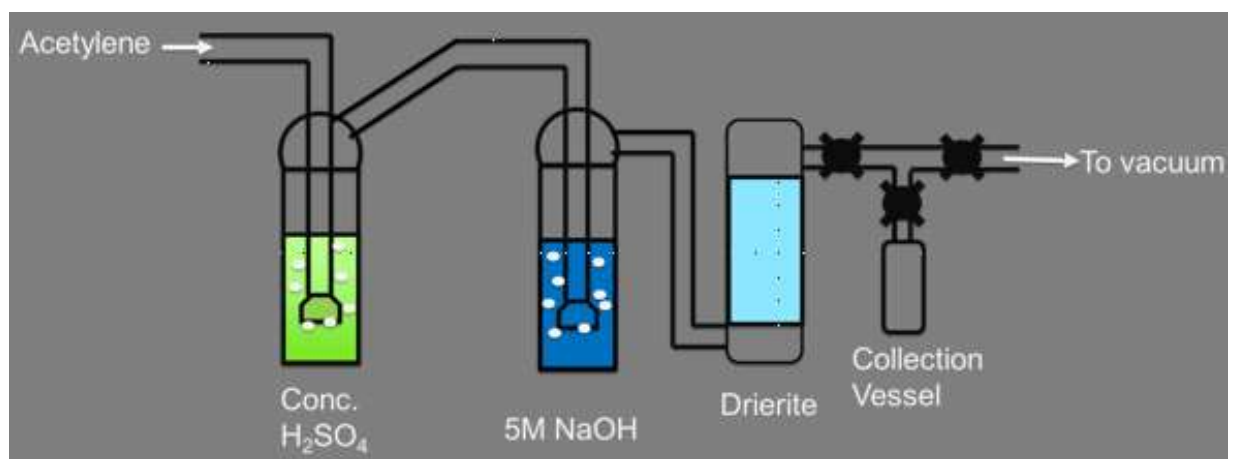


Figure 2.1: Manifold for acetylene purification

Before running a purification, the forward-half of the apparatus containing the two liquid scrubbing baths was purged overnight with nitrogen to displace any other gases in the system. The second-half of the apparatus with the Drierite column and collection vessel was pumped on under vacuum with heat applied to the Drierite using heat tape at around 190 °C to remove any gases that might have been adsorbed on the manifold walls and Drierite. The acetylene was then used to purge the system at a low flow rate for half an hour to purge most of the nitrogen from the system. It was not necessary for this step to remove all of the nitrogen as freeze-pump-thaw cycles on the collected gas could remove this later. After purging with acetylene for thirty minutes, the vent valve for the purge was closed, along with the valves connecting the back-half of the apparatus to the vacuum pump. The valve connecting the front and back halves of the apparatus was opened and a needle valve was used to regulate the flow of gas through the Drierite column. To prevent over-pressurization of the front-half of the manifold, after 1 atm of acetylene was collected in the manifold, liquid nitrogen was used to contain this in a small auxiliary steel volume. The gas flow was then continued until another 1 atm of gas was collected. This would mean 2 atm of gas was collected, which is precisely at the safety limit for acetylene; however, the gas still contained a significant amount of nitrogen that, once removed, yielded closer to 1.8 atm of pressure. The gas was then cumulatively collected with liquid nitrogen and subjected to several freeze-pump-thaw cycles to remove the remaining volatile gas impurities.

2.1.2 – Freeze-Pump-Thaw

Freeze-pump-thaw cycling is a simple purification to remove other gas impurities that may be present in the adsorbate gas, such as nitrogen, oxygen, and hydrogen. Considerations for allene include frequent re-purifications and small volumes of gas. This process has, for this research group, typically been conducted using a separate manifold attached directly to a portable turbo-pump unit. This would have been inefficient with a freeze-pump-thaw cycle for every one to two isotherm measurements. Instead, a stainless-steel volume was kept on the isotherm station itself, along with the lecture bottle source of the gas, and the freeze-pump-thaw distillation was performed using the manifold and vacuum system present on the system. Acetylene was freeze-pump-thawed initially as the final step of the purification procedure described in the previous section. As an added precaution to verify that the gas maintained purity over time, it was occasionally resubjected to the freeze-pump-thaw process. Of note, there was

never any noticeable release of gas from the acetylene during the pumping stage. Owing to the fact that these products have a tendency to be of a heavier molecular weight, however, if any acetylene had undergone a self-induced reaction, this step should not be taken as a verification that the gas remained stable, and instead served merely to confirm that atmospheric gases have not accidentally contaminated the gas over time either through a human error or station leak.

A stainless-steel volume was pressurized with a quantity of adsorbate gas with a maximum pressure of less than 2 atm (standard safety limit for both gases). This vessel was then submerged in a liquid nitrogen bath, which freezes the gases into a solid phase. The vapor pressures of either gas at 77 K are negligible. The condensed gases were pumped on for 10 to 15 minutes while submerged in the liquid nitrogen. This was then removed, but the system was kept open to vacuum for the first part of the warming process until the vapor pressure reached 0.05 torr on a 1 torr capacitance manometer (in the case of allene), allowing for any gas molecules trapped sub-surface and any potential impurities with marginal vapor pressures of 77 K to be removed. Once at 0.05 torr, the valve to the vacuum pump was closed, and the gas was allowed to warm back up to room temperature. The process was similar for acetylene, but this was done on the purification manifold and not directly on the isotherm station. An ion gauge mounted above the turbo pump was monitored and the gas was warmed until the pressure entered the 10^{-4} torr range. This process was repeated at least three times total, with more cycles in some cases being necessary. Completion was determined when a base pressure in the low 10^{-6} torr range was observed during the pumping stage and if the initial pressure spike when opening the frozen system to vacuum did not exceed 1×10^{-5} torr. It was not unusual in the case of allene for five or six cycles to be completed before this requirement was met.

2.2 – Preparation of Surface Substrates

The preparation process of the substrates used in these experiments was crucial to ensure and protect high quality surfaces for the adsorption studies. Graphite is a relatively easy substrate to work with and does not necessarily require completely perfect conditions during the sample preparation steps, though these conditions nonetheless were maintained at the highest quality obtainable as a matter of diligence. MgO surfaces are more difficult to work with, and samples were selected based on the best characterized quality from a pool of a large number of synthetic batches. The graphite used for these studies is an exfoliated graphite foam obtained

from Union Carbide with specific surface area in excess of $20 \text{ m}^2 \text{ g}^{-1}$. The MgO was synthesized for use following the procedure outlined in the following section. The specific surface area for these samples fell within an average range of 6.5 to $7.5 \text{ m}^2 \text{ g}^{-1}$

2.2.1 – Synthesis of MgO (100)

The magnesium oxide substrate used was a powder of nano-cubes with a typical size of a few hundred nanometers along one side. The synthesis method to be outlined here is a patented process known to produce large quantities ($\approx 20 \text{ g}$) of high-purity, low-defect magnesium oxide nano-particles with a small and tunable distribution of size, predominantly having single faceted exposure of the (100) surface²¹⁹. It has a further benefit of bypassing the creation of a liquid magnesium state, resulting in a safer synthetic route to other vapor-based techniques.

The process involves the use of pure magnesium chunks that were around 0.5 cm across, which were washed in dilute hydrochloric acid to remove already-present surface oxidation and any other contaminants on the surface. These were then placed into a graphite crucible along with similarly sized pieces of crushed graphite in alternating layers to ensure an even distribution of magnesium and graphite. The crucible was placed within an induction coil within the quartz chimney reaction chamber shown in Figure 2.2. The system was then slowly purged with argon to remove oxygen and other atmospheric gases. An RF generator tuned to resonate with graphite was used to heat the graphite through the surrounding induction coil. Indirect heating of the magnesium metal power was gradually increased over several minutes, during which time, the melting magnesium reacted with the graphite to create a magnesium carbide intermediate. Upon further heating, the carbide intermediate began to break back down into graphite, releasing the magnesium directly as a vapor. Around the time that vapors were first witnessed, the flow of oxygen gas into the chamber was started. The magnesium vapor quickly ignited in the presence of oxygen producing the magnesium oxide powder.

Following synthesis, the chamber was allowed to cool, continuing the argon flow in order to maintain an inert atmosphere. Once sufficiently cool to handle safely, the powder was collected from the walls of the quartz chimney and transferred into a storage container, which was sealed under an argon atmosphere to prevent hydroxylation of the surface from atmospheric water vapor. The samples were then stored in a desiccator previously purged with argon. A sample of each synthesis batch was reserved before packaging, which was used to characterize

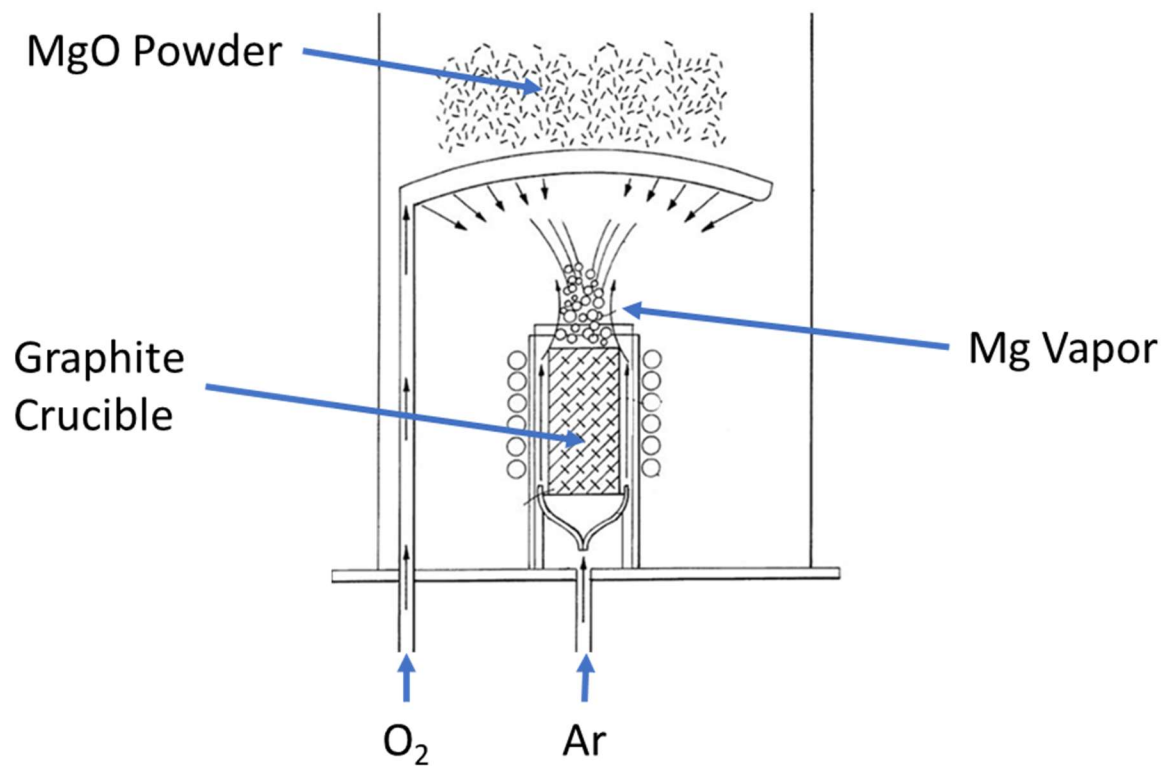


Figure 2.2: Diagram of the MgO synthesis chamber
Taken from patent by Kunmann and Larese (US 6179897 B1)²¹⁹

the quality of the MgO samples using a volumetric adsorption isotherm with methane in a liquid nitrogen bath. The characterization will be further described in section 2.3.3.

2.2.2 – Vacuum Heat Treatment

Before use, samples were prepared using a vacuum heat treatment. The substrate was loaded into a quartz tube with a graded borosilicate transition at the top end to enable coupling with vacuum systems. The tube was placed in a Lindberg/Blue M™ tube furnace, taking care that only the quartz section of the tube was directly exposed to the heated furnace interior. The sample was located at the bottom as near to the thermocouple as possible in order to ensure that the substrate maintained the desired set temperature during the heat treatment process. A compact electric fan was used on the metal vacuum fittings and the glass/Kovar junctions to cool and alleviate stress from radiant heat transferred to these components through the quartz tube.

MgO samples were gradually heated over 8 hours to 950 °C, where they were maintained for at least 48 hours. This process anneals the MgO surface and ensures the uniformity of the (1 0 0) surface exposure. Graphite samples were ramped over an 8 hour period as with the MgO, but a slower rate was used initially over the first three hours up to 250 °C to prevent a rapid release of physically adsorbed contaminants and water vapor, which occurs around 200 °C. The temperature was ramped up over the remaining 5 hours, up to 750 °C, where it was maintained for at least 24 hours. This timeframe is longer than is necessary for the heat treatment of graphite, generally only requiring a few hours at max temperature. The longer time frame, however, does not impair the quality of the graphite and ensures a consistent procedural method that guarantees surface preparation quality.

2.2.3 – Sample Loading

Samples were loaded into an oxide-free, high-thermal conductivity (OFHC) copper sample cell connected to a gas inlet on a mounting ring for the cryostat system of the isotherm stations. The transfer process was conducted inside an argon filled glove box to preserve sample quality (in the case of MgO in particular), and careful atmospheric control was absolutely crucial as even small levels of water vapor or atmospheric gases can degrade the sample. Graphite is less sensitive and was capable of being loaded in a glove bag purged with argon; however, the glovebox was used to load all samples into the sample cell.

Before adding the sample into the copper cell, quartz wool was used to add a gas permeable plug inside the cell at the open end of the steel capillary gas inlet. This would prevent the fine powders of the samples from being able to exit the sample cell into the capillary, where the temperature will not be as maintained, or potentially making its way into the isotherm stations' calibrated volume and damaging components, such as diaphragm valves. Samples were added to the cell and then sealed with a OFHC copper lid using an indium wire gasket to create a cryogenically stable airtight seal. Finally, cells were then removed from the glovebox and leak checks were performed before mounting on the isotherm station.

2.3 – Volumetric Isotherms

The isotherm measurements recorded in these studies were made on custom-built systems described in Mursic and Larese²²⁰. These machines are able to take precise, high-resolution measurements through assessment of pressure and intricate, stable control of temperatures. An automated LabVIEW program provides the ability to obtain a large number of isotherm data points without excessive time of use on the part of the experimenter, and avoids large variances used in determining that equilibrium has been achieved for each step. These instruments deliver precision and reproducibility far above what can be obtained from simpler, commercially-available units.

2.3.1 – Instrumentation

A diagram of the isotherm gas handling system is shown in Figure 2.3 and the sample cell mounting in the displacer is shown in Figure 2.4. The manifolds of the isotherm station are constructed from quarter-inch steel tubing with sections joined by either brazed joints or valves. The systems primarily made use of Swagelok B-4HK brass valves with quarter-inch Swagelok fittings, and the four computer-controlled valves for each station were opened and closed by Swagelok MS-HK-1C pneumatic actuators using compressed air. Alternatively, stainless steel diaphragm valves with pneumatic actuators were also used for controlled valves. An MKS 248D proportional valve was used in the acetylene studies to control gas flow during the pressurization of the calibrated volume at the beginning of each step. The large surface area of rubberized

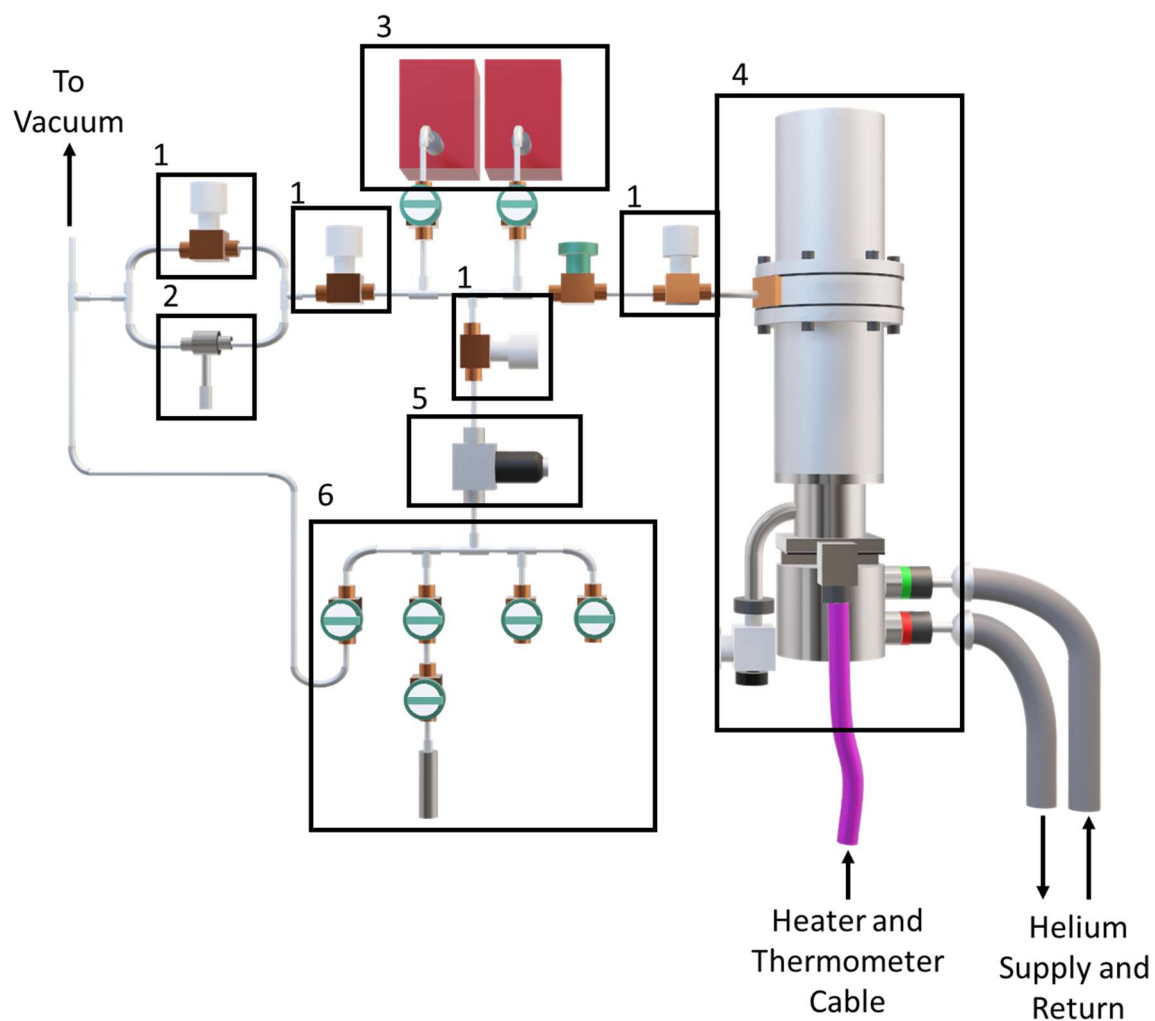


Figure 2.3: Isotherm station diagram

- 1) *Computer controlled Pneumatic valves*
- 2) *Needle Valve*
- 3) *Capacitance manometers*
- 4) *Displex assembly*
- 5) *Proportional Valve*
- 6) *Adsorbate gas source manifold*

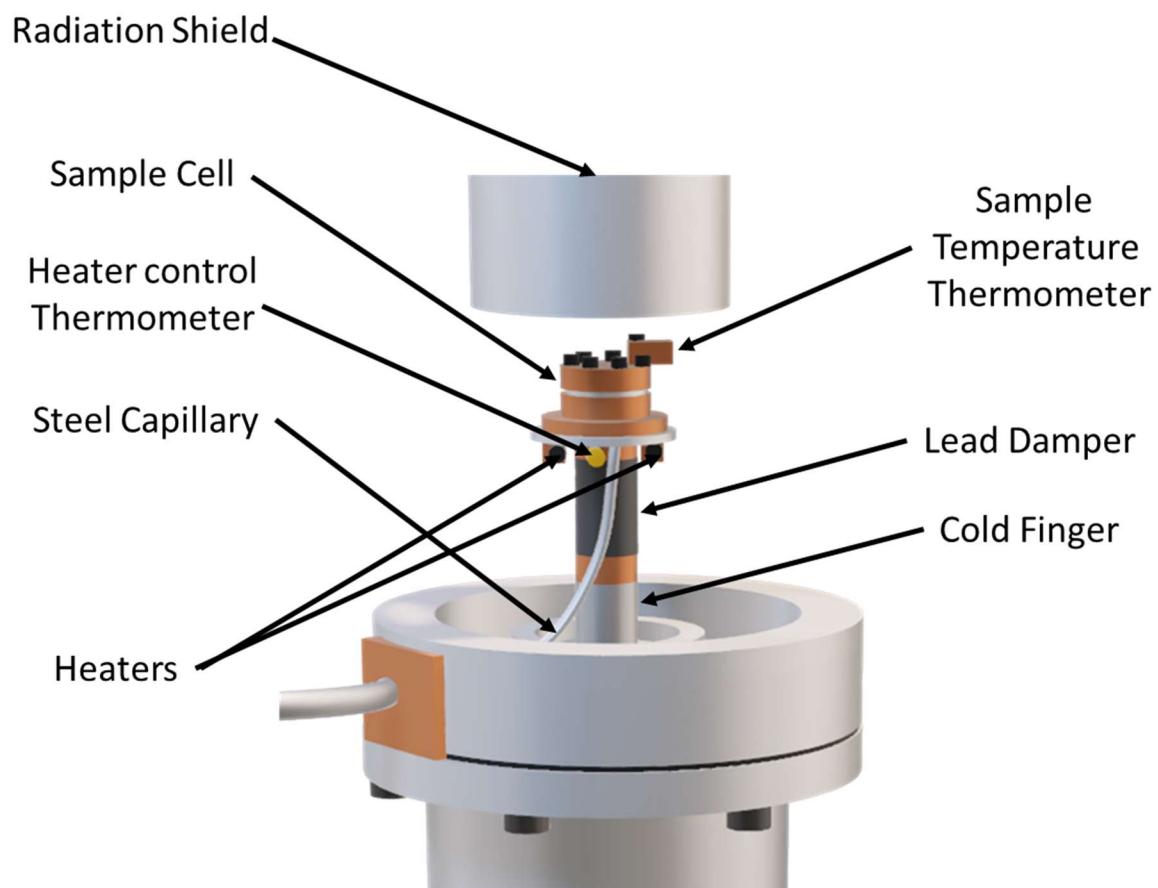


Figure 2.4: Sample cell mounted in displex

gaskets and O-rings were incompatible with allene gas, and the proportional valve was replaced with a Clippard EVP series proportional valve. Pressure was read from MKS Baratron capacitance manometers with either a 1 torr or 100 torr range. The cryostat was an ARS DE-202 closed cycle cryocooler with an attached helium compressor unit. Gas evacuation and vacuum pressure of the system were maintained with Pfeiffer TSH-071 pumping station with a turbomolecular pump.

The electronics systems were controlled through the use of National Instruments modules, which controlled all electronic valves, digitized pressure readings, communicated with the temperature control unit, and monitored the cell temperature. The pressure was read using a 12-bit digitizer which had three modes. The normal output of the manometers spanned 0 V to 10 V over their entire range. In normal mode, the system would digitize the outputs over this entire 10 V span. In high resolution mode, between 5 V and 10 V, the full 10 V range was used, between 1 V and 5 V, the signal was digitized over a range the span of 5 volts, doubling the resolution, and lastly, between 0 V and 1 V, the signal was digitized spanning only this range, giving a factor of 10 better resolution in the low pressure ranges. The high-resolution mode allowed for automatic switching between the different ranges when the signals crossed the threshold values. Temperature controllers were either a Neocera LTC-21 or a Cryocon 32-B, which controlled the temperature based on a silicon diode thermometer placed at the top of the cold finger, directly underneath the sample cell stage. A 50 Ω resistive heating element was used to maintain the control thermometer at the required temperature with fluctuations of < 5 mK. The sample temperature was read from a second diode thermometer located on the top of the sample cell.

The lab view program interfaced with the controlling electronics and monitored and recorded the isotherm process. The gas pressure for each dose was monitored over time to determine when the gas and surface had reached equilibrium, which is determined by monitoring the changes in pressure taken at regular intervals until these changes drop below a predefined tolerance. Most isotherms recorded around 150 data points, but the system automation easily enabled extremely fine pressure dosing and recording of isotherms with hundreds or even up to a thousand data points with no significant intervention required from an operator.

2.3.2 – Determination of System Volume

The calibrated volume of the manifolds was determined through the use of repeated gas expansions using an attached precisely calibrated external glass volume. From the changes in pressure from these expansions, the calibrated volume of the manifold was calculated using the ideal gas law. Similarly, the dead-space volume of the sample cell was measured by gas expansions between the calibrated volume and the sample cell. For accuracy, an ideal gas is required for this process. The adsorbate gases are generally not used for this application as they may not be perfectly ideal in nature, may sorb or damage the substrate at room temperature, or present other issues. The best simple options that were available with these systems was utilization of methane or helium, and while helium is the best option in terms of ideality, methane was used more often as this could be during the preparation of the surface characterization isotherms and is also a well behaved gas.

2.3.3 – Characterization of Substrates

The characterization of substrate sample quality and surface area determination were fulfilled by conducting initial methane isotherms at 77 K. For both graphite and MgO, thin film systems with methane have been well-studied and characterized. Both systems are known to show film structures commensurate with the surface in this range, with an area per molecule of $15.72 \text{ \AA}^2$ on graphite¹⁴⁰ and $17.72 \text{ \AA}^2$ on MgO¹⁴⁸. The surface areas of the substrates were calculated from the monolayer capacity determined from the point B method outlined previously pertaining to these molecular areas. The quality of the surface could be assessed based on the multilayer behavior of the surface. This was more significant for MgO, which had a more variable and sensitive surface that could easily degrade over time during the isotherm process. The indicators to look for with MgO were the obvious formation of at least five distinct monolayer steps, all with similar magnitude to the first step, and sharp, well-defined transitions at the top of the monolayer steps. Poor sample quality or surface degradation over time resulted in loss of distinction and capacity in the higher monolayers, making it important to periodically rerun methane isotherms to check on the status of the sample quality. A comparison of methane isotherms for both substrates is found in Figure 2.5.

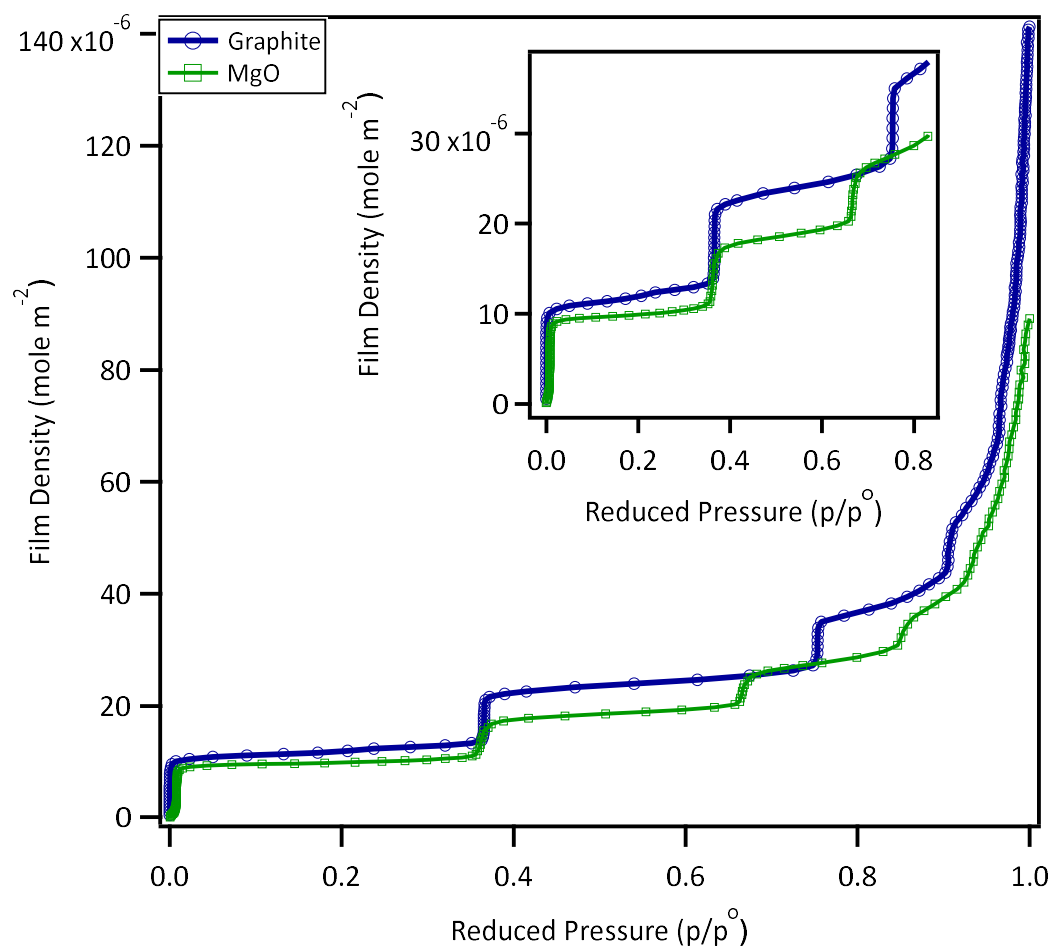


Figure 2.5: Comparison of methane isotherms on graphite and MgO

2.3.4 – Data Analysis

The data was primarily analyzed using Kaleidagraph 4.5 software. The isotherm data was first dead-space corrected and then interpolated to provide both a greater density of data points in the horizontal isotherm regions and a smoothing out of small fluctuations in pressure to improve the quality of the isotherm data and behavior of their numerical derivatives required for peak fitting analysis. Such a process can introduce inherent bias, particular in the analysis of potential subtle features that may be present in the data. In instances where areas were examined in such detail, two separate interpolation algorithms within the software were used and compared: Interpolate, which is a variant of a linear interpolation process, and Smooth, which combines the interpolation with a smoothing algorithm. Both interpolation algorithms could be applied through a single parameter that adjusted the strength of smoothing processes. This parameter was manually adjusted in order to optimize the agreement of the interpolated line with the data points. If a closer inspection of fine details was not warranted with a set of isotherms, only the smooth algorithm was utilized.

In the peak fitting processes used for the FWHM analysis of derivatives or compressibilities, subtle features in one region and shifting peak overlaps in another region of one isotherm system created difficulties beyond what the peak fitting processes in Kaleidagraph were capable of solving. To fit these problematic places, and to keep the data processing methodology the same for all analysis within this dissertation, the peak fitting process was carried out using the multi-peak fitting 2.0 package in Wavemetrics Igor Pro 8.0.

2.4 – Molecular Dynamics Simulations

Molecular dynamics simulations were carried out through the use of Accelrys Materials Studio's Forcite molecular dynamics module. The procedure that has been typically followed by this group in the study of many previous hydrocarbon systems was not perfectly adequate for use in either of these systems and required some extra considerations to obtain more realistic and relevant results. However, while molecular dynamics does provide useful insight into the microscopic behavior of such molecular systems, they are not always trustworthy and should not be interpreted as an absolute reference in this regard. This is perhaps more so true when standardized force fields are edited or modified to try and match the experimental results. For acetylene, where this was heavily explored, simple calculations using other force-fields and

atomic potentials obtained from the literature provided a wider picture of the possibilities and differences of the various force-fields that have been used to describe this system. This section will only describe the simulations conducted within Materials Studio. A report on these extra calculations can be found in Chapter 4.

2.4.1 – Preparation of Simulated System

The preparation of the simulated materials and simulation box parameters needed to be properly and carefully considered in order to construct a realistic size simulation. The conditions must be defined in a way to be the best approximation of reality possible, while remaining simple enough for the computational time of the simulation to remain reasonable. The following example illustrates the need for such considerations. Smaller systems are computationally faster but may result in exaggerated effects if there is a significant mismatch between the lattice structure of the film and the size of the simulation box dimensions. A larger box would help to alleviate some of the mismatch strain, spreading out any compressive or expansive forces created by the boundary mismatch over more molecules, but would take longer to run the simulations. A wise trade-off may be to run simulations with incomplete coverages using smaller simulation boxes, while increasing the size as the system approaches a complete monolayer. An extension of this would be in the examination of commensurate film systems, where the simulation box needs to be an integer multiple of the commensurate lattice structure. The following outlined procedures were constructed to represent the best imitation of real, infinite systems as is reasonably obtainable using molecular dynamics systems on a desktop computational cluster.

The simulations were conducted using the COMPASS force field to define basic parameters of the intermolecular interactions. This force field has been well-validated for accurate representations of the physical properties for many systems, including hydrocarbons. Acetylene has a long history of attempts to describe its properties with different force fields and custom-tailored atomic potentials with varying degrees of success, but no record has been found for a set of potentials that accurately describes acetylene's behavior in all of its phases. Even attempts to define a set of potentials that are able to describe both solid phases has not been entirely successful. Additionally, the COMPASS force field does not contain accurate parameters to control the dihedral angle of the pairs of carbons at opposite ends of the molecular axis, and

in fact allows for free rotation of the cumulated double bonds around the central sp carbon. How these issues were addressed is outlined below.

2.4.1.1 – Surface Construction

The structures for materials utilized in these studies were defined based on the experimentally measured lattice constants and atomic positions. This did not result in significant shifts from the force-field assigned values, but as the atoms of the surface substrate were constrained, the real values would, in theory, present the best representation of the actual surface potential for these simulations.

Supercells of the surface were created to the desired dimensions of the substrate surface within the simulation box. The size of the cell depended on the type of calculation being performed and, where appropriate, lattice considerations were made as was outlined in this section's introduction. The surfaces were then "cleaved" along the c lattice vector (z-axis in cartesian coordinates) to define the surface faces of the substrate, with a substrate thickness of 5 atomic layers. This thickness was set based on the cut-off distances of the intermolecular interaction terms in the calculations; hence a thicker surface would involve more atoms in the system for calculations, while a thinner surface would not represent surface interactions with full accuracy and may allow molecules on opposing surfaces of the substrate to interact with each other.

Vacuum slabs were created at 100 Å in length with the substrate centered along the vertical axis of the simulated volume. The centering of the substrate was not necessary for the accuracy of the simulations, but was used as a reference point in the calculation of the two-dimensional radial distribution functions. The software assigns periodic boundary conditions to the simulation box such that particles leaving the simulation box re-enter along the opposite symmetric edge of the system. When the supercell and simulation space were fully constructed, the constraints were used to fix the cartesian coordinates of the surface atoms.

2.4.1.2 – Preparation of Molecules

Neither molecule was included amongst the preconstructed molecules found within the software's library of structures. The molecules were built using the Materials Studio visualizer, and geometry optimizations were performed with the standard parameters of the COMPASS

force-fields to obtain the proper structure for the molecules. The molecular geometries were compared with those from the NIST CCCBDB values to confirm that the obtained structures agreed with the proper values. This worked well for acetylene; however, allene required an additional restraint to be defined before an accurate molecular structure was obtained. For the calculations of radial distribution functions, the molecules must actually have the identification of a “molecule” object within the Accelrys hierarchy, which sometimes is not generated automatically when molecules are built. Lack of this classification system would not have any effect on the simulations themselves, but was a needed requirement when individually counting objects for use in the custom radial distribution script. If the molecule tag was not automatically created by the software, this was assigned manually in the Morphology Tools module’s crystal graph menu.

2.4.1.3 – Special Considerations for Allene

To obtain a realistic optimization of the structure for allene, a dihedral object was created on the molecule within the visualizer. This object was then used to define a restraint on the molecule, setting the minimum energy orientation to 90° and the force constant was set to 102.09 kJ mol⁻¹ rad⁻¹, which was derived from the rotational barrier for allene found in the literature. The restraint used the same harmonic potential form as the normal dihedral interactions of the COMPASS force-field.

2.4.1.4 – Force-Field Variations for Acetylene

The COMPASS force-field is a proprietary development of BIOVIA (formerly Accelrys when the version of the software utilized was released). Most of the potentials used in the software are not accessible except for a small fraction released by the company in publications on the force-fields validation. This means that direct editing of this force-fields’ parameters was not possible within the software. Not unexpectedly, simulations of acetylene on graphite ran using the standard force-field parameters produced results with clear evidence of an underestimation of the quadrupole interactions.

Within the context of correcting and balancing the quadrupole interactions, the system did allow for two potential types of modifications that did not involve the need to edit force-field defined potentials. The first was the editing of the point charge values assigned to the individual

atoms to increase the quadrupole strength. The second possibility allowed for the modification of the atom type assignments to other alternatives defined within the force-field. The list of atom type equivalencies has been published by the company and was used as a guideline for alternative atom type assignments that might result in subtle changes to the van der Waals energy calculations.

In order to alter these parameters, the force field had to first make the assigned atom types and point charges for the entire simulated system. Therefore, after the simulated system was created and molecules for the desired film density were in place, a simulation of at least one frame had to be performed to allow the force-field to initialize its assignments. To the resulting output, desired adjustments were made, and in the simulation set up, the automatic force field assignments were turned off, preventing the force field from reassigning the current values.

2.4.2 – Energy Minimization Calculations

Energy minimization calculations for a single molecule on the surface were performed using a small supercell approximately 8 to 10 angstroms across. A single molecule was placed onto the surface at one of the high symmetry locations defined earlier. The calculation was then proceeded to optimize the configurational energy of the molecule to the surface using the Forcite module's geometry optimization routine, employing the Smart algorithm. The outputs were examined for the optimized position on the surface and the non-bonding energies were used to assess the binding energy for the molecule-surface interactions of the molecule in the optimized position. This process was repeated by rotating the molecule by several degrees and performing the calculation for each unique high symmetry position of the surface.

Acetylene's symmetry did not require any need for consideration of different molecular orientations about its molecular axis. Conversely, the lower symmetry of allene presented two likely orientations of this axis relative to the surface. To explore both possibilities, the series of calculations were run with the molecule oriented with the planes of the hydrogens each oriented at 45° from the surface, and with the hydrogen planes oriented with one set horizontal to the surface and the other vertically oriented from the surface.

Acetylene did, however, present an issue when analyzing the simulations due to the close proximity of the large point charges assigned to the molecule to simulate its quadrupole interactions. The force-field did not have any settings that allowed for the exclusion of 1-4 atom-

atom intramolecular interactions, resulting in a large repulsive energy being calculated between the positive charges on the molecules' opposing hydrogens. This repulsive energy, being intramolecular in nature, should not have impacted the refined surface configuration, as it did not seem to result in any unphysical distortion of the molecule itself. However, even with the default force field settings that under-represented the quadrupole strength, the magnitude of the repulsive energy was nearly exactly the same magnitude as the surface interactions in the case of graphite, resulting in an apparent non-bond energy that was nearly zero. To remove the artifact of this interaction from the reported energies, the surface was deleted from the calculation output's atomistic document, and an energy calculation was performed using the Forcite module to determine the energy of just the intramolecular interactions of the molecule, which were further subtracted from the non-bond energies of the original optimizations.

2.4.3 – Dynamics Simulations

The dynamics simulations were conducted using a supercell of sufficient size to contain approximately 120 molecules to create a complete monolayer for both surfaces of the substrate used. Considerations for lattice mismatches were made by basing the surface density of a monolayer on the areas per molecule obtained from isotherm measurements. The sizes were also set within this context to ensure there were no issues in commensurate structures, while simultaneously tailoring the supercell size to be an integer multiple of any suspected commensurate relationships.

2.4.3.1 – Simulation Process

The simulations were conducted by placing a predefined number of molecules within the supercell space to achieve a nominal desired coverage to examine. The simulations were run using the Forcite dynamics routine with the Canonical (NVT) ensemble. The calculations were performed with a minimum time span of 100 ps with a 1 fs time step. Temperature was controlled using the NHL thermostat and associated default values for the thermostat constants. The energy calculations were performed using the modules "medium" quality settings, which set the non-bond energy cut-off distance to 15.5 Å.

To remove any bias in the initial placement of molecules within the supercell and simulate the film behavior across a large range of temperatures, the simulations needed to be initiated at

a temperature that was two to three times the bulk triple point. This ensured the thermal randomization of the molecules and that the simulations were conducted from a realistic frame of reference. The triple point for both molecules is such that 400 K was picked as the starting temperature for both molecules. The simulations were then conducted as a series exposed to decreasing temperature with the coordinates and velocities from the last frame of the previous simulation being used to define the starting point of the next simulation at the next lower temperature, most often moving in increments of 10 K. The normal simulation timeframe was 100 ps; however, following the completion of each simulation, the trajectory outputs were examined to determine if the system had reached the equilibrium point for that temperature step. The temperature generally reached equilibrium within the first few picoseconds, with the energy analyses of the trajectories serving as good indicators that the system may have reached the equilibrium configuration at that temperature. In particular, the trends in the non-bond and potential energies were assessed and, if they were seen to still be decreasing by the end of the simulation or seemed to have leveled off in the last 10% of the simulation, the simulation would be continued for a longer timeframe until these energies remained constant with time.

2.4.3.2 – Analysis of Simulation Trajectories

The most heavily utilized methods employed by this research group for examining the trajectories in similar studies are visualization, radial distribution function analysis, and concentration profile analysis. The first and simplest, though the most subjective, involves one of the important and unique aspects that molecular dynamics and other computational methods afford chemists: the visual inspection of the trajectories, both as a stationary frame and an animated movie, provide a visual representation of the molecule's structure and dynamics that is unique. While this step is certainly subjective, it allows for a contextualization of both quantitative analyses of the simulation trajectories and empirical data. It can also highlight certain aspects of the film dynamics that are not as immediately clear in the data from the other methods. A review of the visualization of the dynamics calculations, for example, might reveal a correlation of the direction of motion of the molecules along one particular direction of the surface lattice. Such information may be quantifiable from a vectorized mean squared displacement analysis, but without visualization, would not be obvious in the data. Furthermore, distance or angle measurements could be defined within the system between any objects of

interest, and Forcite analysis calculations allowed for length or angle distributions to be determined on this feature.

The second method used here is the calculation of the radial distribution function of the simulated films. This function provides important time-averaged structural information about the trajectory's structures and the disorder thereof. The default calculation algorithm included in the Forcite analysis package was intended for analysis of three-dimensional systems, and so application to two-dimensional systems resulted in an artifact that drove the intensities towards zero at increasing distances. Though reasonable information about the first coordination shell could be obtained, the errors in intensities of each subsequent shell grew rapidly in magnitude. It was assumed at first that this was the result of the normalization of molecules in a two-dimensional plane over the volume of a spherical shell element for each radius bin in the generated histogram. Such an artifact would be easily corrected for, however, applying such a correction did not remove the artifact and only marginally improved the results. The exact reason for this issue was not determined, but it was suspected that it was the result of a combination of the volume element problem and the way the algorithm dealt with periodic boundary conditions in three dimensions versus two dimensions. While this latter issue should not seem to make a difference in theory, it is noted that the calculations typically resulted in an extra odd feature at a distance correlated with the lengths of the simulation box along in the surface plane, indicating a boundary artifact. A component of the dissertation research contained herein was the development of a script that would run in the Materials Studio platform, capable of calculating the correct two-dimensional radial distribution function from trajectory outputs, which can be found in appendix A.

Concentration profiles were also examined for the axis perpendicular to the surface. This yielded information in regards to the orientation and disorder of molecules away from the surface plane of the film, which is not obtainable within the radial distribution functions and is hard to quantify from visual inspections.

Further analyses were examined in some cases where the information they provided would help elucidate aspects of the simulations not obtainable with the previously mentioned methods, and also for their potential usefulness in the analysis of molecular dynamics within Materials Studio in future studies. The previous two methods described provide useful

information about structure, but do not contain any direct information about the dynamics of the system. Mean squared displacement calculations are a common tool for examining simulation dynamics and diffusion. Forcite can calculate these quantities vectorized for each direction (xx, yy, zz), as coupled crossterms of two directions (xy, xz, yz) and as the total. Spatial orientation correlation functions in Materials Studio are an expression of the orientational order in the system. This is similar to the bond angle correlation function discussed in the previous chapter, and can be used to examine the orientational ordering of the molecules, or of the lattice, but does not have the specificity of the bond angle correlation functions to specific bond ordering. Rotational time correlation functions were also examined as a means to assess potential aspects of hindered or free rotations within the system for analysis of potential aspects of different phases in the films.

The analyses contained within the proceeding results chapters focus primarily on the three primary methods: visualization analysis, radial distribution functions, and concentration profiles. A summary of the potential uses of these other methods is discussed in chapter 1.

2.5 – Neutron Diffraction

This dissertation includes the analysis of data that was previously collected for the systems of acetylene on graphite and MgO collected at the High Flux Beam Reactor (HFBR) at Brookhaven National Laboratory before its decommissioning that had hitherto gone unpublished. These data were also supplemented with recently collected, though more limited, measurements conducted at the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory.

The majority of this data focused on the acetylene on graphite system and was collected in two separate sets of experiments that each examined the system over a wide range of temperatures utilizing the H5 beam line at the HRBR facility in the late 80s to early 90s, set to a wavelength of 2.865 Å. The first set was performed preceding an upgrade to the beamline, consisting of the installment of an improved multidetector. Following this upgrade, a second set of experiments mirrored the first set, but with significantly improved data quality. These experiments were conducted at a 0.7 monolayer coverage relative to a commensurate $\sqrt{3} \times \sqrt{3}R30^\circ$ lattice. They spanned a temperature range from 4 K to 165 K, with the second set of experiments focusing more on the region around the melting transition for this system. Both

experiments were collected as difference measurements to remove the higher intensity signals of the substrate and sample container from the obtained spectra. This process collects backgrounds of the bare substrate system that could then be subtracted from scans of the adsorbed system in order to isolate the diffraction pattern of the film itself. Films were annealed at 165 K for two hours and then slowly cooled at 1K/min to the data collection temperature. The data consisted of the averaging of six scans taken at each temperature point and were corrected for detector efficiency.

Two diffraction profile measurements of acetylene on MgO were also performed for coverages of 0.7 and 1.0 monolayers on the same beam line following the detector upgrade. These measurements were only performed at 10 K. The shutdown of the HFBR facility in the mid 90s prevented further measurements to be taken for this system.

Follow-up measurements were also made using the HFIR HB-2C beamline employing the Wide Angle Neutron Diffractometer (WAND). These measurements were conducted as difference scans for acetylene adsorbed on both graphite and MgO at 10 K and a wavelength of 1.487 Å. WAND covered a much larger range of Q-space than the previously measured data and was useful in adding verification of previous results and confirming the absence of any other significant diffraction peaks outside of the original data's scan window.

The primary contribution of this dissertation towards the elucidation of neutron diffraction results for these systems was not in the collection of data, but in the analysis of the data. Heretofore, a Fortran program called 2dim that generates calculated diffraction profiles for two-dimensional systems for both neutron and x-ray diffraction experiments, has been used for the analysis of diffraction studies amongst this research group. The program was originally developed by James C. Newton as part of his dissertation work at the University of Missouri and was modified by John Z. Larese and his research team at Brookhaven National Laboratory, which included the addition of two non-Warren, Lorentzian and Lorentzian-squared lineshape possibilities. This program generated lineshapes that accounted for lattice parameters, molecular positions and orientations, fixed or free molecular rotations, three possible lineshape functions (mentioned above), disorder terms (coherence length and mean squared displacements), multilayering corrections and background corrections, substrate preferred orientations, and instrument-specific parameters.

A drawback of this program, in the absence of further refinement, is that it requires manual input for specific potential lattices and other settings, one value at a time, and then further manual analysis of each resulting output. Though this limitation has not prevented the use of the program in the structural refinement of many systems in the past with very good agreement, it lacked the elegance of the Rietveld refinement process used for the analysis of powder diffraction data in three dimensions. To establish similar abilities for the analysis of two-dimensional systems, a Matlab application was developed to add a GUI and more functionality to the original program. This program allows the user to specify all the initial input settings required by the 2dim program, as well as particular parameters and ranges for a refinement process. Following this, the program initiates a loop over the permutations of all the selected parameters, from which it generates the input files for 2dim, runs the program, then uploads the resulting calculated diffraction profile. It then uses a least-squares fitting process to scale the calculated intensities to the diffraction profile, along with a selected baseline function, and, selectably, a disordered background function. The process then repeats the loop for the next iteration, tracking the goodness-of-fit for each structure tested. While this method is a “blunt force” method of approaching a least-squares fitting, the program in its current form functions primarily as the interface of the 2dim program that has already been established and worked within the confines of the current functionality of that program. One modification to the original source code was made by the author of this dissertation that allowed for the source code to be compiled using the Intel’s Ifort compiler instead of the opensource gfortran compiler previously utilized. The new compiler has inbuilt features that allow for the optimization of vector algebra and the automatic parallelization of processes within the program. This resulted in a benchmarked speed increase in the program efficiency by a factor of 20 for a comparatively small system. A more optimized and direct approach for Rietveld refinement is possible for two-dimensional systems, but if implemented in the future, will require a significant overhaul or replacement of the 2dim program source code.

In the process of fitting the experimental data, one additional aspect required further functionalities of the program. In the refinement of the acetylene on graphite data, diffraction profiles at multiple temperatures showed an evolving, two-phase coexistence region with overlapping diffraction features. First attempts to use the developed refinement program to fit

the data in this region employed a pre-fit disordered background of the liquid diffraction profile after the complete melting of the system. This, however, resulted in poor quality fitting, which grew worse as the temperatures approached the pure solid phase, and did very poorly at describing the diffuse disorder background present in the solid phase. The functionality of the refinement application was extended to include a simultaneous two-phase refinement that enabled fitting of both phases simultaneously. Further description on how this was able to be used effectively while avoiding false solutions inherent to optimizations of systems with too many degrees of freedom is described in Chapter 3.

Chapter 3 – Adsorption of Acetylene on Graphite: A Thermodynamic, Neutron Diffraction, and Modeling Study

3.1 – Abstract

A detailed investigation of the phase behavior of acetylene films adsorbed on graphite's basal plane between 119 K and 141 K is presented. Volumetric adsorption isotherms show four distinct features in the monolayer regime. A potential fifth feature appears in the first step. A notable change in the isotherm behavior takes place between 132.5 K and 134.5 K, where the system undergoes a 2D melting transition. At temperatures above 134.5K, the adsorption traces exhibit three features, with a second melting transition at 140.5 K. Neutron diffraction data at sub-monolayer coverage has been used to analyze the structure of one of the previously observed solid phases. The neutron diffraction data confirms that the transition at 133 K recorded in the isotherm data is associated with the melting of the monolayer solid. Companion molecular dynamics simulations were performed over a temperature and coverage range consistent with the adsorption and neutron diffraction measurements. At low coverages, the quadrupole-quadrupole molecular interactions are comparable in magnitude to the molecule-surface interactions, leading to a solid with significant rotational disorder. These simulations find that as the film density is increased, the solid film becomes more rotationally ordered, leading to a hexagonal solid structure, symmetric with the graphite surface.

3.2 – Introduction

Understanding the behavior of molecules adsorbed on a solid surface plays an important role in current basic scientific and technological issues. Examples where these investigations are most relevant include catalysis¹¹, gas separation¹¹, gas storage¹⁴, and optoelectronics¹⁶. By expanding the fundamental knowledge base on how molecules interact with (and perhaps modify) a material's surface, an ideal platform is established with which to probe and test theories of intermolecular interactions and in principle subsequently lead to technological advancements. One interesting area involves examination of the interplay of molecule-molecule and molecule-surface symmetries, especially in cases where the two symmetries are incompatible. Archetypal surface substrates like MgO (100) and graphite basal plane have

recently been undertaken to probe how the relative size of these two interactions influence the properties of adsorbed molecular films. Graphite is one of the most widely studied surfaces due to its chemical stability, the availability of uniform, single facet high surface area materials (i.e. predominantly basal plane exposure), and relative ease of preparation and maintenance of clean surfaces.

For this study, the focus was an examination of the adsorption of acetylene films on the surface of graphite. As such, it is one component of an ongoing series of investigations which examine the behavioral trends of a homologous family of molecules adsorbed onto surfaces of varying symmetry^{154, 156-158}. This study represents the first step in an examination of the adsorption properties of linear, quadrupolar hydrocarbons, of which acetylene may be considered the prototypical molecule. It is a small, highly symmetric molecule similar to other molecules that have previously been studied, such as N_2 ^{164, 165}, C_2N_2 ¹⁷⁸, and CO_2 ^{177, 178}. Linear molecules of these types all belong to the same point group ($D_{\infty h}$), the common symmetry which prevents the formation of any type of static dipole moment. These small molecules can, however, display charge distributions with higher order electrostatic moments (e.g. a quadrupole moment), and in cases where this electrostatic property is substantial, a notable influence on their intermolecular interactions and resulting condensed state properties. Acetylene distinguishes itself from these other molecules as a result of its small size and large quadrupole moment, which is approximately 5 times greater than that of nitrogen^{95, 209, 211, 221-223}. This means that the quadrupolar interaction between molecules should be a key factor in the resulting surface structure and behavior of adsorbed acetylene films. Notably, acetylene is considerably smaller and lighter than CO_2 , which also has a sizable quadrupole moment. It is nearly small enough to adopt a $\sqrt{3} \times \sqrt{3}$ $R30^\circ$ commensurate lattice on graphite while lying flat²¹⁴, suggesting that the six-fold symmetry of the surface will influence the physical properties of the film as well.

The minimum energy configuration for two interacting linear quadrupoles is such that they adopt a T-shaped arrangement. Extending this effect in two dimensions would result in the formation of a stable, ordered square lattice containing two molecules per unit cell in the T-shaped configuration, with four-fold symmetry²²⁴. It is well known that graphite forms a hexagonal or “honeycomb” lattice, with a weakly corrugated, nonpolar surface plane. Thus, the 6-fold surface symmetry would naturally “steer” molecules towards structures which would favor

a similar arrangement. The juxtaposition of these two different structurally favorable symmetries underscores one of the underlying purposes for investigating acetylene film adsorption on the graphite basal plane (i.e. 4-fold versus 6-fold symmetry, respectively). Depending on the relative size of the molecule-molecule and molecule-surface interactions and the surface density, a “tug of war” between the preferred molecular orientations can result, producing a solid film that is structurally frustrated⁵¹. For example, nitrogen, which has a weaker quadrupole moment compared to other molecules of similar size, readily forms a monolayer solid that is commensurate with the graphite (hexagonal) surface⁵¹. In the current study, acetylene, with its larger quadrupole moment, has a phase diagram with fascinating structural and physical properties.

Earlier, less comprehensive thermodynamic and microscopic studies suggested that this is a system that is poorly understood and complex^{27, 107, 213-217, 225}. The thermodynamic investigations revealed several adsorption features that may be related to phase transitions within the monolayer phase. Preliminary neutron data identified two solid phases (referred to as S_1 and S_2), as well as one liquid phase²¹⁶. A more recent neutron study broadened this picture, by introducing phase transitions and mixed solid phases²¹³. Although these studies have revealed the complexity of this system, they have not represented a detailed enough paralleled thermodynamic, microscopic, and modeling investigation in order to provide a more complete picture of the structural, thermodynamic, and phase behavior for this system.

The present investigation presents a comprehensive examination of the adsorption of acetylene films on graphite using thermodynamic, neutron scattering, and molecular dynamic modeling techniques aimed at the monolayer (and beyond) behavior. Thermodynamic measurements were made using high resolution volumetric isotherms in a temperature range of 119 K to 141 K. From these data, potential phase transitions, surface densities, and differential enthalpies and entropies were obtained. Molecular dynamics simulations were performed over a range of coverages above and below monolayer completion to illuminate the structure and subtleties of the film behavior. Single molecule geometry optimizations on graphite were also performed to identify preferred binding sites and energies. Lastly, neutron diffraction data at low coverages were obtained to provide structural information and additional evidence concerning 2D melting.

3.3 – Experimental

3.3.1 – Acetylene Purification

Most commercially available acetylene gas (pressurized over 2 atm) is dissolved in acetone to stabilize it and allow for safe storage at higher pressures. For this study, atomic absorption grade (99.7 % purity, Airgas) was used. Before use, the gas was purified following a procedure described by Hyman et al.²¹⁸, shown to effectively remove the contaminating acetone vapor as well as several other contaminants common to acetylene production. The resulting gas was then subjected to several freeze-pump-thaw cycles to remove any remaining volatile gases.

3.3.2 – Volumetric Isotherms

The graphite sample used was an exfoliated foam provided by Union Carbide with a surface area around $20 \text{ m}^2 \text{ g}^{-1}$. The graphite sample was heat-treated *in vacuo* inside a quartz tube at 750°C for 24 hours. The sample was then transferred into an argon filled glove box, where it was loaded into a OFHC copper sample cell and subsequently sealed with an indium gasket. The sample cell was then mounted on a cold finger inside an ARS™ 4K based closed-cycle helium cryostat. A Neocera™ LTC-21 controller was used to regulate temperature to a stability of less than $\pm 5 \text{ mK}$ using a silicon diode thermometer mounted at the top of the cold finger. The sample temperature was monitored with a second silicon diode attached to the top of the sample cell.

As in the past, adsorption experiments were performed using an automated, high-resolution isotherm apparatus controlled by a custom LabVIEW program to regulate and record gas dosing, pressures, and temperature²²⁰. Pressure readings were made using either a 1 or 100 torr MKS baratron capacitance monometer. This system has been shown to produce highly stable and precise measurements, across a wide range of temperatures and pressures. A methane isotherm at 77K was initially performed to characterize the quality and surface area of the heat-treated sample after mounting the sample in the cryostat. In order to monitor if surface degradation took place, methane isotherms were performed periodically. Greater than twenty isotherms were recorded within the temperature range of $119 \text{ K} > T(\text{K}) > 141 \text{ K}$. Sample temperatures were established using saturated vapor pressures (SVP) for each isotherm employing parameters determined for acetylene by Menaucourt et al²¹⁴.

3.3.3 – Computational Modeling

Molecular modeling studies were performed using the Forcite Module in Accelrys' Materials Studio 6.0 software. As performed similarly in our previous studies, the COMPASS forcefield was used to define the intermolecular and molecule-surface interactions in the simulations known to realistically describe the interactions of many hydrocarbons and small molecules⁹⁰. Two types of computations were performed in this study: geometry optimization of a single molecule on a graphite surface was used to identify favorable surface binding sites and energies, and molecular dynamics (MD) simulations were conducted at various temperatures and for several fixed numbers of molecules to gain insight regarding possible film structure and attendant molecular dynamic behavior.

For both types of simulations, the initial preparation of the graphite surfaces and acetylene molecules was the same. An optimized graphite unit cell ($2.46 \times 2.46 \times 6.80$ Å) consistent with crystallographic data was used to create a larger supercell of the graphite substrate, within which the atomic positions of the C atoms were constrained to remain fixed in their optimized positions. A vacuum slab was created above the surface with periodic boundary conditions to create an infinite xy-plane of the graphite surfaces, with the z direction connecting the vacuum space of the top and bottom surfaces of the simulation box. Likewise, individual acetylene molecules were constructed and optimized and then transferred onto the graphite surface within the simulation box.

For the geometry optimization calculations, acetylene molecules were placed onto the surface of a $9.84 \times 9.84 \times 17.00$ Å graphite supercell with a 20 Å vacuum slab having the molecular center of mass positioned over high symmetry points of the graphite surface, those being the center hollow of the hexagonal unit, the mid-point of a carbon-carbon bond, and directly on top of a carbon atom. Calculations were run for various initial molecular orientations over these fixed points using the Forcite module's Smart algorithm.

MD simulations were performed using a $36.90 \times 36.90 \times 17.00$ Å supercell with a 100 Å vacuum slab. To investigate the density dependence of a single layer of adsorbed molecules on the graphite surface, five different groups of acetylene molecules (over an approximate range of 0.3 to 1.2 monolayers) were placed randomly within the simulation box. Simulations were performed using the NVT (canonical) ensemble with a Nose-Hoover-Langevin (NHL) thermostat

for temperature regulation. Simulation times ranged from 50 to 250 ps depending on equilibration times, with a 1 fs time step. Equilibrium was determined to be reached when the non-bonded and potential energy terms remain constant with time. In order to eliminate any unintended bias of the starting position of any molecule within the ensemble, each MD simulation was initially performed at 400 K. The system was incrementally cooled by using the final velocities and positions from the end of each simulation as the start point of the next simulation at lower temperature. This process ensured that the simulations were conducted from a suitably random arrangement of molecules that then incrementally approached equilibrium with the surface as the temperature was lowered.

3.3.4 – Neutron Diffraction

Elastic neutron diffraction data was collected using the powder diffractometers TAMPA located at the High Flux Beam Reactor (Brookhaven National Laboratory) and WAND² at the High Flux Isotope Reactor (Oak Ridge National Laboratory), which were operated at fixed wavelengths of 1.63 Å and 1.5 Å, respectively. The sample cells were loaded in a glove box and mounted on a custom cryostat insert²²⁶. The adsorbed films were prepared *in situ* as in the past, using a custom-built gas handling system²⁴. All quantities of C₂D₂ gas are quoted in fractional coverages where one monolayer refers to the quantity of gas needed to form a $\sqrt{3} \times \sqrt{3}$ R30° commensurate lattice (as determined using a N₂ isotherm at 77.4K). Films were annealed for ~ 2 hours at (165 K) and then slowly cooled at 1K/min to the data collection temperature. Diffraction profiles were recorded within a temperature range between 160 K to 4 K. The diffraction data was evaluated by subtracting off the signal from the sample cell containing the bare graphite.

3.4 – Results and Discussion

3.4.1 – Thermodynamics

As noted above, twenty-seven volumetric isotherms were recorded between 119.69 K < T(K) < 141.62 K. Once the raw data was corrected for molecules that occupied the dead space, these data were reduced using the interpolation routine described in our earlier work¹⁴² to obtain smooth curves that accurately represent the experimental data. The inset to Figure 3.1 shows four different isotherms to illustrate how the interpolated curves match the behavior of the

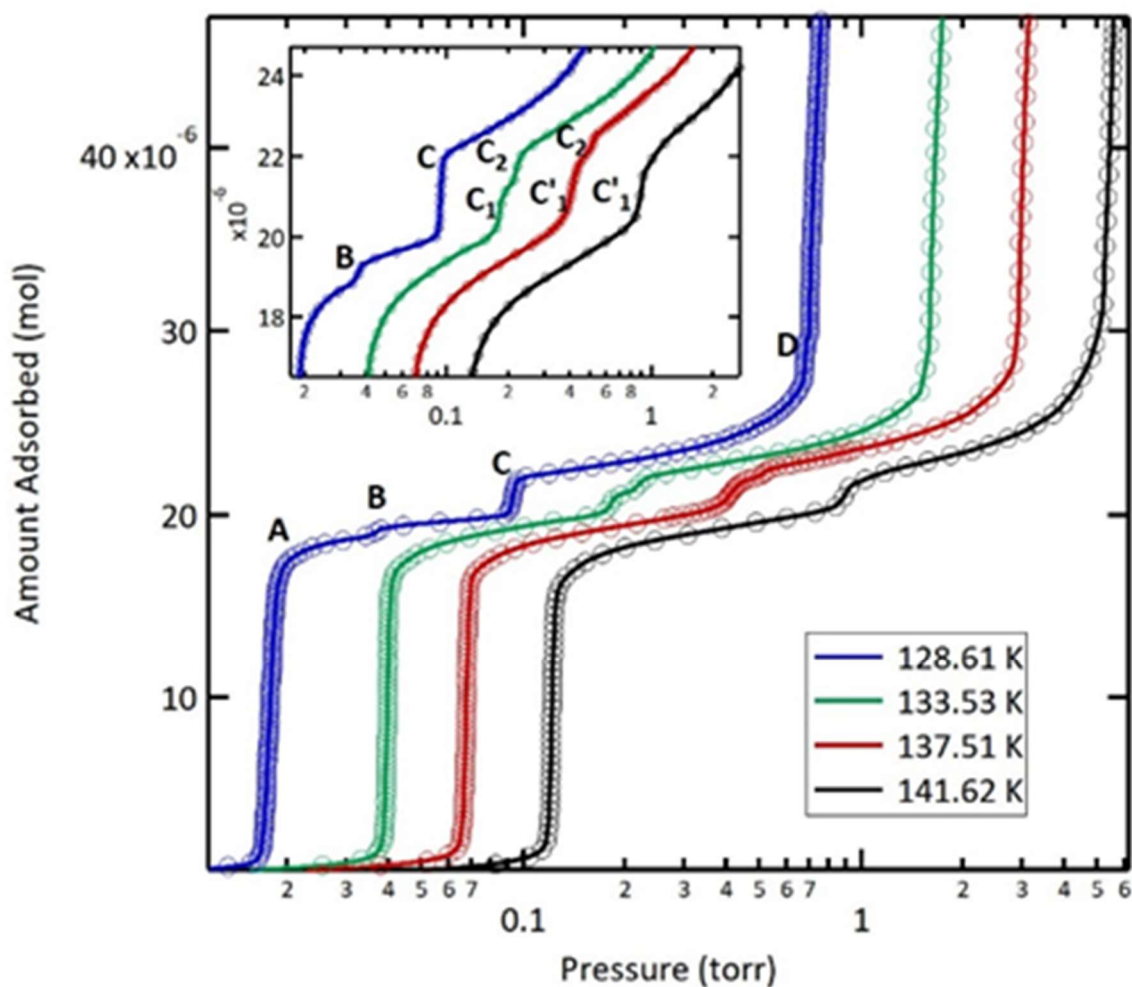


Figure 3.1: Selected isotherms for acetylene on graphite
Interpolated fits (lines) with matching raw data points (circles) at four selected temperatures within the analyzed range. Transition features of the first monolayer are labeled here as A through D.

experimental data (solid circles). Figure 3.1 also indicates that at temperatures < 132.63 K, four prominent features (labeled A through D) are recorded. Between 132.63 K and 134.52 K, these features exhibit noticeable changes: feature B broadens and disappears while feature C splits into two sub-steps (C_1 and C_2). Furthermore, above 134.52 K, feature C undergoes another change in behavior as a function of coverage for the lower step (labelled C_1'). Lastly, the substep identified as C_2 disappears between 140.61 K and 141.62 K.

When the isotherm temperature is > 132.63 K, the slope of initial step A appears to be less vertical and becomes progressively less steep as the temperature is decreased. This behavior can be associated with a decrease in film density as well (see example in Figure 3.2). Previous investigations have led to uncertainty in the critical temperature, T_{c1} , associated with the first acetylene layer. Recent investigations^{14,20} indicate that T_{c1} is at 155 K. The study by Peters et al.¹⁰⁷, who reported T_{c1} to be at 120 K, based their conclusion on an apparent splitting and reduction in slope of the initial riser (labeled feature A in Figure 1, found at ~ 120 K). In the high-resolution measurements reported here, a similar (albeit subtle) feature associated with step A appears in all traces < 132.5 K. It is important to note that this feature is barely visible in the raw data; however, by taking the numerical derivative of the interpolated fits, this feature is readily observable (see example found in bottom trace of Figure 3.2). The heat capacity study by Alkhafaji and Migone²⁷ provides additional information in terms of the order of the monolayer melting behavior of acetylene. Similar behavior may have been observed in the study of sub-monolayer ethylene on graphite^{160, 161, 227}.

Surface coverages corresponding to the various monolayer substep features were identified using the point B method. The area per molecule (APM) was determined by comparing the substep locations to the initial 77 K methane calibration isotherm where the $\sqrt{3} \times \sqrt{3}$ $R30^\circ$ commensurate structure and $15.72 \text{ \AA}^2$ APM is well-established. All coverages are reported as a fraction, where 1.00 monolayer is the coverage when the $\sqrt{3} \times \sqrt{3}$ commensurate phase is completed, consistent with earlier published measurements^{27, 214, 217}. These values are summarized in Table 3.1. Notably, the coverage/APM value for phase A has a lower surface density in the low temperature regime than in the high temperature region. The C and C_2 phases have similar densities (i.e. $\sim 5\%$ lower than the $\sqrt{3} \times \sqrt{3}$ $R30^\circ$ phase and where C_2 is slightly more

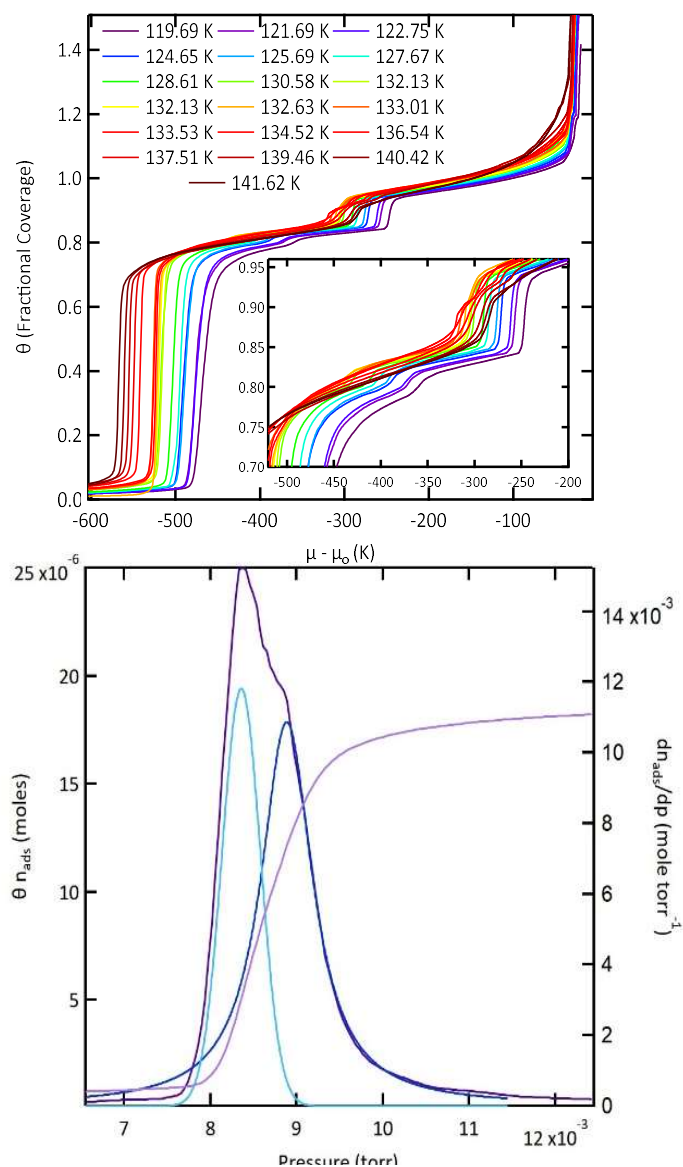


Figure 3.2: Acetylene on graphite isotherms plotted vs chemical potential (top) plot of isotherms over the full temperature range examined plotted as a function of chemical potential. (bottom) First monolayer step of isotherm at 124.64 K with numerical derivative. Peak fitting results showing two distinct peaks are in blue showing two distinct sub-features. FWHMs for two peak fit solution: 5.2274E-4 and 7.4087E-4. **FWHM for one peak fit solution: 1.0176E-3**

Table 3.1::Thermodynamic quantities for acetylene on graphite

Phase	Coverage (Relative to CH ₄)	APM Å ²	A ⁽ⁿ⁾	B ⁽ⁿ⁾	ΔH kJ mol ⁻¹	ΔS J mol ⁻¹ K ⁻¹	Q _{ads} kJ mol ⁻¹	Temperature Range Observable K
A	0.790 ± 0.007	19.92 ± 0.15	2673.0	17.532	1.247	35.484	22.223	≥ 133.53
A₁	≈0.57 [†]	≈28 [†]	2810.0	17.795	0.108	33.298	23.362	≤ 132.14
A₂	0.762 ± 0.007	20.66 ± 0.22	2723.8	17.170	0.825	38.494	22.646	≤ 132.14
B	0.824 ± 0.004	19.1 ± 0.10	2384.8	15.199	3.643	54.881	19.827	≤ 132.14
B'	‡	‡	5219.0	36.670	-19.920	-123.63	43.391	132.63 – 133.70
C	0.950 ± 0.002	16.56 ± 0.04	2496.8	17.035	2.712	39.616	20.758	≤ 132.14
C₁	0.896 ± 0.005	17.57 ± 0.11	2764.9	19.016	0.483	23.146	22.987	132.52 – 133.77
C'₁	0.923 ± 0.006	17.06 ± 0.12	3788.2	26.644	-8.025	-40.439	31.495	≥ 136.54
C₂	0.959 ± 0.008	16.42 ± 0.15	4051.2	28.789	-10.21	-58.107	33.682	≥ 136.54
D	1.202 ± 0.019	13.10 ± 0.25	2821.7	21.550	0.0108	2.079	23.460	≤ 133.01
Layer 2	-	-	2804.0	21.453	0.158	2.885	23.313	Full range
Layer 3	-	-	2827.1	21.742	-0.034	0.482	23.505	Full range
Layer 4	-	-	2859.5	22.015	-0.304	-1.788	23.774	Full range
Bulk	-	-	2823.0	21.800	-	-	23.470	-

Coverage and thermodynamic data for observed phases. Coverages for multilayers are excluded due to overlap with capillary condensation within the vermicular graphite structure. († estimate based on best fitting isotherms data, ‡ feature is visible in only two isotherms weakly, coverage and thermodynamic values are should be regarded as estimations).

dense). The density associated with feature D is significantly higher than in the other monolayer films and may signal that the molecules are tilted away from the graphite surface or that feature D corresponds to the onset of molecules being promoted to a second layer.

While earlier adsorption studies^{26, 213} reported substeps in the monolayer regime, the results presented here track the evolution of these features as a function of temperature and coverage through monolayer completion and beyond. This includes evidence that these substep features are present at the onset and within the second acetylene layer. However, the present study is focused on developing a more detailed understanding of the monolayer regime and a discussion of these bilayer features will be left to a future publication.

The data plotted in Figure 3.3 correspond to the location of the peak in the numerical derivatives associated with each of the adsorption features (A-D) discussed above. These data are analyzed following the formalism introduced by Larher⁹, which employs a Clausius-Clapeyron analysis utilizing linear fits of the natural logarithm of the pressure values plotted against the inverse isotherm temperature (found in Figure 3.3), :

$$\ln(p_f^{(n)}) = B^{(n)} - \frac{A^{(n)}}{T} \quad (3.1)$$

The thermodynamic values summarized in Table 3.1 and depicted in equation (1) include both the differential enthalpy, $\Delta H^{(n)}$, and entropy, $\Delta S^{(n)}$, and the heat of adsorption, $Q_{ads}^{(n)}$, where the slope, $A^{(n)}$, and y-intercept, $B^{(n)}$, represent fits determined for each of the nth adsorbed layers. The differential enthalpy ($\Delta H^{(n)}$) and entropy ($\Delta S^{(n)}$) are calculated relative to the bulk acetylene ($n = \infty$) values. These relationships are given in equations (2) through (4) below:

$$\Delta H^{(n)} = -R(A^{(n)} - A^{(\infty)}) \quad (3.2)$$

$$\Delta S^{(n)} = -R(B^{(n)} - B^{(\infty)}) \quad (3.3)$$

$$Q_{ads}^{(n)} = RA^{(n)} \quad (3.4)$$

The values summarized in Table 3.1 illustrate that film thermodynamics primarily are characterized by positive values of the differential enthalpy and entropy, indicating the processes are entropically driven and likely partially disordered. Some notable exceptions to this trend are associated with the B', C₁, and C₂ features. It appears that these transformations evolve from high energy and disordered structures at lower temperature, to a lower energy, more ordered phase at higher temperature. Interestingly, bulk acetylene undergoes a solid-solid phase

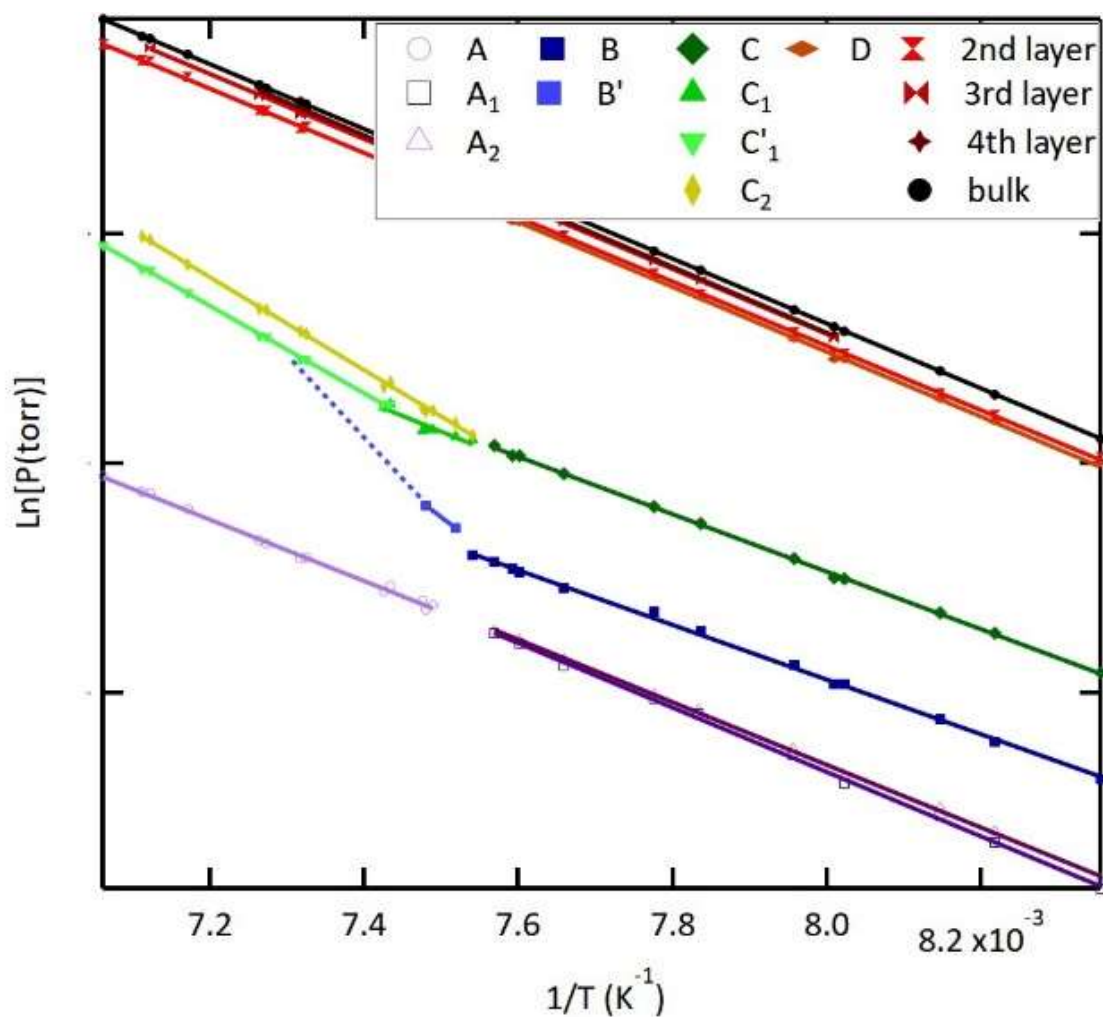


Figure 3.3: Clausius-Clapeyron plot for acetylene on graphite

Clausius-Clapeyron plot of different phases whose positions were obtained from the maxima present in the numerical derivative. Numerical results are found in Table 1. Note, the phase demarcated as B' was only fully resolvable at two temperatures, and the dashed line is a projection based on other empirical data.

transition at 133 K from a low energy, disordered orthorhombic phase at low temperature, to a high energy, disordered cubic phase at high temperature^{196-198, 208}. Interaction of the film with the substrate is known to modify the bulk behavior and is likely related to the behavior recorded here, especially when one considers that the solid-solid transition in the bulk occurs at approximately the same temperature as the transitions observed in these isotherm measurements. Hence, the magnitude of the intermolecular quadrupole-quadrupole interactions relative to molecule-surface interactions is the most likely explanation of this behavior.

The isosteric heat of adsorption is defined as the amount of energy required to move a molecule from the gas phase into the surface film at constant coverage:

$$Q_{st} = RT^2 \left(\frac{\partial \ln(p_f)}{\partial T} \right)_\theta \cong RT^2 \left(\frac{\Delta \ln(p_f)}{\Delta T} \right)_\theta \quad (3.6)$$

The numerical derivative versus temperature between two isotherms closely spaced in T can be used to approximate the value for $Q_{st}(T_{avg})$, where T_{avg} is the average of the two isotherm temperatures used to calculate Q_{st} . Figure 3.4 displays the isosteric heats for several temperatures between 122K and 142K. The NIST Webbook¹⁹² lists both 22.1 and 23.5 kJ/mole for bulk molar heat of acetylene at 130 K. The isosteres shown in Figure 3.4 converge towards the bulk values at higher coverage. Peaks in the isosteric heats indicate that adsorption is energetically favorable at those points. One prominent feature in the isosteric heat traces is the large, broad peak located near $\theta \sim 1$ at temperatures < 132.5 K. This is the region where the isotherm plateaus between steps C and D, corresponding to a surface coverage where a commensurate $\sqrt{3} \times \sqrt{3}$ R30° phase would form. The behavior of isotherm feature C suggests that the film may undergo a continuous transition to a commensurate hexagonal structure if the molecular axes are no longer parallel to the graphite basal plane.

In the Henry's law (low coverage) regime, the molecule interaction with the surface plays a dominant role. The binding energy of an isolated molecule to the graphite surface is Q^0 , i.e. the heat of adsorption in the zero coverage limit. The Henry's law constant $K(T)$ is given by:

$$K(T) = K^* \exp \left(\frac{Q^0}{RT} \right) \quad (3.6)$$

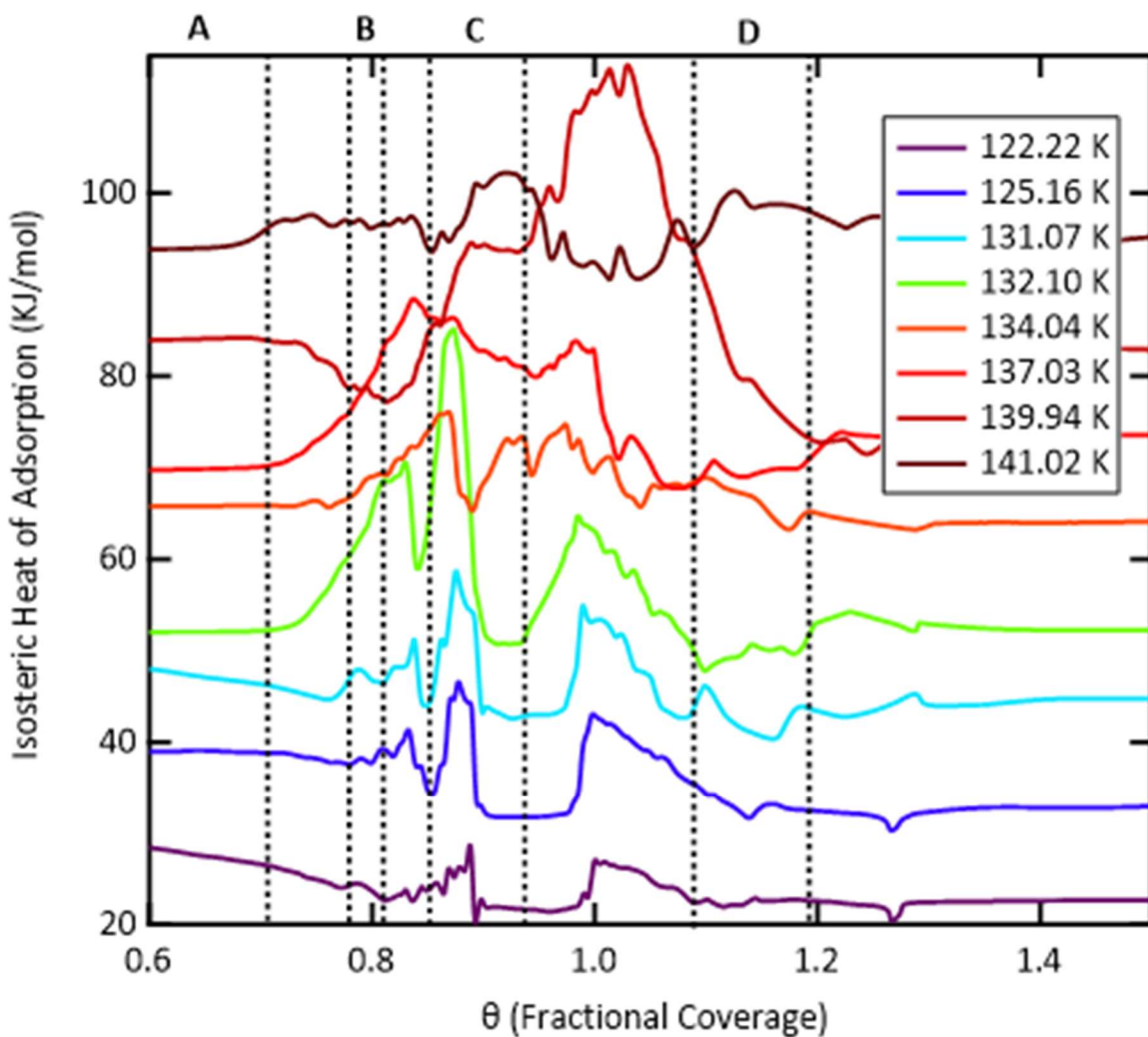


Figure 3.4: Isosteres of acetylene on graphite

Isosteric heats of adsorption over the monolayer range. The plots are offset vertically by 10 units for clarity. Vertical lines mark upper and lower bounds of each adsorption step

where K^* is a constant of integration, R is the gas constant, T the isotherm temperature and, as noted above, Q^0 is the heat of adsorption in the zero-coverage limit. See supplementary information for results of this analysis.

The 2D isotherm compressibility (K_{2D}) given in equation (3.7) can be used to better understand the nature of the phase behavior and transitions of the adsorbed film:

$$K_{2D} = \frac{A \cdot p_f}{N_A \cdot k_B \cdot T \cdot n_{ads}^2} \cdot \frac{\Delta n_{ads}}{\Delta p_f} \quad (3.7)$$

where A is the surface area of the substrate, p_f is the vapor pressure, N_A is Avogadro's number, k_B is Boltzmann's constant, T is the temperature in Kelvin, n_{ads} is the moles adsorbed, and $\Delta n_{ads}/\Delta p_f$ is the numerical derivative of the isotherm. Figure 3.5 shows a plot of the K_{2D} for each of the observed monolayer features (steps and substeps) as a function of temperature. Remarkably, the K_{2D} -associated step A exhibits a sharp increase in intensity at 132.63 K. Such behavior would be consistent with being at or near a first order transition phase where compressibility should theoretically be infinite.

Additional analysis of K_{2D} was performed by examining the functional form and changes in the width of the compressibility peaks as a function of temperature. The comprehensive results are summarized in the supplementary data, however, Figure 3.6 shows the behavior of the widths of the numeric derivative peak of Step A as a function of temperature. The derivative was used instead of the K_{2D} function in this case because it enabled better fitting of the subtle features and K_{2D} is proportional to the slope of the isotherms

In earlier studies, we have used the temperature dependence of K_{2D} peak widths to identify where possible phase transitions occur. For the A step, for example, both A_1 and A_2 exhibit abrupt changes in slope at 133 K, while A_1 also shows a change in slope at 126 K. The supplementary data displays the temperature dependence of features B, C, and D. Step B exhibits both a discontinuity at 126 K and a change of slope at 132 K. The C step and its corresponding substeps show a much greater deal of complexity. With increasing temperature, the first change occurs at 132.5 K, where C_2 shows a discontinuity with an increase in the FWHM, and where C_1 continues along the same line as before. Then at 134.5 K, both C_1 and C_2 go through another discontinuity point, where the value for C_1 increases and C_2 simultaneously decreases. From there, the C_1 FWHM decreases with temperature while C_2 stays relatively constant. Then at 140.7, the FWHM of C_2 sharply increases, joining with the C_1 line into a single peak. For step D,

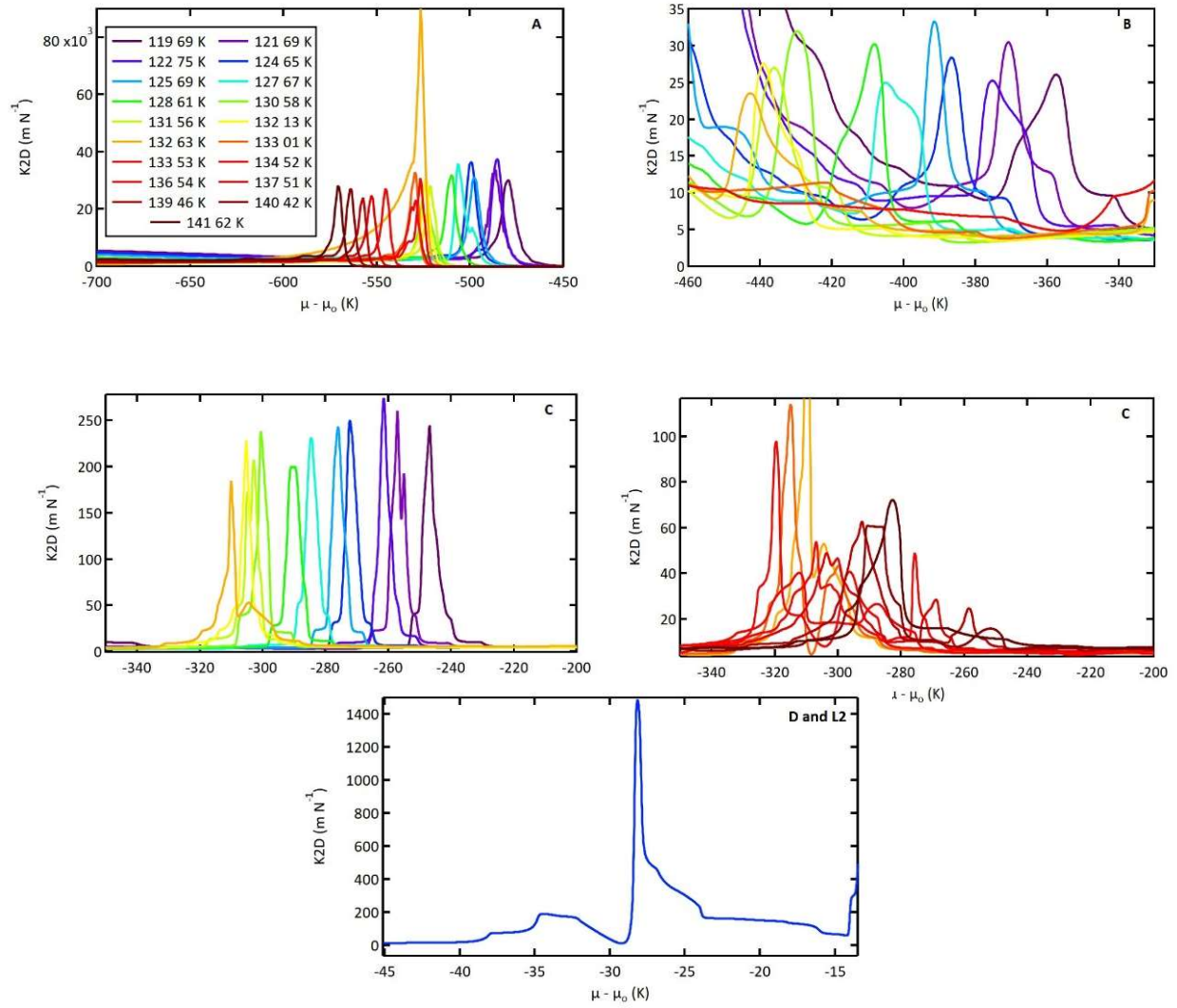


Figure 3.5: Two-dimensional compressibilities for acetylene on graphite

The K_{2D} peaks corresponding to steps A through D with C sub-step and the second layer peak (L2). D and L2 are shown at 124.65 K only due to overlap of different temperatures

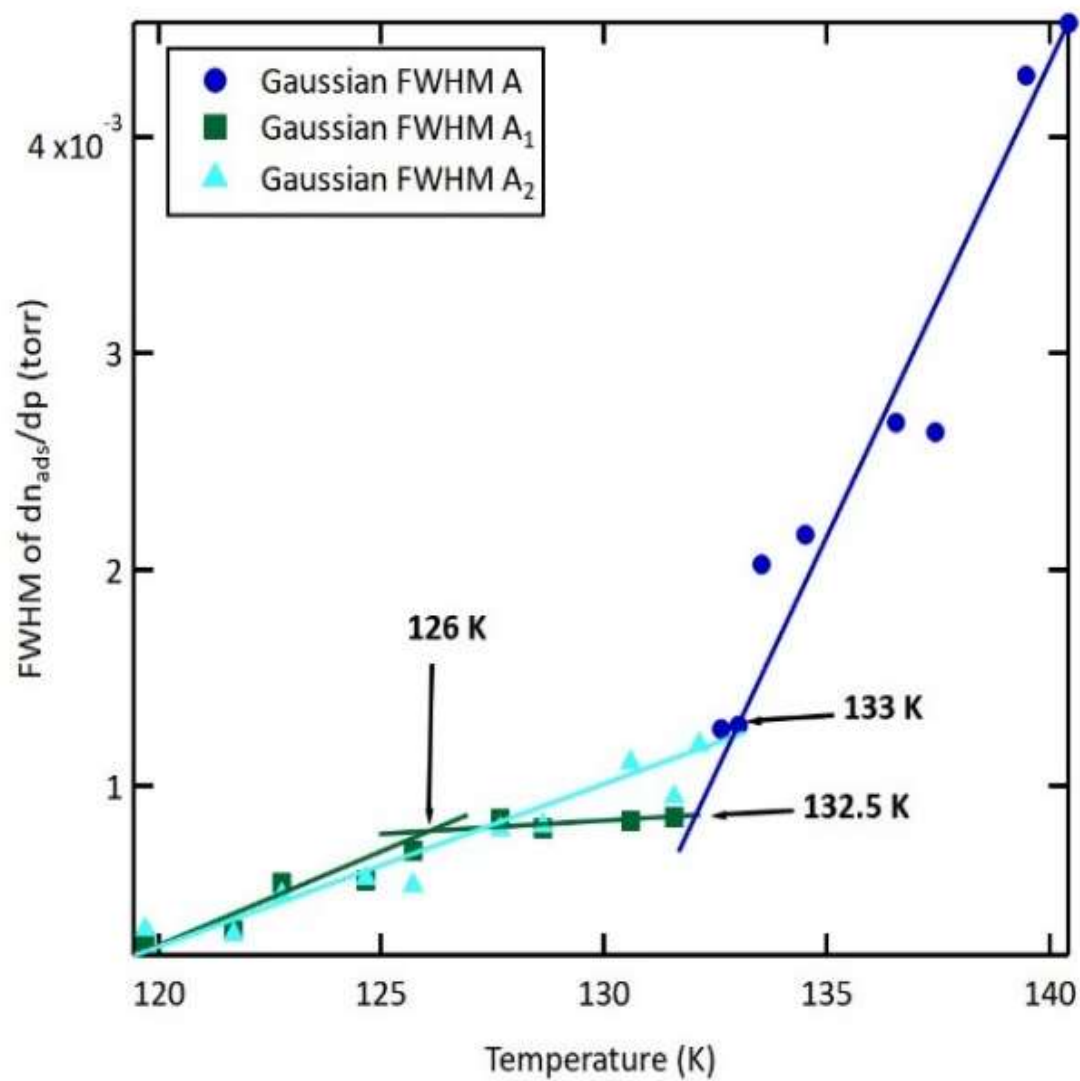


Figure 3.6: Plot of FWHM analysis for first isotherm step for acetylene on graphite
*Plots of FWHM values for the first monolayer step (A) with secondary features.
 Temperatures of possible phase changes are labeled*

the peaks were the most challenging to fit and have the largest degree of error, but a change seems to occur there as well, with notable features at 126 K and 130 K. To attach meaning to these observations and put them into a greater context, a proposed phase diagram will be discussed later in this report.

3.4.2 – Computational Modeling

3.4.2.1 – Single Molecule Energy Minimizations

To examine how the graphite surface influences the behavior of an isolated adsorbed acetylene molecule, a geometry optimization was performed using Accelrys Materials Studio 6.0. Acetylene is a challenge to simulate accurately, in large part due to limitations in computational models that appropriately reflect its large quadrupole moment^{107, 210, 211, 228}. This is primarily due to the difficulty of accurately describing the quadrupole interaction of a small molecule using only 4-point charges located at the centers of the atomic nuclei. The addition of a fifth point charge located at the center of mass of the molecule improves these models, but the functionality of the version of Forcite used here can only place point charges on atomic centers. In these simulations, the values of the point charges assigned by the COMPASS forcefield were $\pm 0.223 e^-$, with the positive poles placed on the hydrogen atoms. These point charge values are considerably lower than the more accurate point charge models in the literature, with charges around $\pm 0.3 e^-$.

One complication that arose in these calculations is in treating the electrostatic interaction energies. The Accelrys software does not allow for the exclusion of intramolecular 1-4 atom-atom interactions. Hence, the positive charges located at the hydrogen atom positions lead to a large, positive electrostatic energy term. Although this does not affect the minimized positions of the molecule relative to the graphite surface, the effect on the energy values had to be subtracted for meaningful interpretation of the binding energies. This was addressed by removing the surface from the simulated space after optimization and performing an energy calculation on the molecule that remained in the absence of the surface binding interactions. The binding energies could then be calculated:

$$E_{binding} = E_{non-bond} - E_{molecule\ non-bond} \quad (3.8)$$

where E_n is the energy of the corresponding interaction term.

These results (see Figure 3.7) show a remarkable agreement with the Henry's law analysis value of 21 kJ mol⁻¹. Furthermore, the difference between the lowest and highest binding energies from these calculations is 0.213 kJ mol⁻¹, consistent with the expectation of the strength of the intermolecular interactions and the molecule-surface interactions.

3.4.2.2 – Molecular Dynamics

Using the Accelrys Materials Studio Forcite package, MDs were used to model the microscopic behavior of the acetylene films on graphite as a function of temperature and surface densities. In terms of fractional surface coverage, θ , between $0.25 \leq \theta < 1.25$, $\theta = 1.0$ corresponds to a commensurate $\sqrt{3} \times \sqrt{3}R30^\circ$ monolayer. While quantitatively precise descriptions of the energetics and thermodynamic quantities require additional microscopic data, the MD simulations presented serve as a guide for understanding the trends in the adsorption properties and in the analysis of neutron scattering investigations of the microscopic structure and dynamics of the films.

First, to elucidate the microscopic behavior, creating a movie composed from a set of sequential MD time snapshots of the molecular trajectories as a function of temperature and fixed surface coverage is a good starting point. Next, using the molecular centers of mass (CoM), the 2D radial distribution functions (2D RDF) can be evaluated. In contrast to the 3D RDF, the 2D RDF is normalized over a circular surface element such that:

$$g(r)_{2D} = \frac{1}{2\pi r \rho_{2D}} \times \frac{dn_r}{dr} \quad (3.9)$$

where ρ_{2D} is the areal number density of the molecules and dn_r is the number of molecules in a circular shell between radii of r and $r + dr$. Additionally, molecular concentration profiles normal to the surface plane, labelled $C(z)$, are used to quantify the orientation and vertical distribution of molecules within the film. $C(z)$ is particularly useful for determining if increases in surface density drive changes in the molecular orientation relative to the surface plane or the vertical displacement of molecules (i.e. layer promotion or film roughening). These analyses are also used to identify solid and liquid structural features and/or the location of phase changes such as commensurate and incommensurate, order-disorder transitions, melting, etc.

The identification of the long-range ordered solid and local structures the molecules are likely to adopt is another important piece of information that can be obtained from the MD simulations. In the absence of a substrate, the acetylene quadrupole-quadrupole interaction

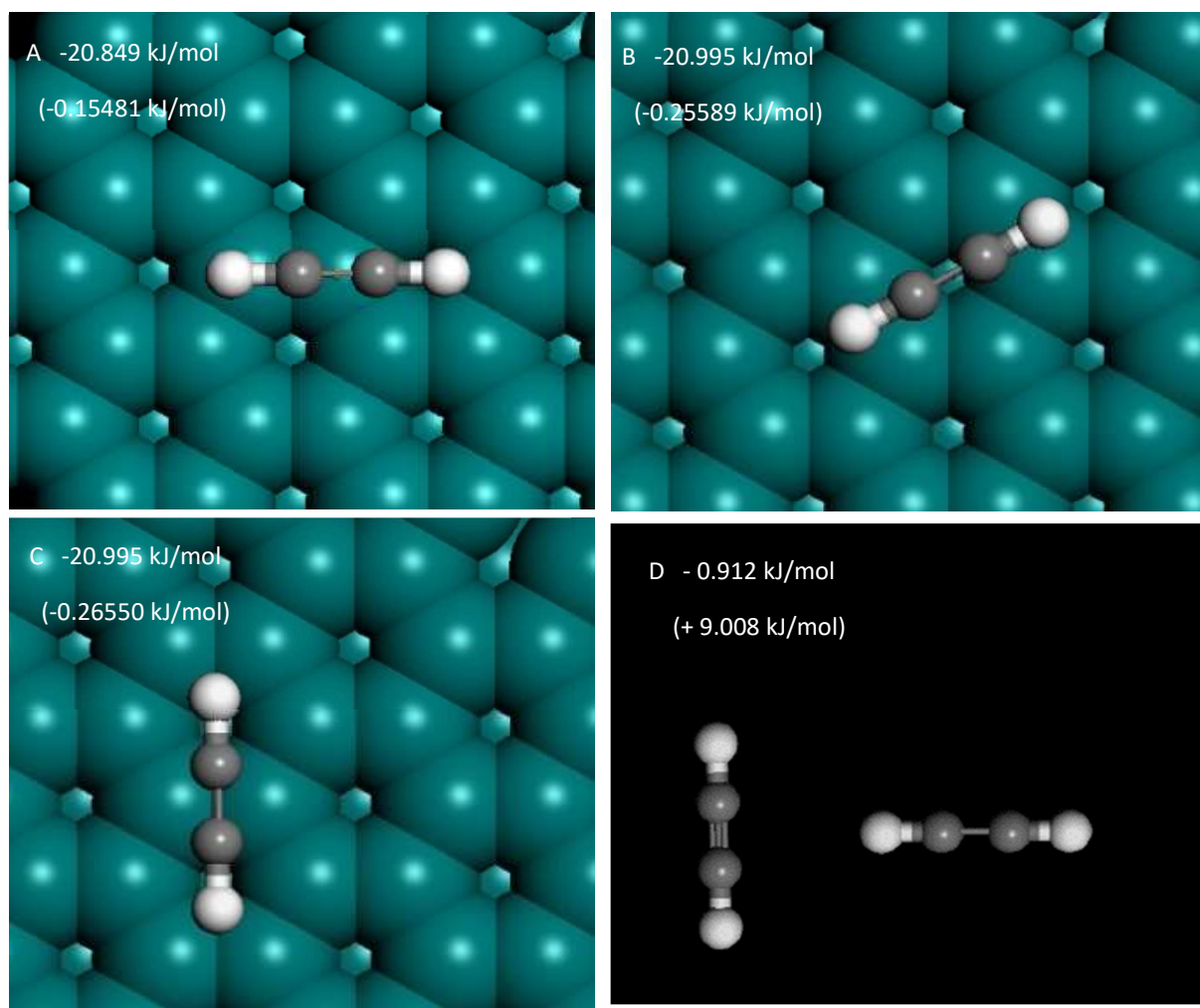


Figure 3.7: minimum energy configurations for acetylene on graphite

The most optimized energy configuration angle and binding energies for each high symmetry site A) on carbon atom, B) on hollow, and C) on $\text{C}=\text{C}$ bond. and also D) The optimized angle for two interacting acetylene molecules and their interaction energy. (original, unsubtracted binding energies are in parenthesis for comparison)

would favor the formation of a square-T lattice structure for a 2D film. However, as in the case of monolayer nitrogen films on graphite, the six-fold graphite surface potential would tend to favor the formation of a hexagonal herringbone arrangement. It is reasonable to assume that there will be situations where, depending on the surface density and temperature, some expression of both of these lattice structures will be present. Figure 3.8 shows a centered rectangular unit-cell along with calculated RDF for the centered rectangular lattice having theta values between 90° (square lattice) and 120° (hexagonal). This simple model offers a more rigorous method of using RDFs to analyze the structure from numerous simulation trajectories quickly. RDFs have an advantage over visual analysis in regards to analyzing structure and order in that they provide the time average of all the molecules in the simulation over the entire time window. To further improve the quality of the analysis, the structures can be analyzed at 5K to limit thermal disorder contributions.

Using the standard parameters assigned by the COMPASS forcefield, only a herringbone ordered phase was observed, regardless of coverage. To enhance the accuracy of these simulations, point charges corresponding to stronger quadrupole moments were examined. Shown here is the set with point charges of $\pm 0.298 e^-$, which best match observed experimental behavior. A comparison of the forcefield assigned charges versus the modified charges is located in the supplementary information.

The first set of these simulations span coverages within the range of the A and B steps from the isotherms ($0 < \Theta < 0.85$), the range of the S_1 phase in previous neutron experiments^{213, 216, 225}. RDF and concentration profile results at 5 K are shown in Figure 3.9. The supplementary information contains further RDF and $C(z)$ results at multiple temperatures for each coverage, along with accompanying simulation snapshots. These results show a tendency for the film to form the square-T configuration. *For all coverages examined in this range, structural defects are a prominent part of film structures.* In addition to the quadrupole's optimal square-T configuration, 3, 5, and 6 molecule pinwheel structures are also observable. In the latter case having a molecule in its center that is highly tilted relative to the surface plane. This can be seen in the simulation snapshots, the effect of which is further demonstrated in the nearest-neighbor coordination numbers from the RDFs, which fall between 2.8 and 3.5. For the simulations corresponding to the lower half of the A step ($\Theta = 0.26, 0.33$), formation of triangular pinwheel

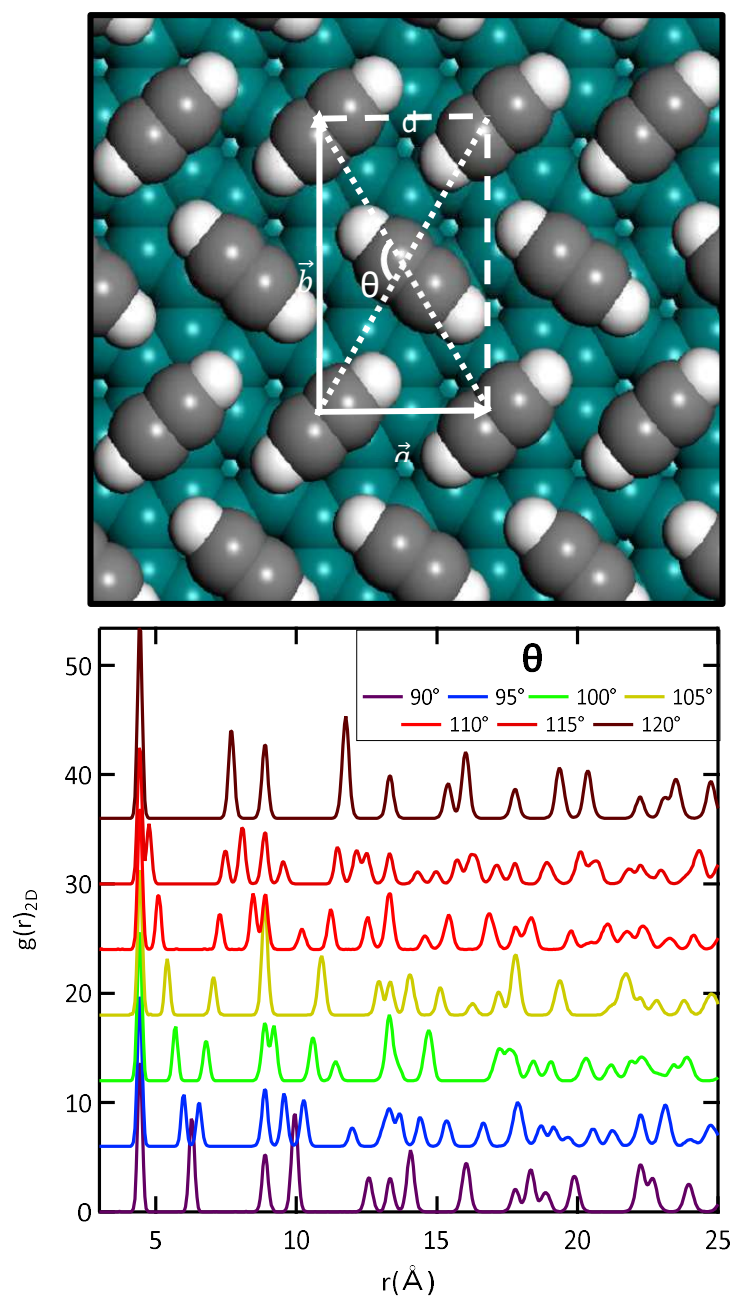


Figure 3.8:Radial distribution functions for various types of rectangular lattices.

(Top) generic face-centered lattice template assumed as a starting point model for structural analysis. (Bottom) Calculated radial distribution functions for the centers of mass for different possible lattices based on this model, and the nearest neighbor peak position based on simulation result.

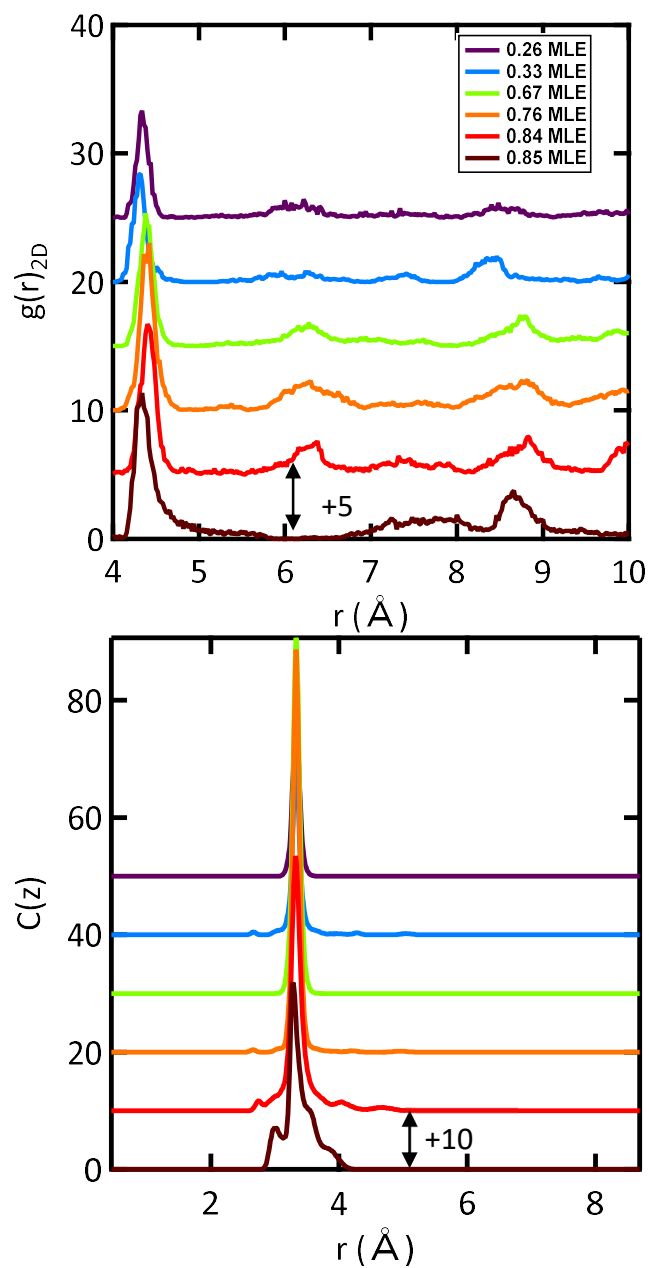


Figure 3.9: Low coverage RDFs and concentration profiles
(top) COM 2D RDF and (bottom let) concentration profiles for simulated coverage ranges of the S1 phase at 5 K, vertically spaced for clarity.

structures is the dominant structural motifs. Furthermore, trajectories show molecules in this regime are orientationally dynamic even at low temperatures, with local structure in constant rearrangement. Corresponding to the region at the top of the first monolayer step are $\Theta = 0.67$, 0.76 . Here a definite favoritism for the square-T arrangement emerges. The transition to solid behavior and the emergence of long-range order also begins is 30 degrees warmer than at lower coverages. At $\Theta = 0.84$, the square lattice is still present, however, the molecules have adopted a twisted-T shape, several degrees off from the ideal right angle. Following this, at $\Theta = 0.85$, though marginally different in coverage, falls with the lowest portion of substep C. Here, the preferred square symmetry of the lattice is broken, becoming a face-centered rectangular lattice, with a herringbone molecular configuration, and the molecules tilted away from the surface.

Results for four higher coverages are shown in figure 3.10 that cover from the completion of substep C up through substep D. The overall pattern here is in favor of a FCR herringbone lattice. For $\Theta = 0.95$, 1.01 , and 1.38 , the film lattice has a $\sqrt{3} \times \sqrt{3}$ $R30^\circ$ commensurability with the surface. Concentration profiles demonstrate that the molecules are tilted away from the surface. The sharpness of the second peak relative to the others indicates that during libration of molecules relative to the surface, the pivot point of the molecule lies at or near the carbon atom closest to the surface, and not at the molecule center of mass. Interestingly, however, $\Theta = 1.05$, does not form a perfect FCR lattice, most easily observable in the splitting of the primary coordination peak in the RDF. This splitting is the result of a distortion to the FCR structure, which has become an oblique lattice with an angle of 88° . The symmetry breaking in the lattice structure would explain previously observed diffraction patterns at this coverage for the so called S_{12} state, previously believed to be a mixture of the other two observed solid phases S_1 and S_2 ^{215, 216}. This distorted phase is likely the result of increased strain in the film structure because of increasing density. Furthermore, the reentrant behavior of the FCR phase occurs as a second monolayer begins to form (as seen in $C(z)$), indicating a stabilizing effect caused by this second layer.

While these simulations do elicit behaviors that would explain other observed experimental phenomena, they do fall short in a few key points. Firstly, the diffraction pattern for a twisted-T shaped lattice seen at $\Theta = 0.84$ is not currently seen in the diffraction experiments around this coverage. It might be in this case that if the angle of the twist is small enough, it would be difficult to distinguish from the square-T case²¹³. Secondly, the commensurate

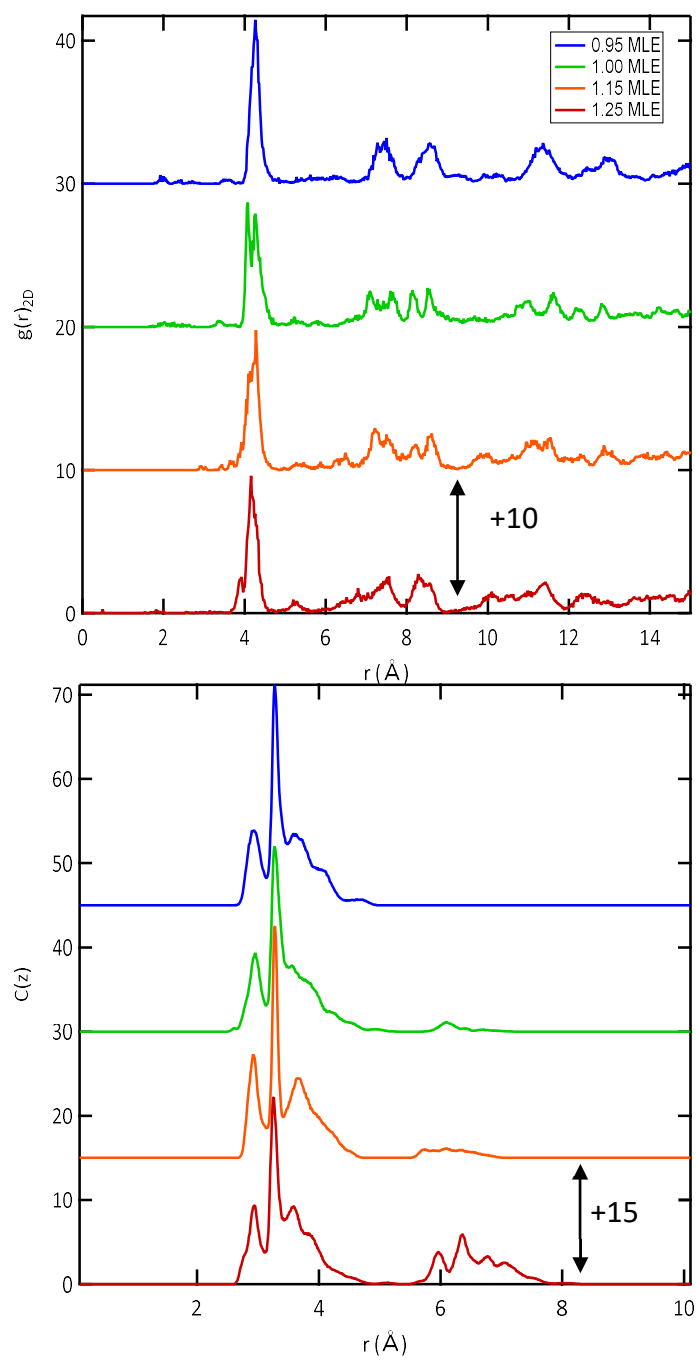


Figure 3.10: High coverage RDF and concentration profiles
(top) COM 2D RDF and (bottom left) concentration profiles for simulated coverage ranges of the S2 phase at 5 K, vertically spaced for clarity.

structures seen at higher coverages are not fully in agreement with diffraction experiments either^{213, 216}; however, this also could be due to the limited scope of previous experiments not covering those temperature ranges. Increasing the quadrupole strength did elicit very similar behavior, with two notable distinctions. The films were all much more disordered, the oblique phase occurs at 5% less coverage. Additionally, it is likely that a simple point charge system for describing acetylene's quadrupole distribution is insufficient for accurate simulations^{52, 95, 107}.

3.4.3 – Neutron Diffraction

Neutron diffraction data were recorded at $\theta = 0.7$, over the temperature range of 10K to 165K. A more closely spaced set of traces were recorded between 124K to 138K.

As in the past, analysis of these diffraction profiles was performed using a 2D line-shape formalism, but modified to employ an iterative least-squares algorithm similar to the Rietveld refinement process. This includes the simultaneous fitting of both liquid and solid phases. While the refinement of two phases simultaneously can be problematic, the pure solid and liquid phase structures were refined first. It was found that a Lorentzian squared function provided the best description of the lineshapes. We note that Halperin and Nelson^{84, 87} suggested utilizing a Lorentzian lineshape. Warren's original lineshape formulation³² has been used on adsorbed systems in previous works²²⁹. Lorentzian line shapes have also been used in the past with excellent agreement to observed data⁸⁶

The diffraction results can be divided into three sections. Below 124 K, the diffraction data shows a mixture of a solid phase with a diffuse, weakly disordered background. Above 135 K, only a liquid-like diffraction profile is recorded. Between 127 K and 132 K, a coexistence of both liquid and solid phases is observed (see figure 3.11).

Figure 3.12 shows the fit to the diffraction pattern at 10 K. The lineshape results from a "square T" configuration with two molecules per unit cell and a lattice constant of 6.1339 Å. We note that the quality of the lineshape fit to the solid phase at 10K is excellent. A compilation of the fit parameters used to describe the diffraction data can be found in Table 3.2. A more detailed description of the liquid phase region can be found in the supplementary information. It is worth noting that the diffraction patterns associated with the liquid phase indicate that the d-spacing is 4.26 Å in the (11) direction, suggesting that the molecules form a lattice-like liquid (i.e. a partially commensurate structure in that direction). Furthermore, the molecule orientations

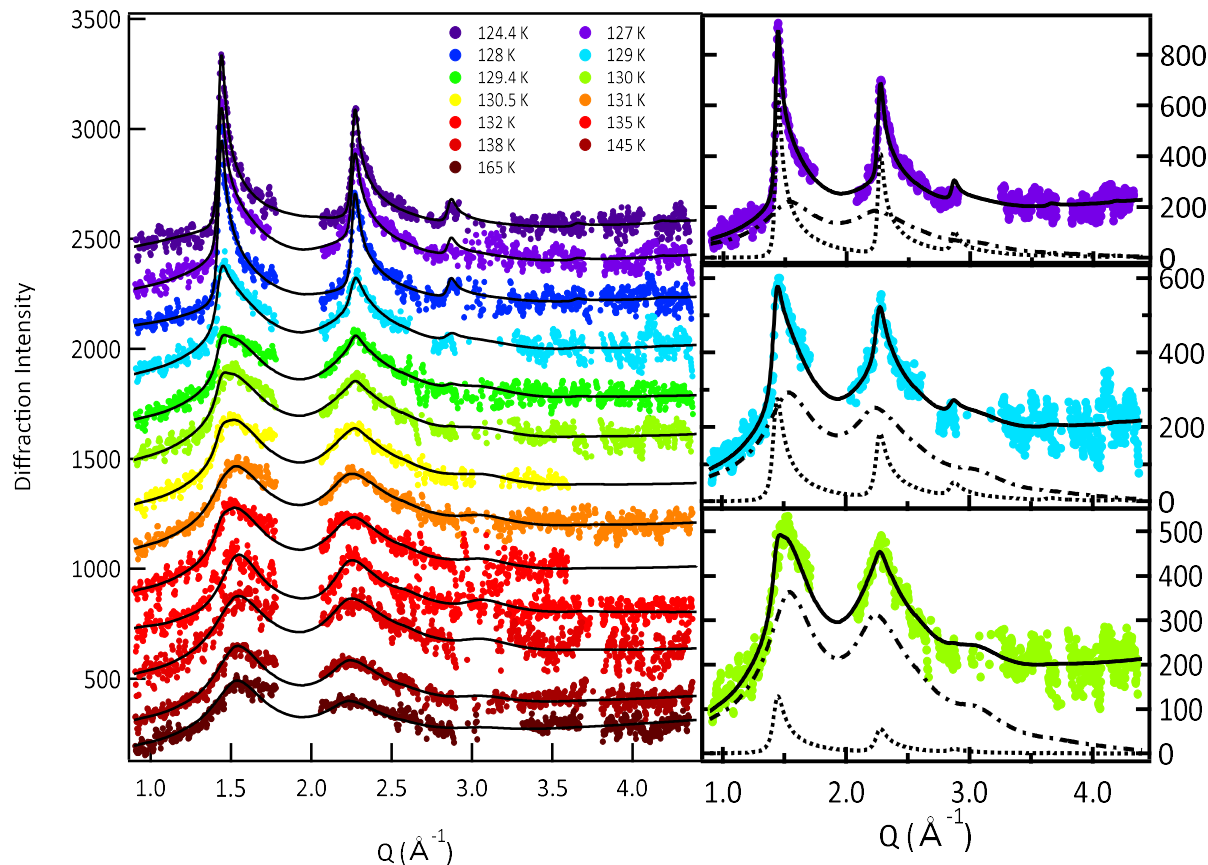


Figure 3.11: Two phase neutron diffraction fits for the solid-liquid coexistence region for acetylene on graphite

(left) Neutron diffraction data and fits for spanning the melting transition range; (right) selected temperatures showing the evolution of the melting process at 127 K (top), 129 K (middle) and 130 K (bottom). The solid line represents the diffraction fit results and the dotted and dot-dashed lines are the individual solid and liquid structural components, respectively.

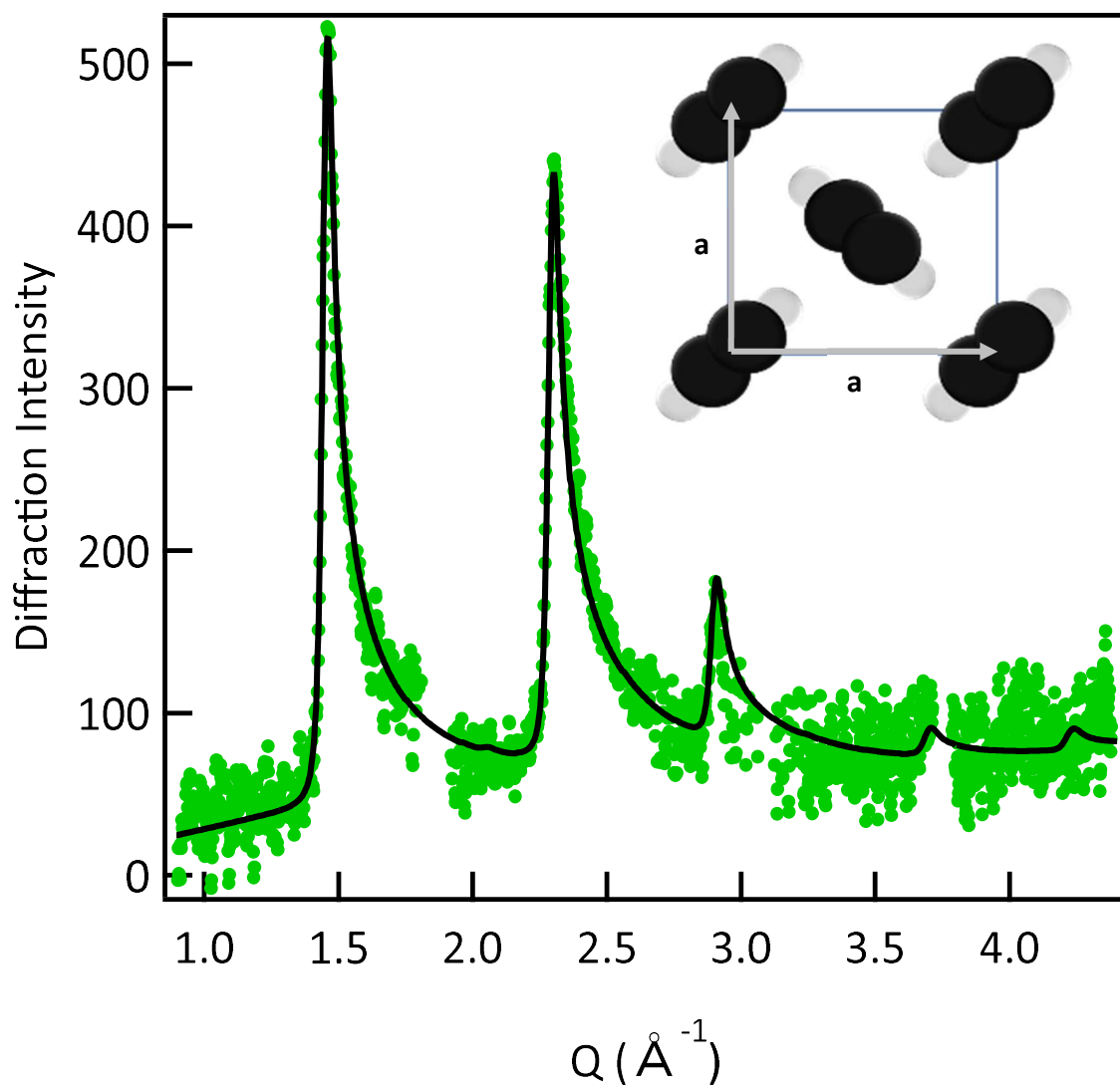


Figure 3.12: Neutron diffraction data and fit profile at 10 K for 0.7 MLE coverage

Table 3.2: Summary of diffraction fitting for solid phase (10 K to 124 K) and liquid phase (> 135 K).

Temp (K)	$Q_{hk} (\text{\AA}^{-1})$	$ \vec{a} (\text{\AA})$	$ \vec{b} (\text{\AA})$	$\gamma (^{\circ})$	Molecules Per Unit Cell	Area Per Molecule ($\text{\AA}^2$)	Molecule Positions			
							X	Y	Z	ϕ
10 K	(11): 1.4594 (21): 2.3033 (22): 2.9054	6.1339	6.1339	90	2	18.8124	0 3.067	0 3.067	0 0	45° -45°
99 K	(11): 1.442 (21): 2.2716 (22): 2.8746*	6.2070	6.2070	90	2	19.2634	0 3.104	0 3.104	0 0	45° -45°
124 K	(11): 1.4387 (21): 2.755 (22): 2.8746	6.2127	6.2127	90	2	19.2988	0 3.106	0 3.106	0 0	45° -45°
135 K	(11): 1.539 (21): 2.2573 (20): 3.0598*	5.2381	6.7195	90	2	17.599	0 2.619	0 3.360	0 0	51° -34°

Reflection not visible in diffraction data due to graphite scattering background

result in a nearly perpendicular T configuration, similar to the solid phase, but only along the diagonal axis of the unit cell. This recommends that the melting is approximately uniaxial, as the intermolecular quadrupolar interaction attempts to maintain the preferred “T” orientation while the surface corrugation influences the intermolecular separation (i.e. $4.26\text{\AA}$). The liquid phase is nearly 10% more dense than the solid phase, a density consistent with the C_1 substep in the isotherm data.

Between 99 K and 124 K, the lattice constant of the solid phase change is only 0.1%. There is no discernable change in the lattice constant for the disordered phase between 135 K and 165 K. To simplify the refinement process, between 127 K and 132 K, the diffraction patterns were fit using structures where the lattice parameters were fixed at constant values from the refinement of the solid and liquid phases. At 135 K, no evidence of a solid phase was present. Figure 3.11 shows the results of these refinements.

The temperature dependence of coherence length and mean squared displacement as a function of temperature is available in the supplementary information. The coherence length values used to fit the diffraction lineshapes were analyzed using the formalism described elsewhere^{84, 87}. The temperature dependence of the coherence length agrees well with the model where the melting point is ~ 126 K, further in agreement with the 126 K isotherm results. The mean squared displacement (MSD) for the solid phase component of the fits remains relatively constant below 129.4 K, above which it sharply increases. As expected, the mean squared displacement for the liquid phase remains constant over the entire range, and at > 129.4 K, distinctly less than the solid phase component fits.

The temperature dependence of the coherence length and the MSD suggests that spatial order is lost first, followed by an increase in the translational diffusion. If it is assumed that the increased mobility would correlate to a weakening of orientational ordering as well, then this trend aligns with predictions made by KTHNY theory indicating a possibility of tetratic phase-like behavior⁸⁷, also hinted at in the simulation results. However, the applicability of KTHNY remains questionable because of the first order transition to the liquid state occurring at 132.5 K. It seems plausible that the disruption of the solid phase may occur following a defect propagation process as described by KTHNY theory, as suggested by the neutron data and simulation results. However, this disruption does not lead to the growth of an isotropic liquid phase as predicted by

this theory, but a bond-ordered rectangular liquid phase. The structure of this liquid phase suggests two possible contributing factors to this preservation of order. First, the molecules along one diagonal axis retain a nearly perpendicular T-configuration. Second, the intermolecular spacing along this same diagonal suggests a uniaxially commensurate relationship with the surface. It seems likely that the retention of local organized local structure in the liquid phase is mediated both by the strong molecule-molecule interactions along with influences of the molecule-surface interactions. That being said, the dynamics of this melting process are clearly complex and warrant a more exhaustive investigation which is beyond the scope of the current study.

Finally, Figure 3.13 illustrates the correlation of the diffraction data and isotherm substep region at 0.67 MLE between ~ 120 K and 160 K. The curve shows how the integrated diffraction intensity between $Q = 1.31$ and $1.63 \text{ \AA}^{-1}$ behaves as a function of temperature. A large decrease in intensity occurs around 133 K, matching the observed sharp transition in the isotherm data. The smaller drop in intensity at ~ 126 K correlates with the secondary feature within the first step described previously.

3.4.4 – Phase Diagram

Based upon the adsorption isotherm results discussed above, a tentative phase diagram is shown in Figure 3.14. This diagram is consistent with the results reported in this work and those of previous investigations^{27, 107, 207, 213-217, 225}. Because no microscopic experimental data exists primarily in the region between the B and C substeps of the isotherm, the diagram remains incomplete.

A description of the various color-coded regions of Figure 3.14 follows. Region A is best described as a square-T phase (blue) with moderate long-range order, but a density based on the isotherms lower than that obtained from the diffraction fits. The diffuse background included in the diffraction fits for the solid phase at 124.4 K indicates that there is a reasonable amount of disorder, a fact that most likely explains the density difference. This phase undergoes a transition between 126 K and 133 K (blue-purple) as observed in diffraction measurements (see Figure 3.13). A first order transition occurs at ~ 132.5 K, above which a liquid phase with substantial bond ordering is observed (purple), most likely uniaxially commensurate with the graphite surface. These bond correlations in the liquid phase result from the strong quadrupole interactions, a

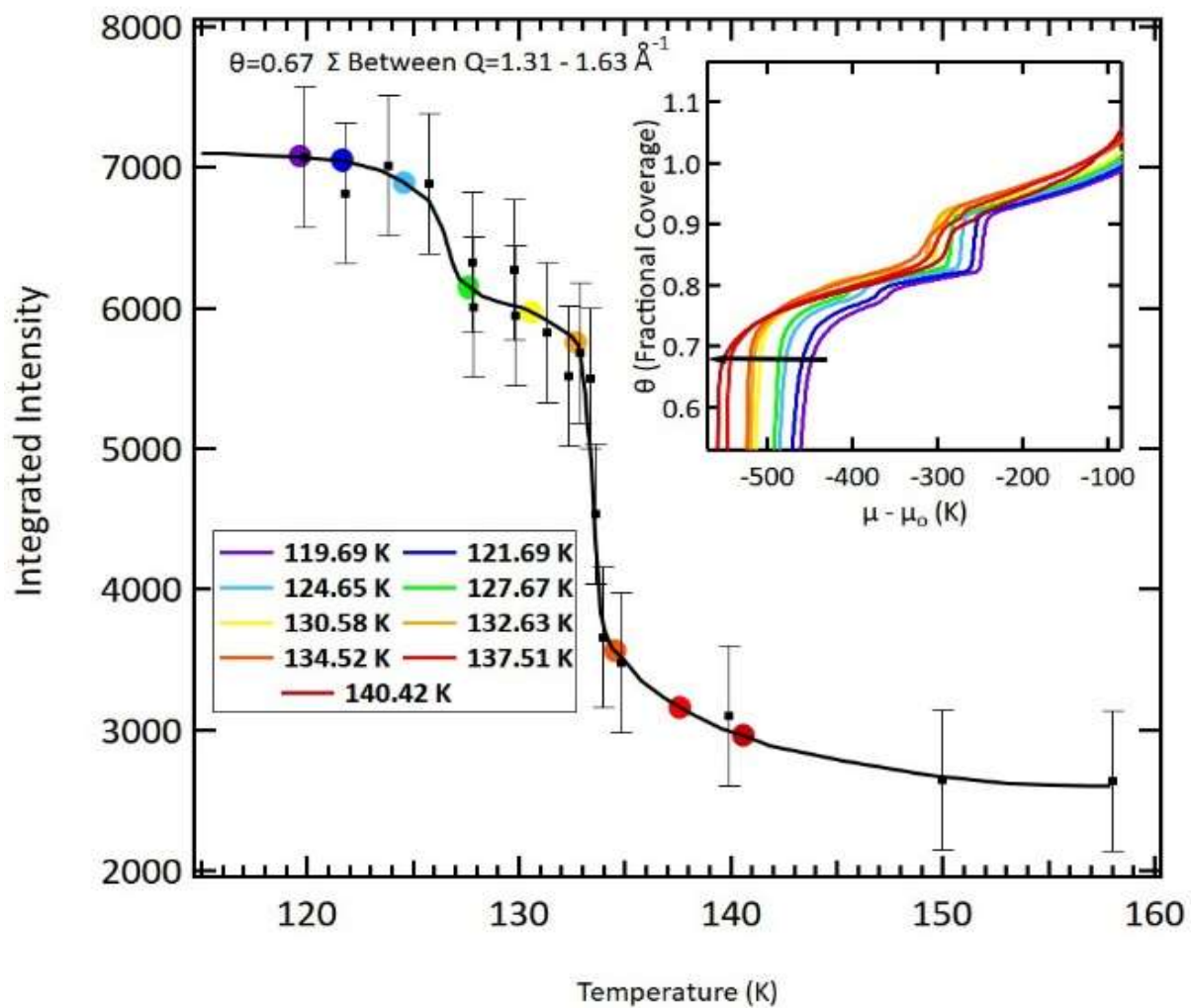


Figure 3.13: Integrated neutron intensity of most intense diffraction peak as a function of temperature

Neutron diffraction intensity versus temperature at 0.67 coverage showing two melting transitions: a continuous transition at 126 K and first order transition at 133 K.

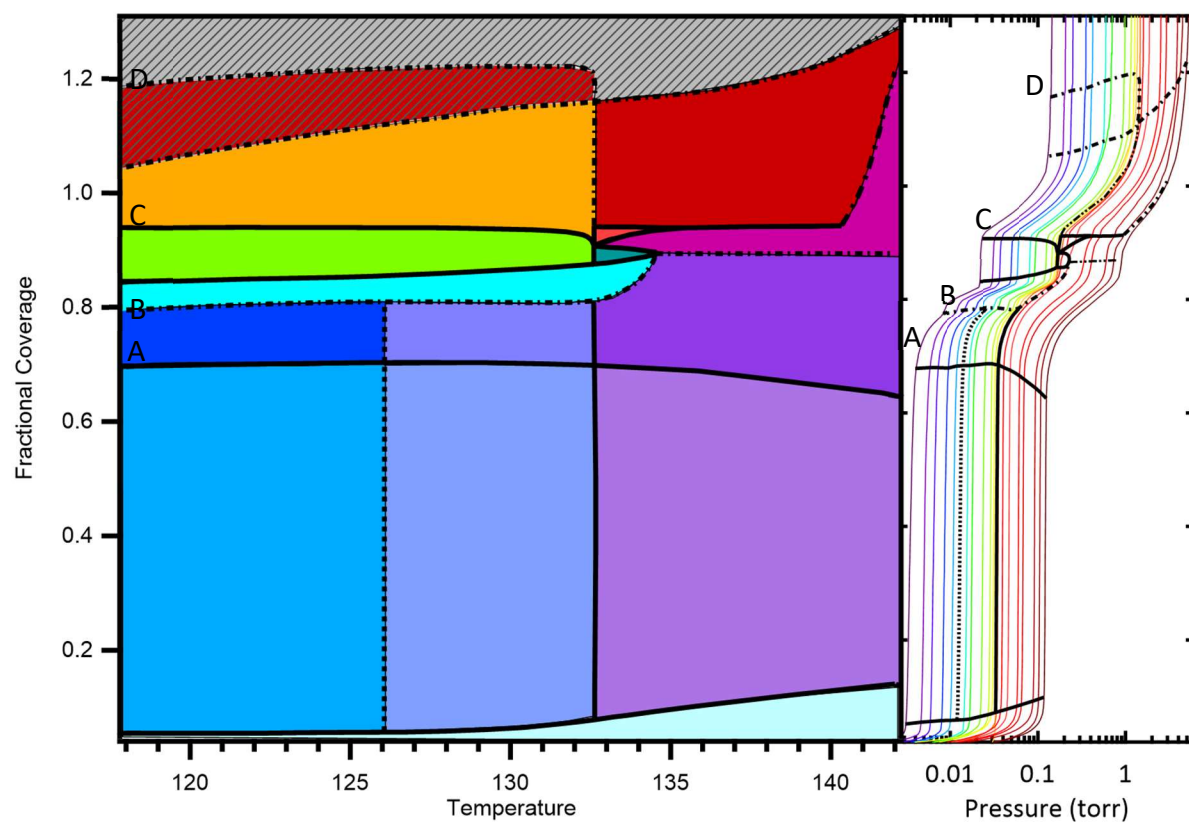


Figure 3.14: Proposed phase diagram for the acetylene on graphite system

Regions are labeled by corresponding isotherm step feature. Dashed line represents the beginning of continuous melting region, Solid lines are probable first order transitions, and dot-dashed are probably continuous transition. See text for color coded phase descriptions

finding consistent with the investigation by Bruch who indicated that total orientational disorder is not possible in a 2D system of quadrupoles⁵¹. The lighter shaded areas of each subsection of region A correspond to the 2D vapor-condensed phase coexistence areas of the first monolayer step.

Region B (turquoise) correlates well with the density of the solid structure observed in the diffraction data (Figure 12). Trabelsi et al. also record a diffraction pattern that indicates this phase (S_1) forms in this region as well; hence, the substep signals the formation of the completed “square-T” lattice. This phase may not undergo the same microscopic behavior at melting (i.e. near ~ 126 K) based on the isotherm behavior, but exhibits instead a (melting?) transition between 132.5 K and 134.5 K.

Below 132.5 K, Region C correlates with the S_{12} phase of the earlier neutron studies^{215, 216} Trabelsi et al. and Thorel et al. both attributed this to be a mixture of both the S_1 and S_2 phases from their studies. Their suggestion is inconsistent with the density of the phases reported in our isotherm data. Within 1%, S_{12} is nearly the same density as the S_2 phase; however, the square-T phase of S_1 is 15% less dense. An explanation consistent with the earlier neutron studies and the current isotherm and MD study is that the S_{12} phase is an oblique distortion of the S_2 structure with a 1 to 2 degree tilt of the lattice vectors (orange). S_1 and S_{12} are in coexistence during the corresponding isotherm step (light green).

Above 132 K, the phase diagram is less certain and more speculative. The lower sections (fractional coverage on phase diagram between 0.85 and 0.9) correspond to isotherm steps C_1 and C_1' . Their completion corresponds to observed densities that are a close match for the bond ordered liquid phase from diffraction data (Figure 3.11). The completion of the C_1 and C_1' substeps (magenta) may be associated with the bond order in the liquid phase. The B substep in the isotherms following the 132.5 K transition curves upwards and merges with the C_1 features at 134.5 K. The C_1 subsection (teal) is tentatively assumed to be the melting transition of the S_1 solid and the high-density bond ordered liquid phase.

Completion of the C_2 substep (red) appears to correspond to the S_2 solid phase region observed by Trabelsi et al. where melting was observed at 141 K at lower coverages (but not observed at higher coverage). The 141 K transition is observed in our isotherm data. Neutron diffraction data of Thorel et al. and Trabelsi et al. is consistent with a slightly incommensurate,

or uniaxially commensurate, rectangular herringbone structure which would also be consistent with S_{12} phase structure being an oblique distortion of the S_2 phase. The C_2 step itself (light red) is the coexistence between the S_2 and high-density bond ordered liquid phases.

Region D cannot be correlated to any features in the first layer with a density that is physically realistic. Thorel et al. and Trabelsi et al. both observed a reentrant appearance of the S_2 phase diffraction signal below 132.5 K. The D substep (red with gray stripes) likely corresponds to promotion of some molecules to the second layer that stabilize the S_2 structure at the expense of the S_{12} phase. The second layer region is identified using the striped gray coloration.

3.5 – Conclusions

The adsorption behavior of acetylene films on the graphite basal plane was examined between 119 K to 141 K using volumetric isotherms, MD modeling, and neutron diffraction. Detailed thermodynamic analysis of these isotherms provided quantitative values for the heat of adsorption and differential entropy and enthalpy for the monolayer and bilayer regime, including the locations and likely nature of several phase transitions. The isotherm investigation reveals multiple sub-steps within the monolayer regime that evolve with temperature. A prominent melting transition occurs at 132.5 K. A third substep in the monolayer region illustrates that the thin film properties of acetylene on graphite are complex. Here, several distinct phase transitions occur (as signaled by the substep feature behavior) over a fairly narrow temperature range.

Careful microscopic studies in the future would be required to understand this regime. Binding energy calculations and molecular dynamics simulations were performed using the COMPASS force field within the Accelrys Materials Studio software package. While this force field is known to be highly accurate in simulating the behavior of hydrocarbon molecules, acetylene is known to be difficult to model effectively. The simplicity of the 4 point-charge method for modeling a quadrupole interaction used by the Accelrys software may have limited the quantitative accuracy of the MD results; however, the MD results broadly matched most of the observed empirical data collected.

Detailed neutron diffraction data at $\sim \theta = 0.7$ MLE was recorded and analyzed over a temperature range in the neighborhood of the observed melting transitions investigated in the isotherm studies. These data showed three distinct regions: a purely solid phase at $T < 124.4$ K, a purely liquid region at $T > 135$ K, and solid-liquid coexistence between 127 K and 132 K. A

Rietveld-like modification of our previously employed 2D diffraction lineshape algorithm enabled a simultaneous two-phase refinement of the diffraction data. These results show a well-defined set of transitions whose onset occurs at 126 K and completes near 132 K. In this temperature range, our analysis indicates that spatial ordering is lost at a lower temperature than where orientational ordering decays, reminiscent in some way of the KTHNY model for 2D melting and the suggestions of Bruch. The first order transition at 133 K signals the end of this region.

The combination of high-resolution adsorption isotherms, MD modeling, and the neutron diffraction investigations reported here have added to the understanding of the adsorbed properties of acetylene on graphite, including a further illustration of the complexity and uniqueness of this system. The need for further microscopic studies of the structure and dynamics of the monolayer phase transitions, along with robust molecular modeling, are necessary to more fully understand the details of the acetylene on graphite system.

3.6 – Supplementary Information

Henry's Law results: results and shows a discontinuity at 133 K. This suggests that a fundamental change in the molecule-surface interaction at that point, and the molecules become more weakly bound to the surface above this temperature. These values are both higher than a previously reported value of 19.4 kJ/mol. While these values are quite different, the ones reported here were obtained at a much lower temperature range, and with significantly more data points.

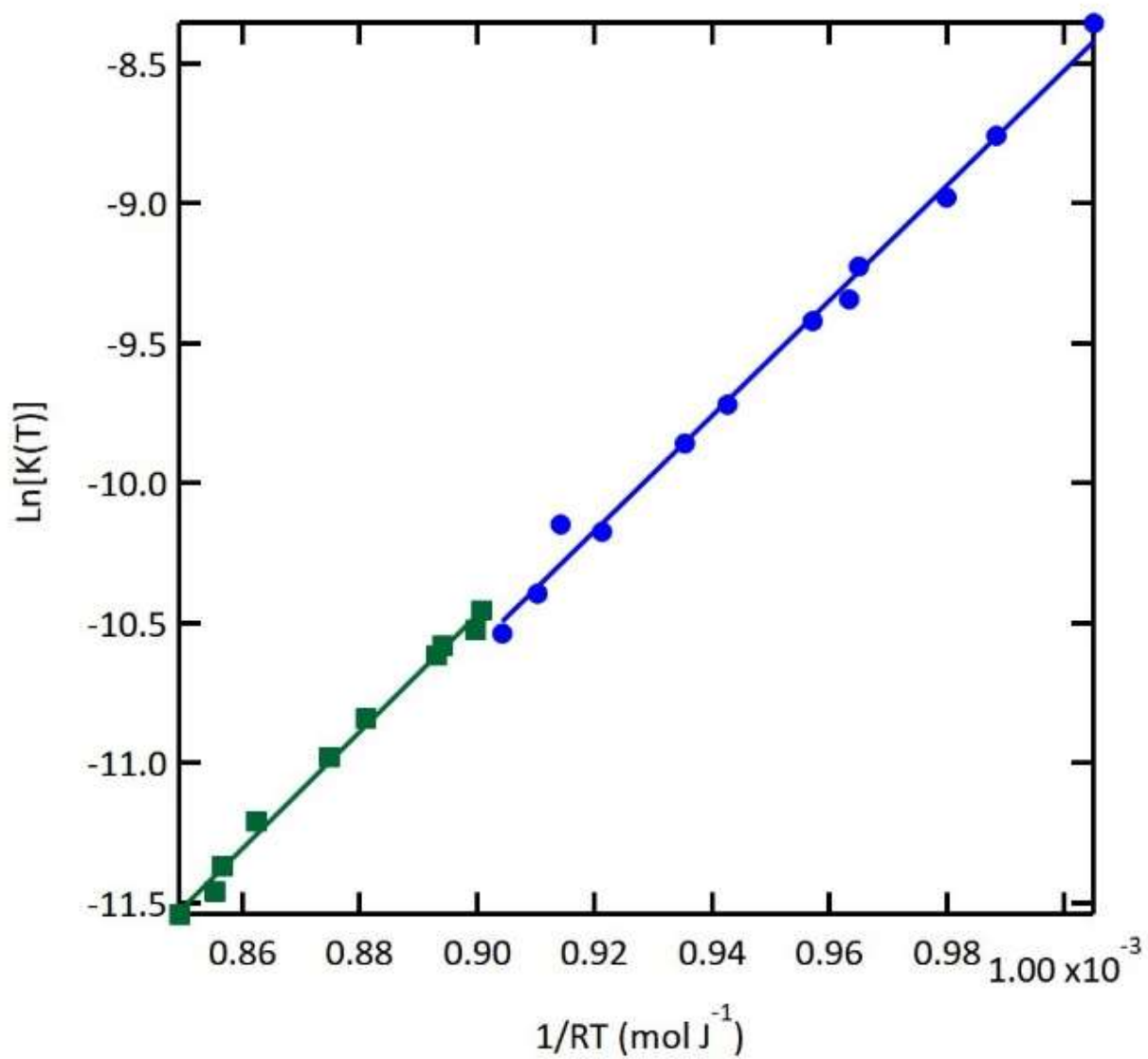


Figure 3.15: Henry's Law fit for acetylene on graphite

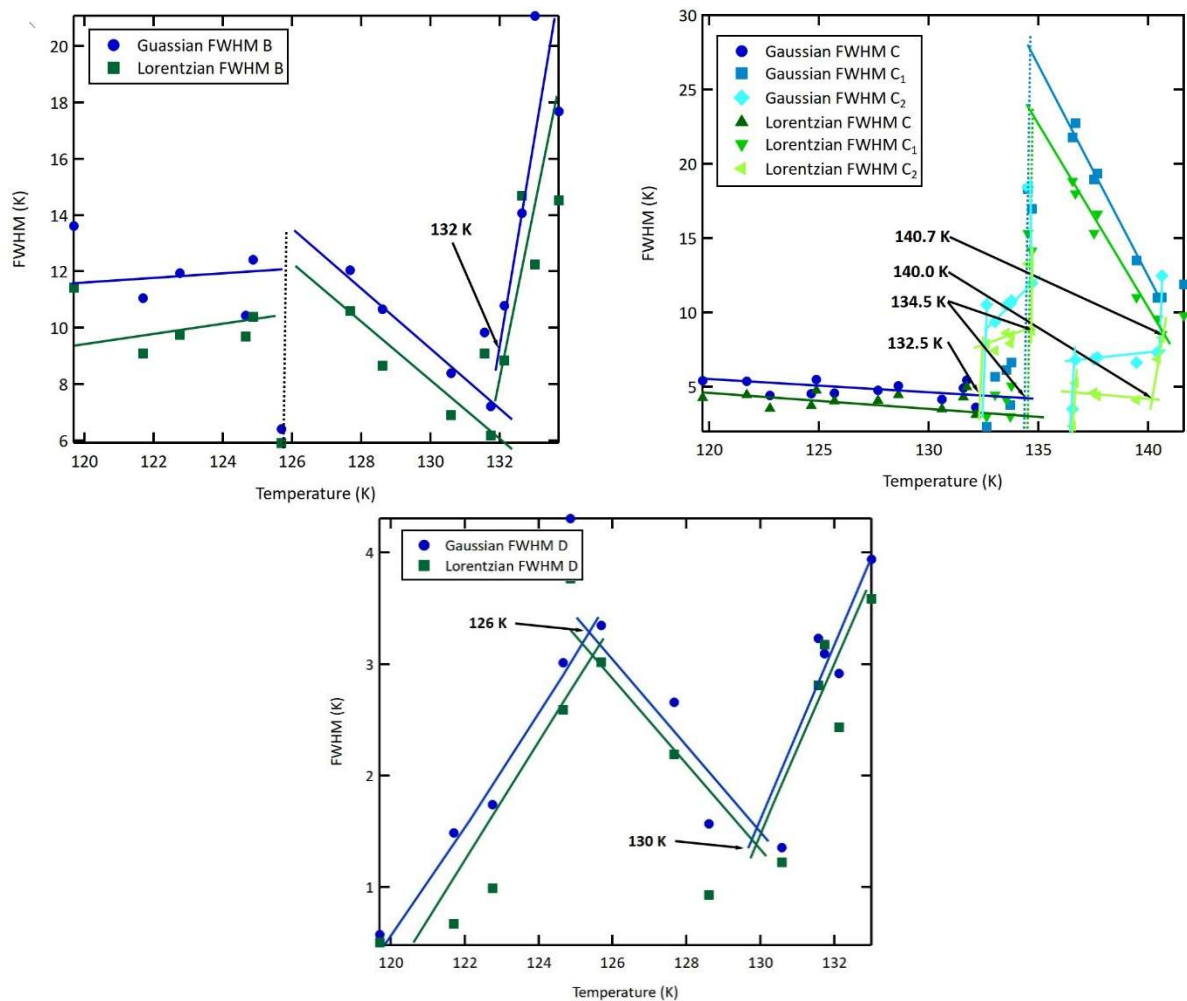


Figure 3.16: Plots of FWHM values for the secondary monolayer features (B through D).
Temperatures of possible phase changes are labeled

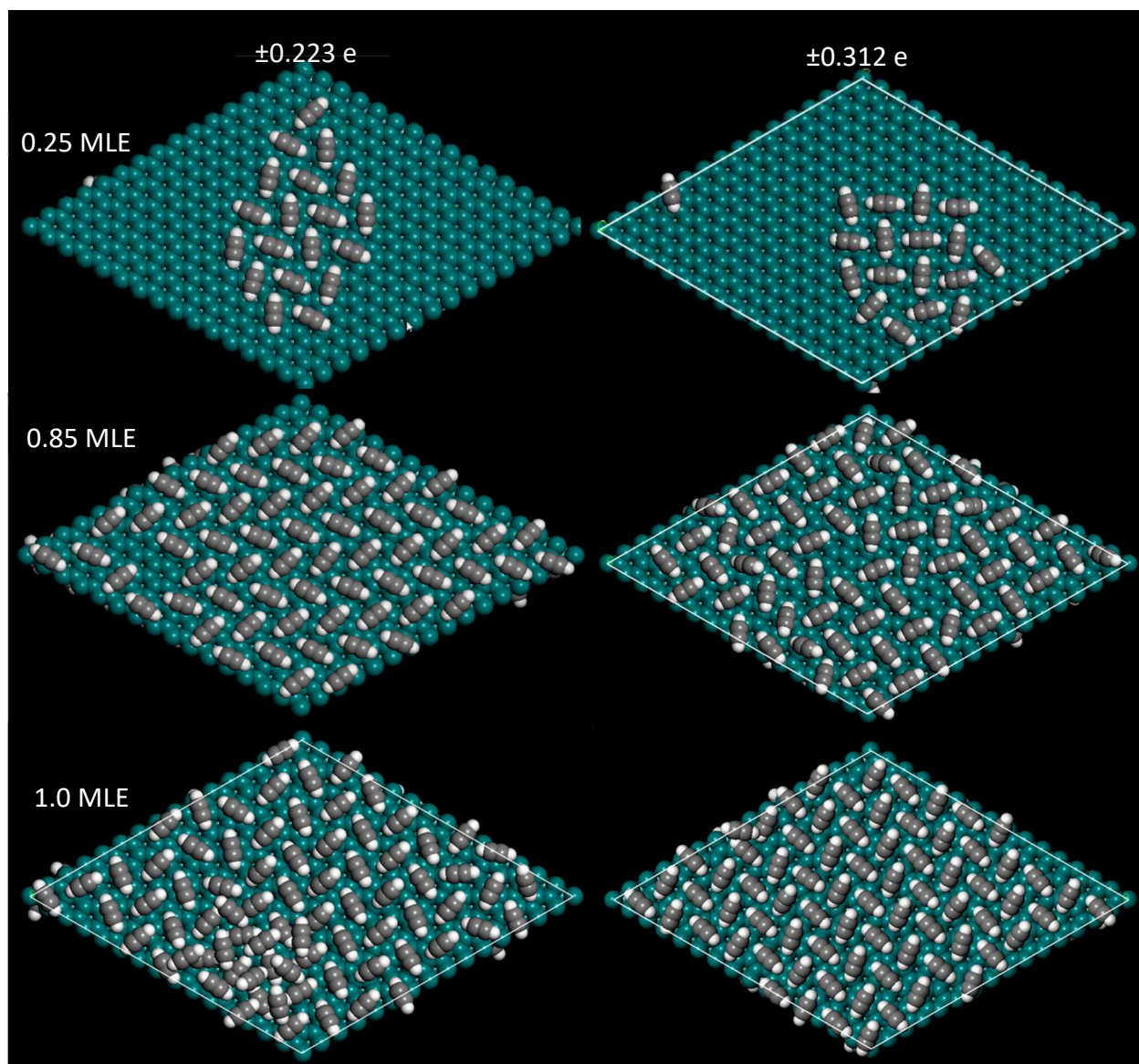


Figure 3.17: Comparison of simulation results at 5K for selected coverages of forcefield assigned point charges ($0.233 e^-$) vs stronger quadrupole value ($0.312 e^-$)

Molecular Dynamics: Given previous studies difficulties in attempts at the accurate modeling of acetylene and the peculiar behavior in the repulsive electrostatic non-bond energies, the results herein should be analyzed with some skepticism. With that being said, some interesting parallels between the thermodynamic data and these simulations can be seen.

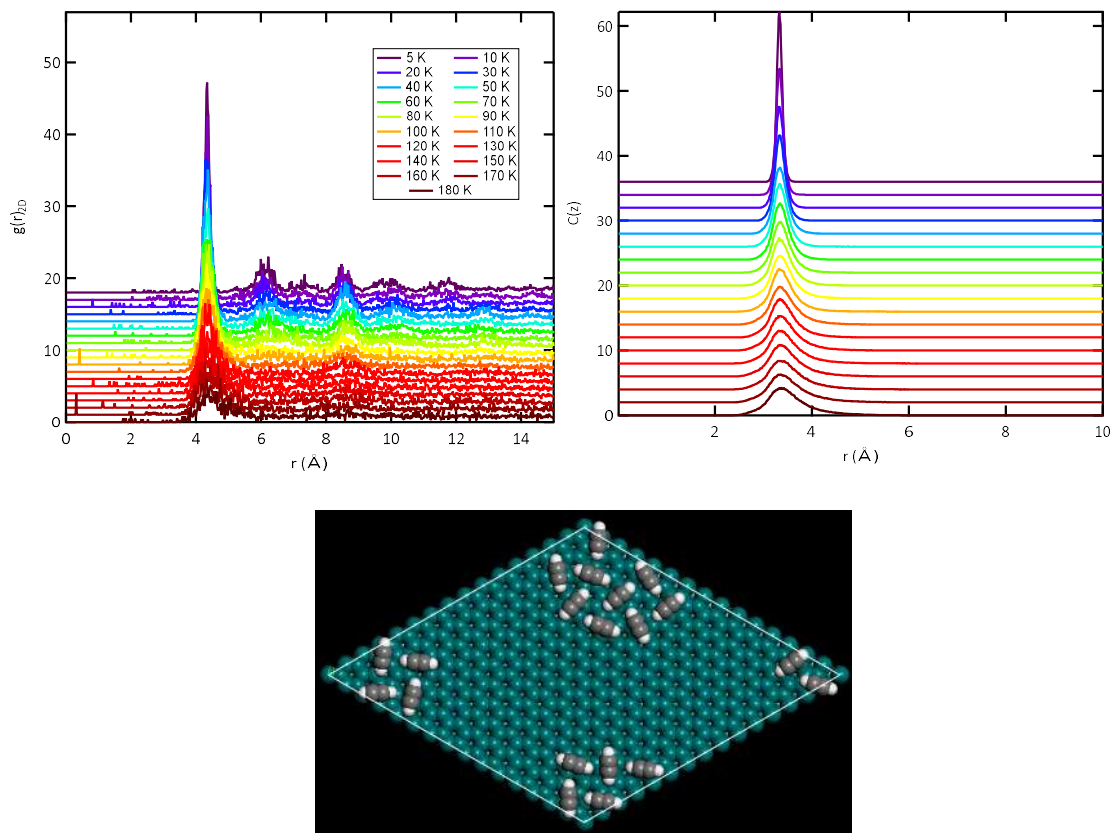


Figure 3.18: RDF profiles of 0.26 MLE as a function of temperature.

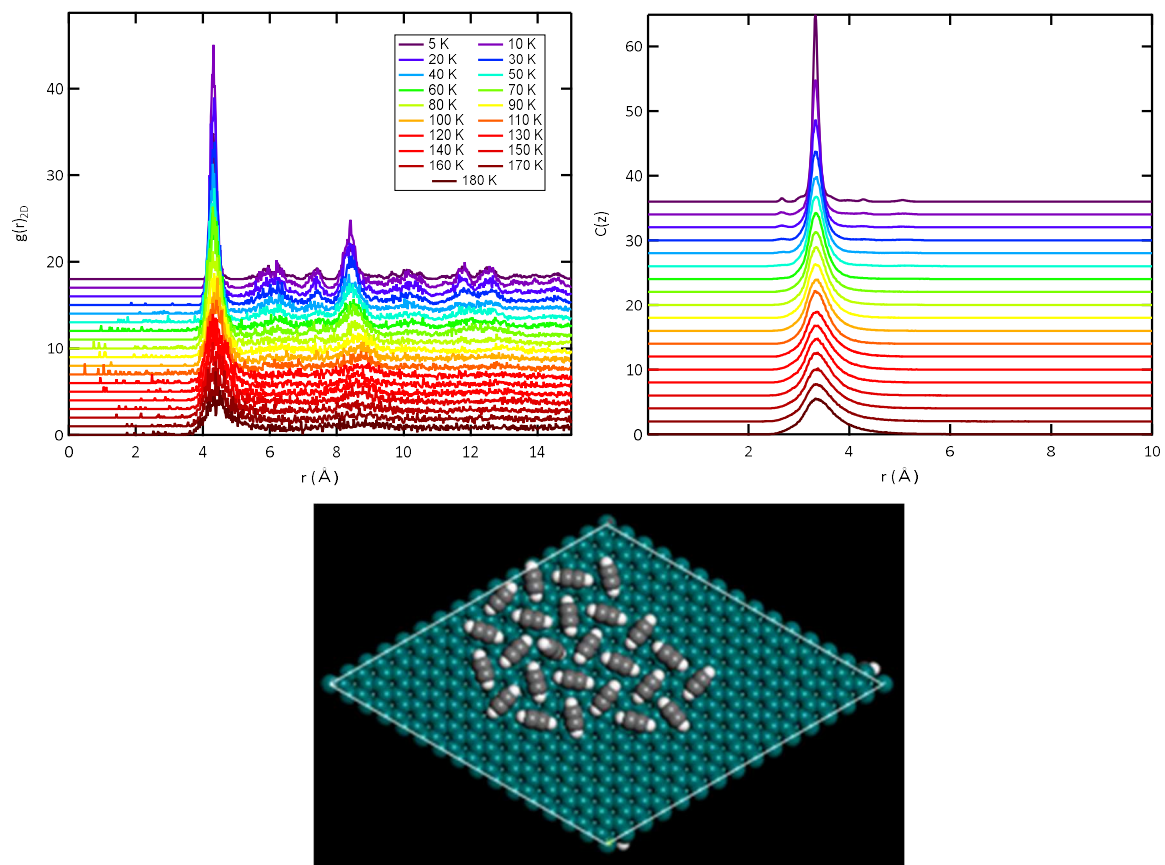


Figure 3.19: RDF profiles of 0.33 MLE as a function of temperature.

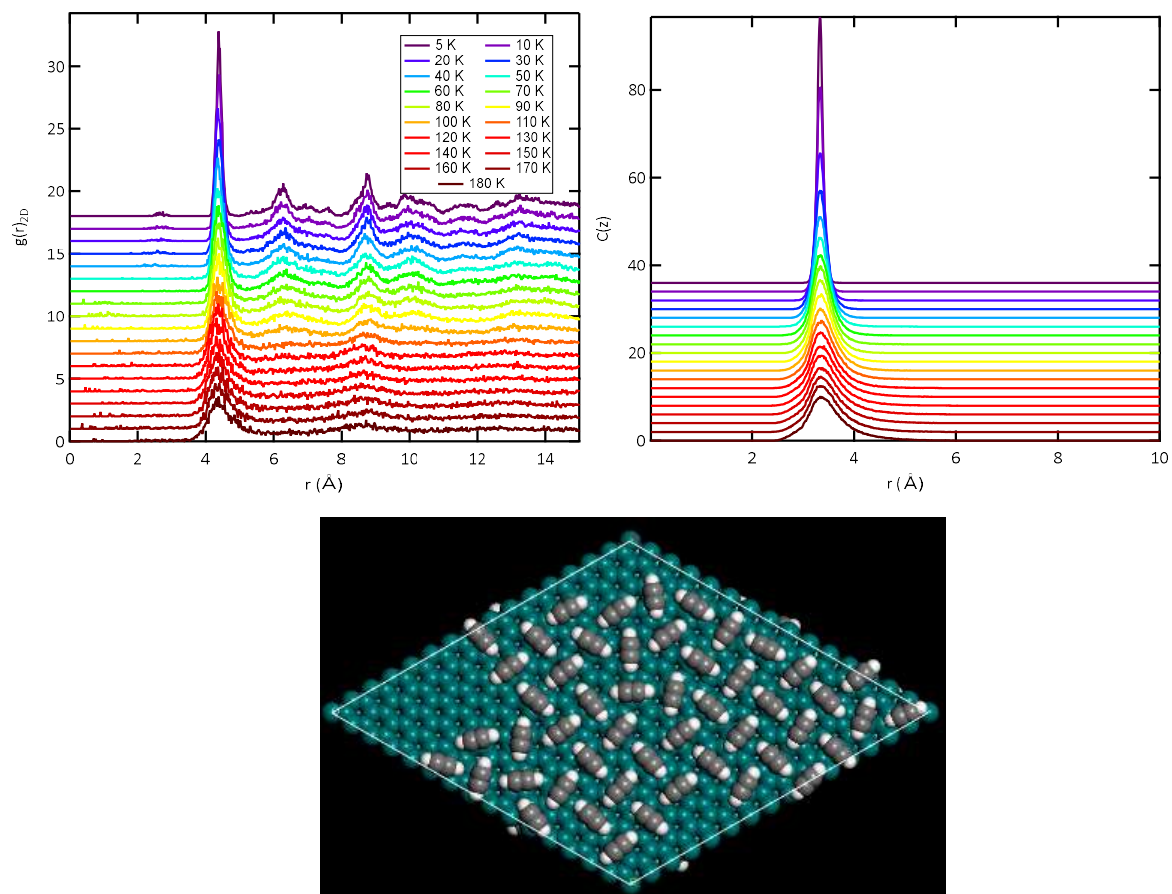


Figure 3.20: RDF profiles of 0.67 MLE as a function of temperature.

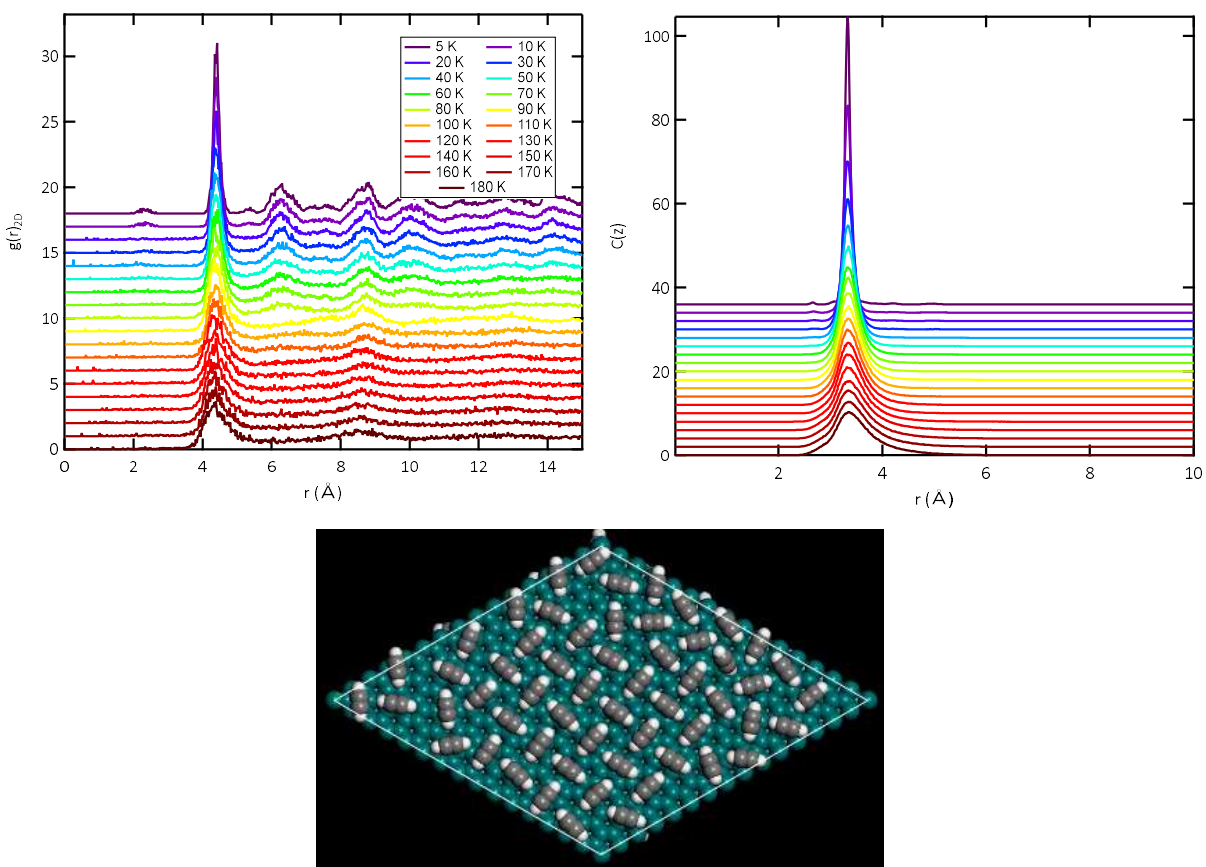


Figure 3.21: RDF profiles of 0.76 MLE as a function of temperature.

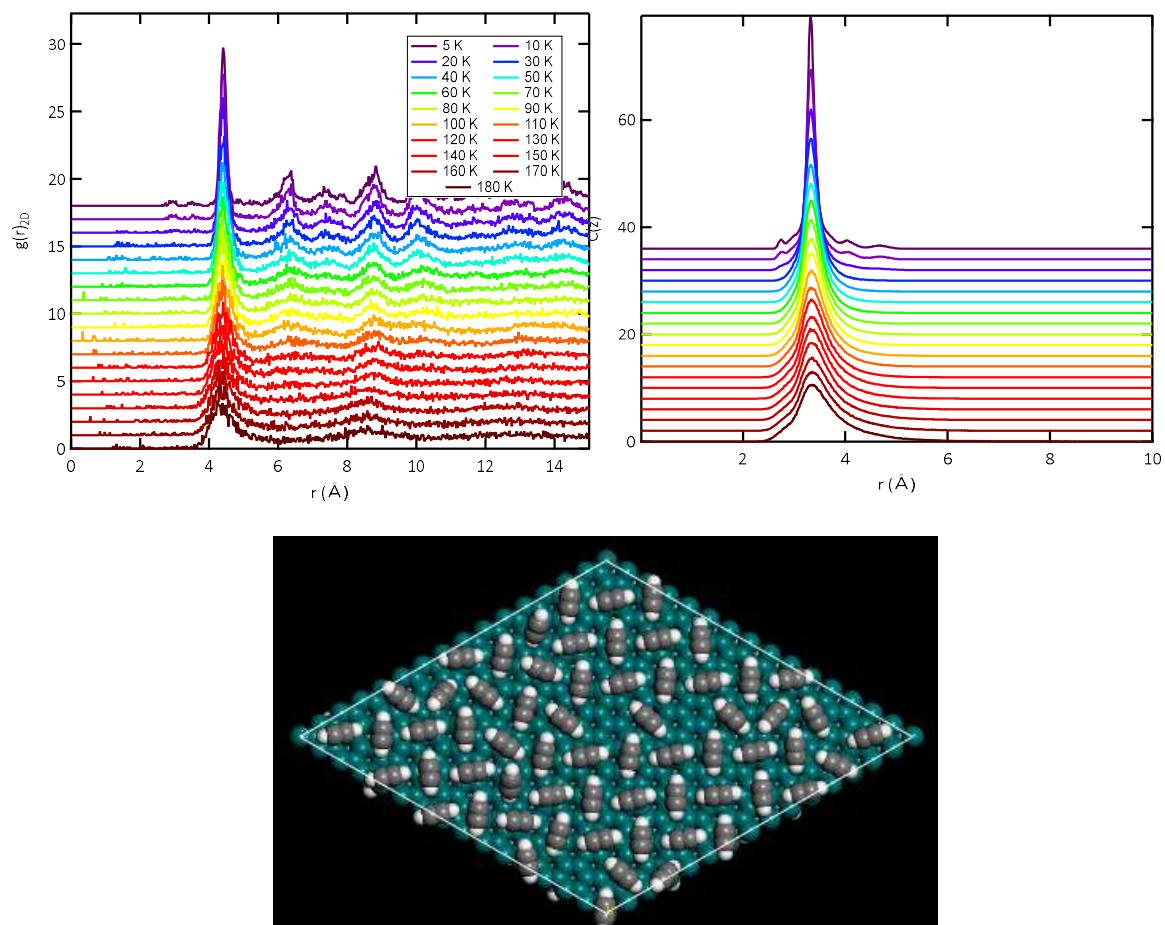


Figure 3.22: RDF profiles of 0.84 MLE as a function of temperature.

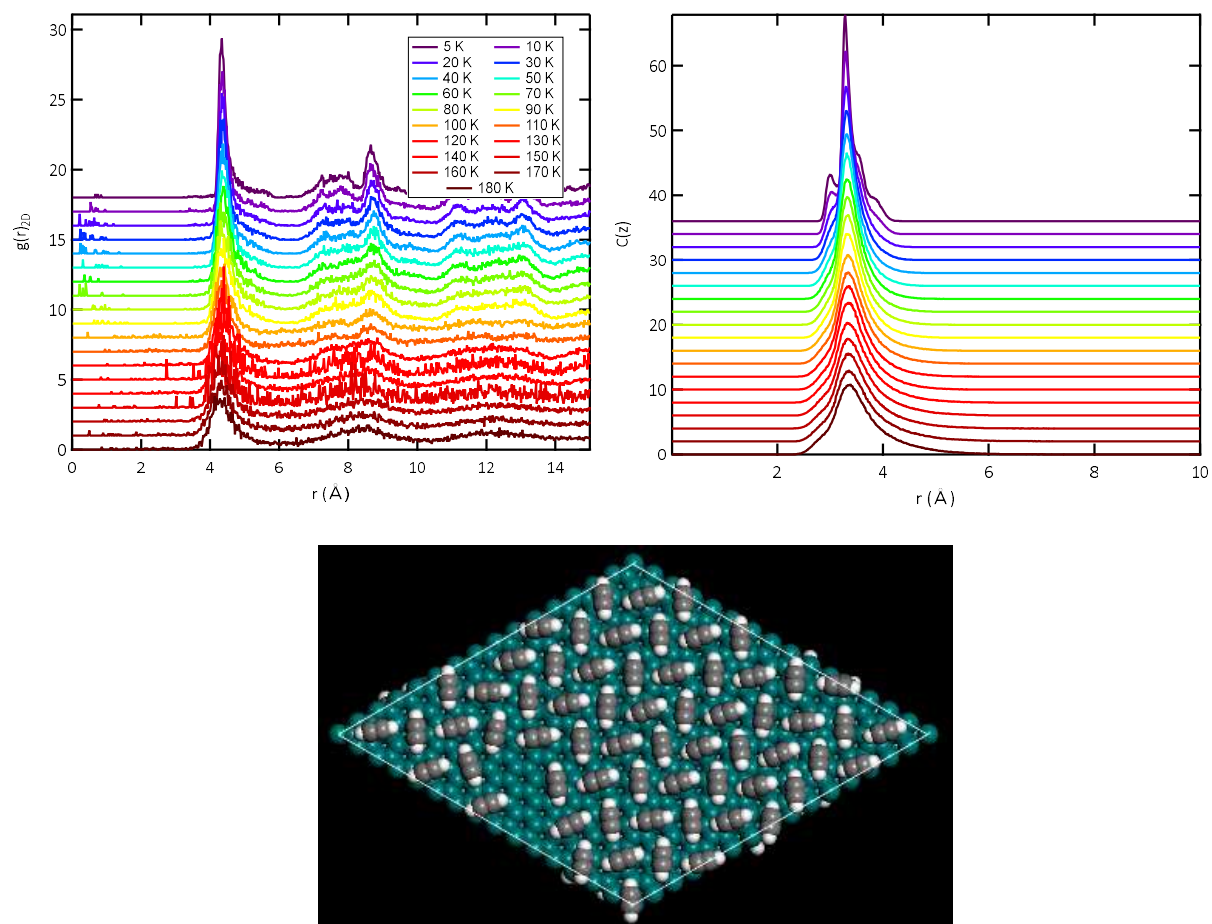


Figure 3.23: RDF profiles of 0.85 MLE as a function of temperature.

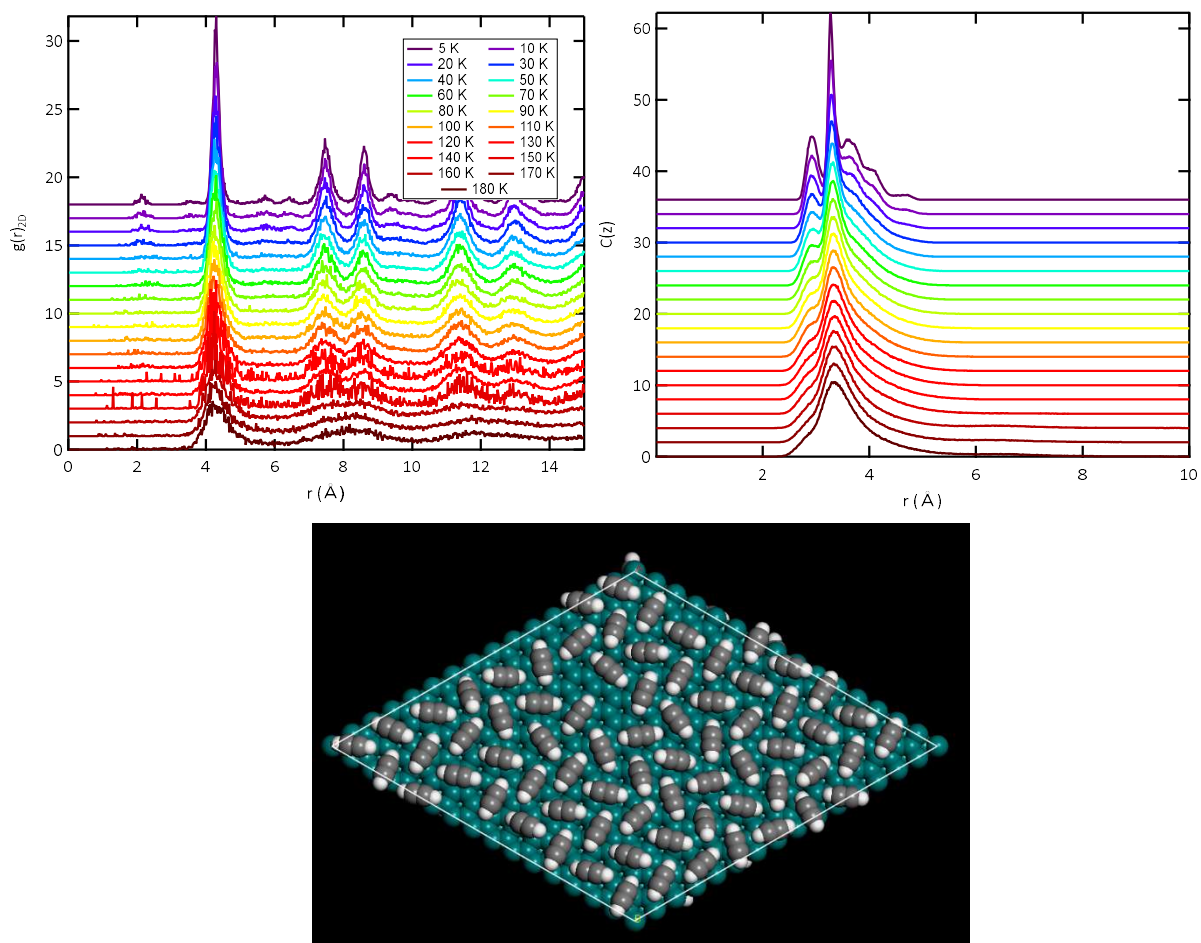


Figure 3.24: RDF profiles of 0.95 MLE as a function of temperature.

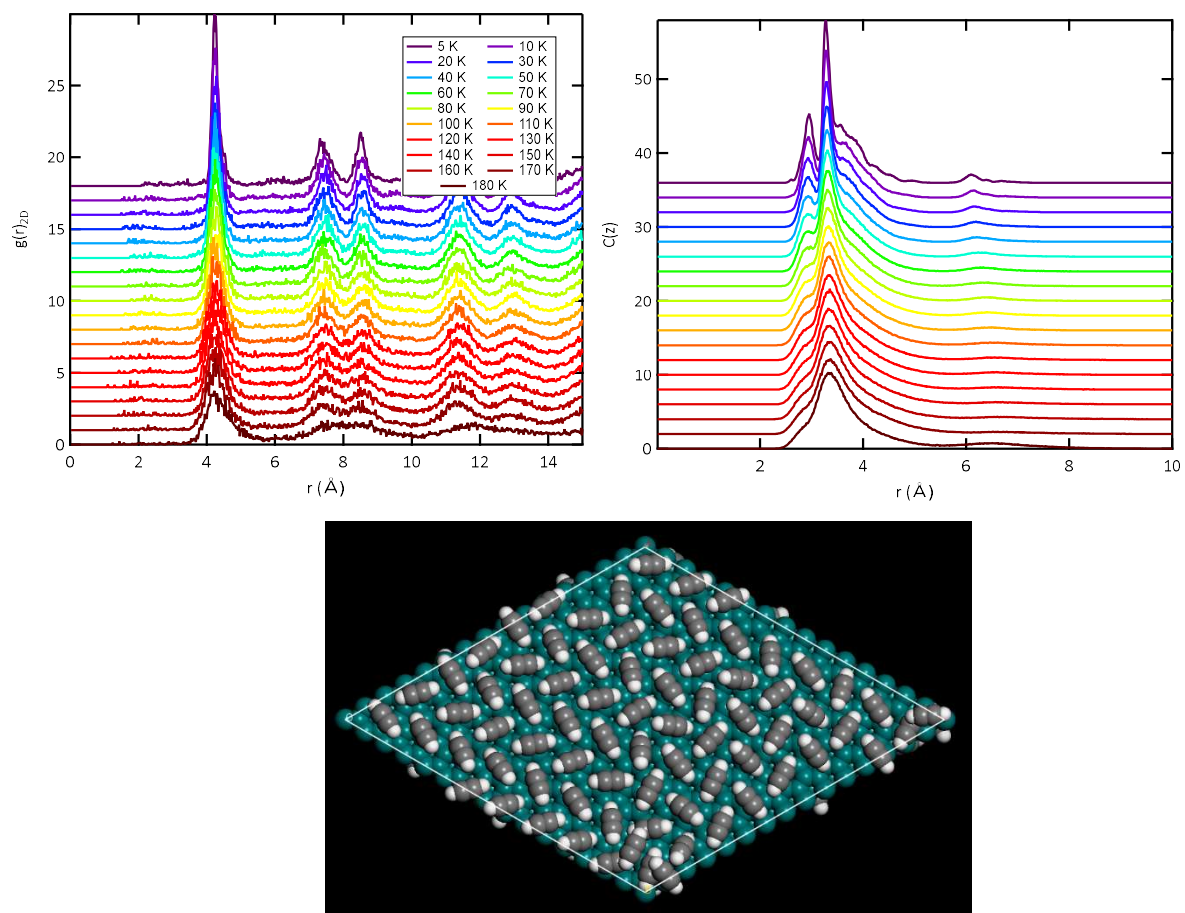


Figure 3.25: RDF profiles of 1.01 MLE as a function of temperature.

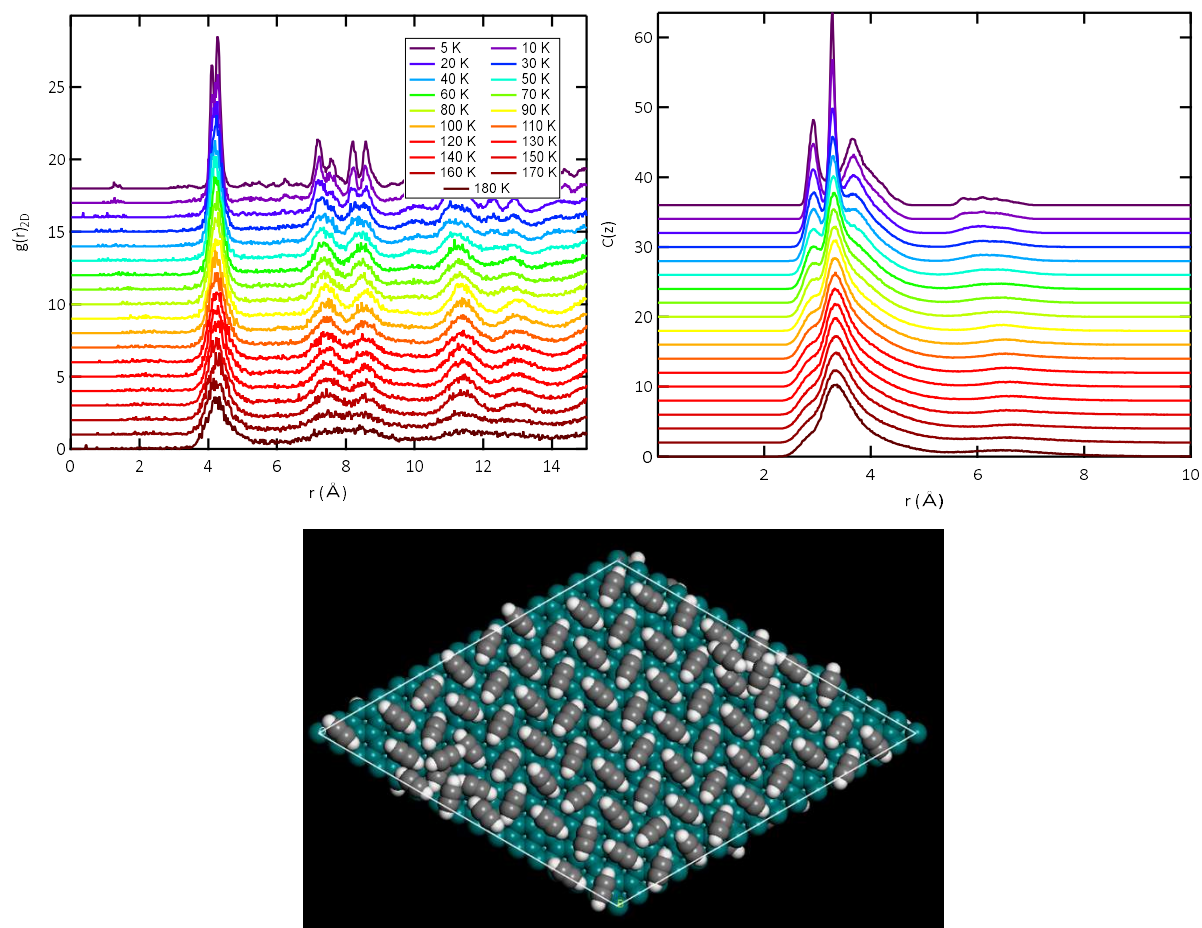


Figure 3.26: RDF profiles of 1.05 MLE as a function of temperature.

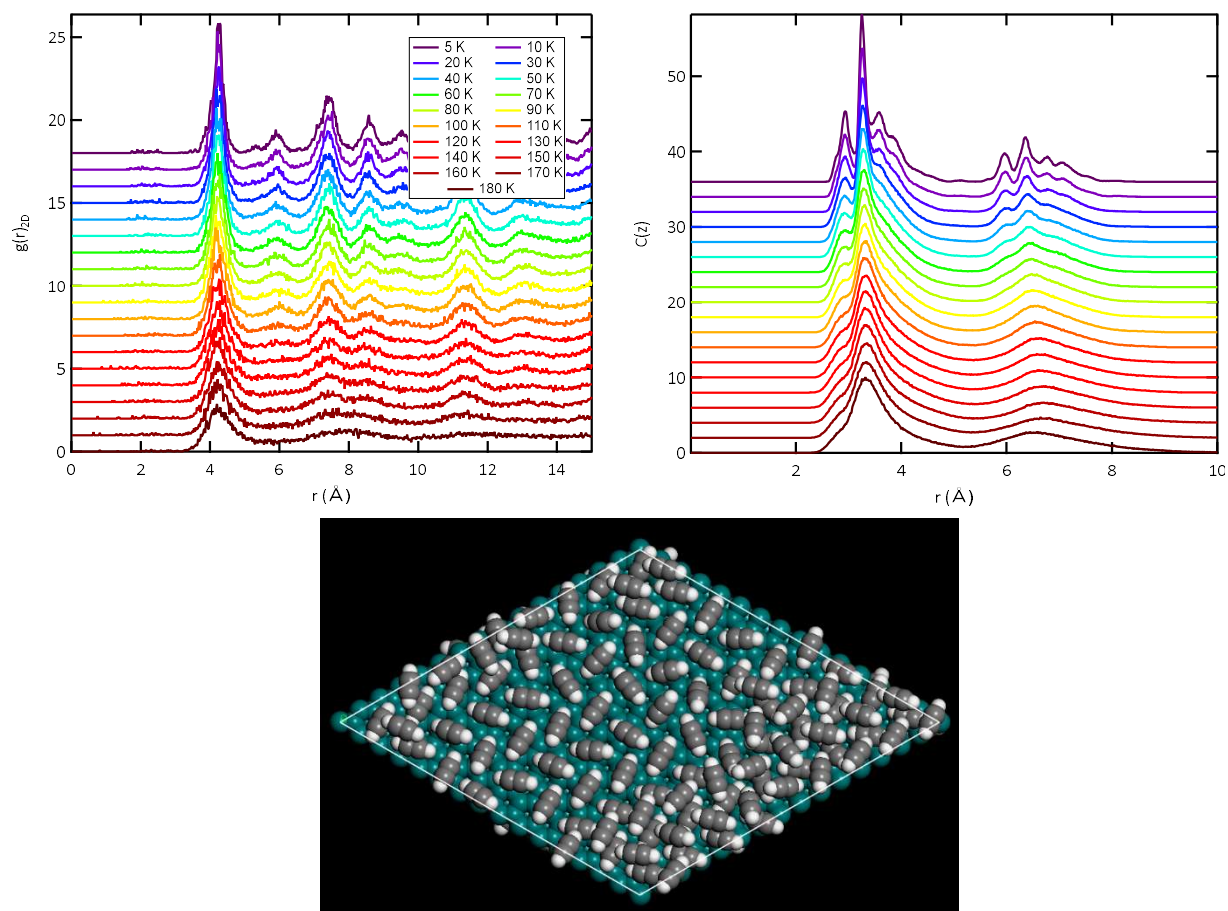


Figure 3.27: RDF profiles of 1.38 MLE as a function of temperature.

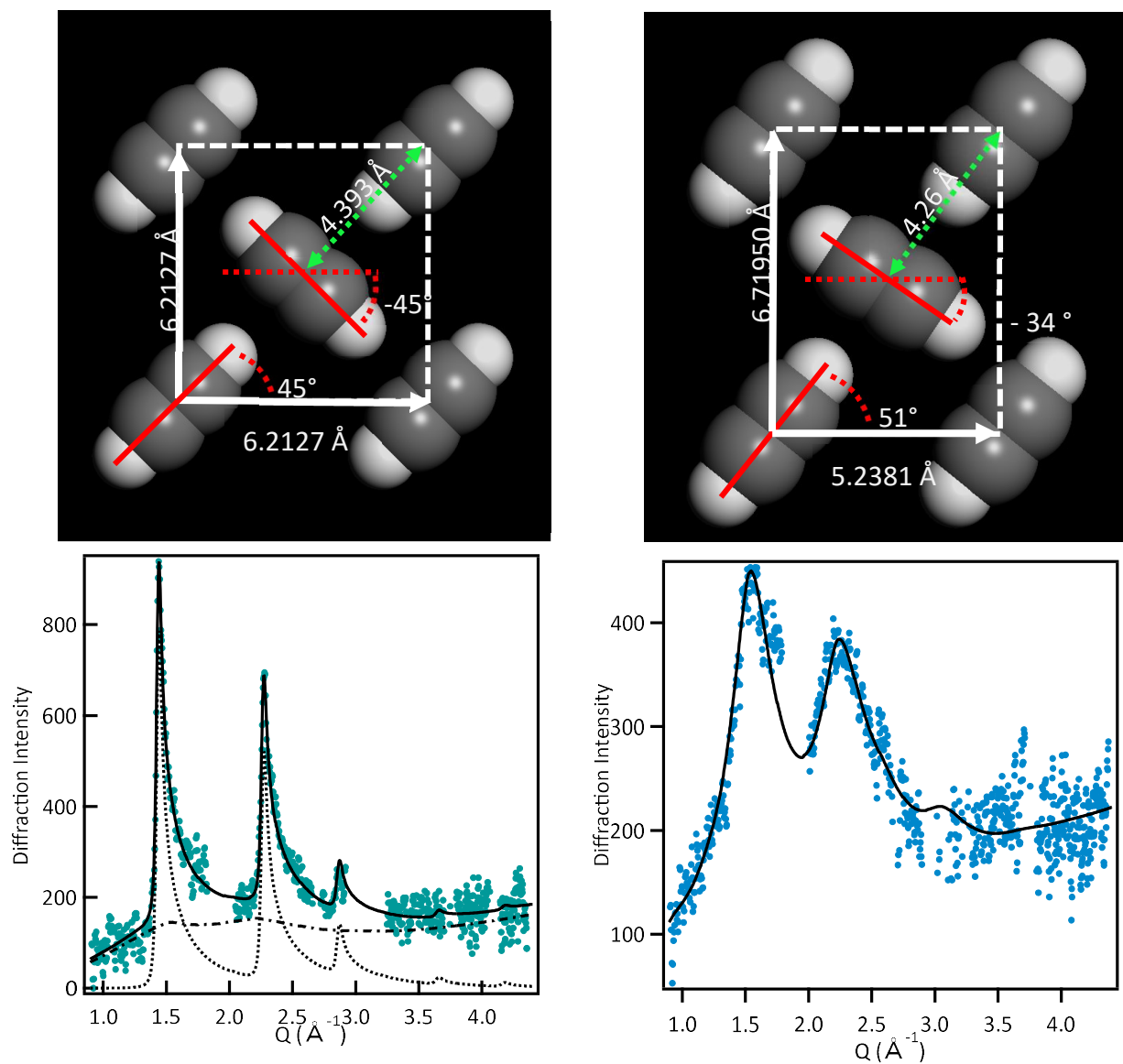


Figure 3.28: Structures and Diffraction profiles for solid and liquid phases of acetylene on graphite
(top) unit cell and (bottom) diffraction results and 124.4 K (left) and 135 K (right) for the solid and liquid phases respectively

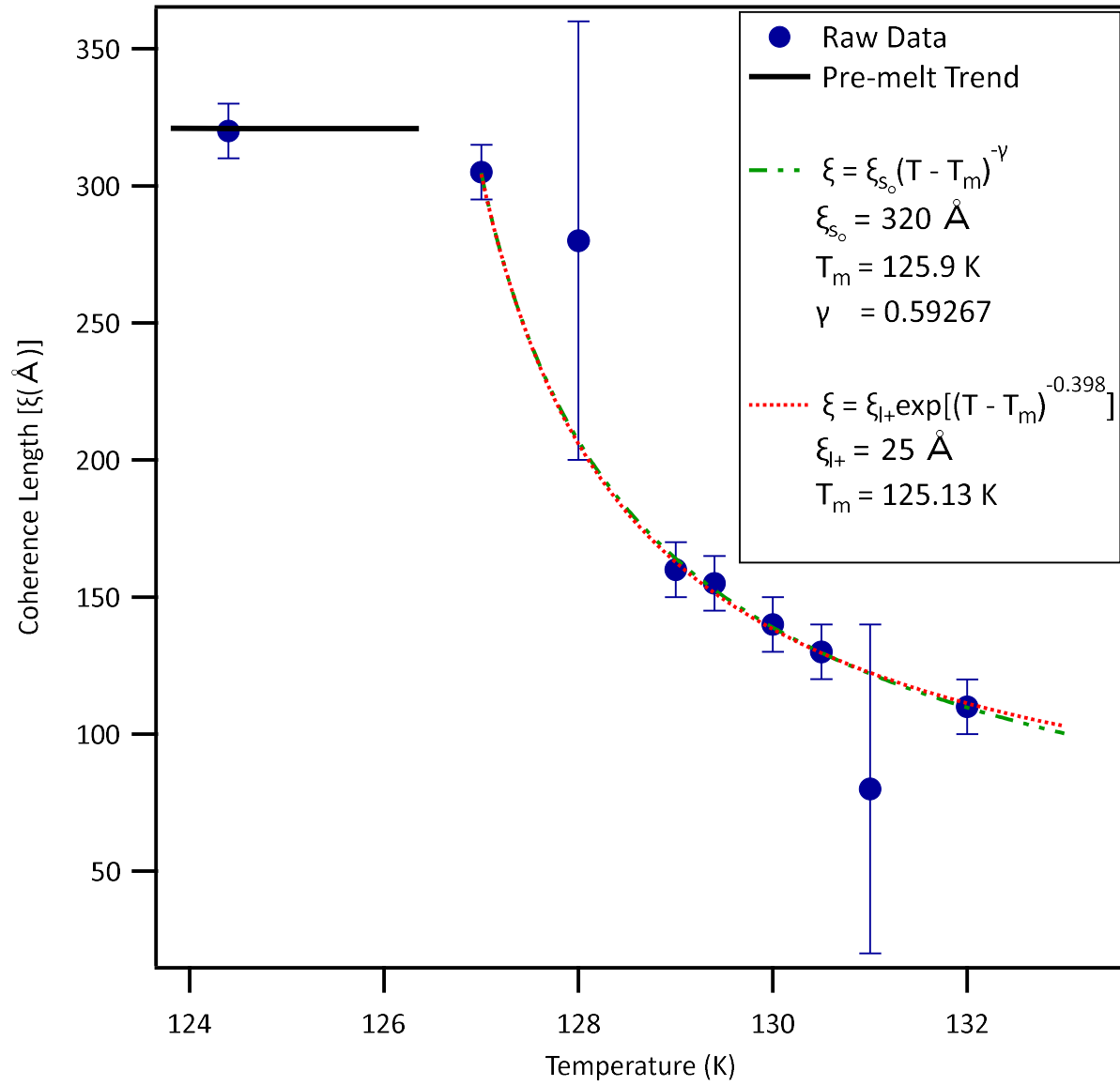


Figure 3.29: Behavior of coherence length of the solid phase as a function of temperature during the melting process.

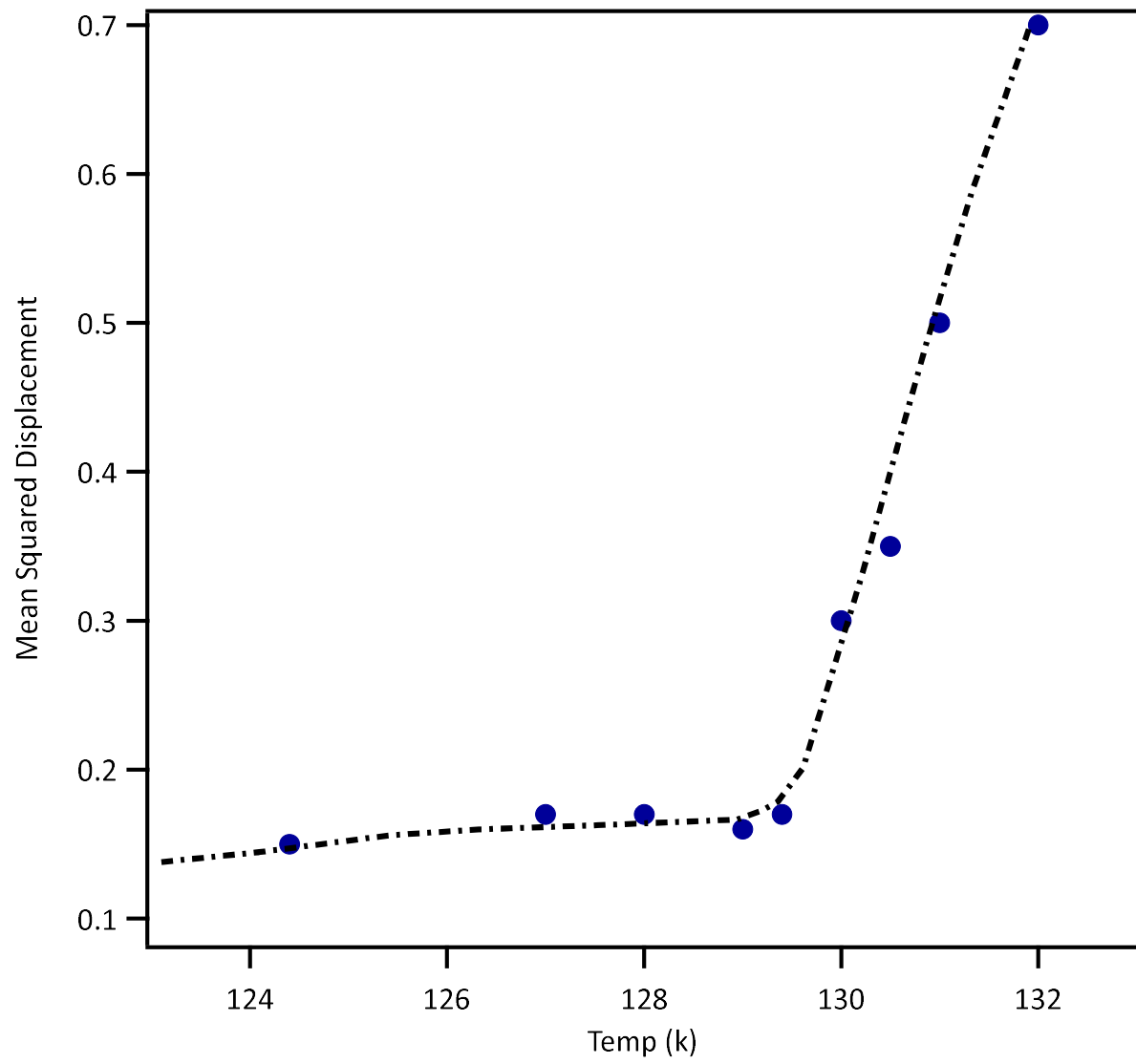


Figure 3.30: Behavior of the mean squared displacement of the solid phase as a function of temperature during the melting process.

Chapter 4 – Simulations and Force Field Trials of Acetylene on Graphite

4.1 – Introduction

This chapter discusses the attempts to modify the intermolecular interactions of acetylene in the molecular dynamics studies of its adsorption on graphite. It has already been mentioned in previous chapters of this dissertation that the creation of accurate force fields to describe the behavior of acetylene has been notoriously difficult. Most of the work on molecule-specific parameters for acetylene was done in an effort to describe the bulk thermodynamics and phases of acetylene and not the interaction of the molecule with other systems, such as a surface. Many of these efforts have succeeded in producing accurate results for the liquid phase of acetylene and/or one of the two solid phases.

Difficulty has come in achieving accurate force field results for both solid phases of acetylene with parameters that are physically reasonable and in keeping with the known attributes of acetylene molecules, such as its quadrupole moment. This latter property also presents issues in the description of acetylene. While one thing these studies have in common is that acetylene indeed has a large quadrupole moment, the exact value of this moment is not agreed upon. Disagreements in this value may not be entirely surprising, as the quadrupole moments for gas and condensed phases will not always be equivalent in calculations. Additionally, the values range over a multitude of conditions, and the available quadrupole moments used to develop potentials do not present a clear trend on the range of the values cited as to whether they refer to the condensed phase or not. Furthermore, the cited values vary in magnitude by approximately 30%. For the efforts of the simulations presented later in this chapter, the value of the quadrupole moment was not assumed to be any specific value, but was instead the focus of the parameter adjustments.

The trustworthiness of results in terms of the molecule-molecule interactions should already be treated with some reticence, and the difficulties lying therein should further cast doubt on the molecule-surface interactions as well. The hope of this exploration was not to produce a set of force field parameters that was perfectly refined to fit the experimental data but to work within the restrictions of the COMPASS force field to survey possibilities of behaviors as a function of these parameters. The results explicated in the previous chapter did display the series that was the best apparent fit to the other available experimental data; however,

insufficient data is available for the higher density regions of the monolayer for even those results to be anything more than a possible, though imperfect, representation of the system.

4.2 – The Solid-Solid Transition of Bulk Acetylene

Empirical studies on the solid phases of acetylene themselves have been a challenge to fully understand. For simplicity of the following discussion, the higher temperature solid phase will be referred to as “solid I” and the lower temperature phase as “solid II.” The solid-solid transition of bulk acetylene has been studied extensively over the past 100 years. One of the first direct observations of this transition was made in 1913 using polarized light, where a transition from an optically isotropic solid I phase to an optically anisotropic solid II phase occurring at 88 K was noted. Follow-up X-ray powder diffraction experiments in the 1930s were not conclusive but suggested that the solid II phase belonged to a lower-symmetry lattice structure¹⁹³.

A study in the 1950s by Sugawara et al.¹⁹³ using single crystal diffraction determined the structure of solid I to have a cubic lattice, with solid II possibly being orthorhombic. The difficulty in the diffraction from the solid II phase involved problems maintaining a single crystal as the acetylene crossed the transition point. They reported that as the acetylene underwent the transition, the transparent single crystals would shatter into an opaque powder. Powder diffraction was run on the resultant materials, but the authors were not able to make any definitive structural determinations from the data. The temperature reported in this study for the transition was 133 K. Though this value is 45 K higher than the value originally reported in 1913, the accuracy of their temperature measurements was much better and likely the source of discrepancy between these measurements. Follow-up spectroscopic studies in the subsequent two decades supported the determinations regarding the orthorhombic lattice for solid II and were able to conclude a probable space group for the structure as Cmca.

A highly detailed neutron powder diffraction study was conducted in the mid-1970s by Koski et al.¹⁹⁵⁻¹⁹⁸ to examine the structure of both phases. Their findings for solid I agreed with the findings of Sugawara et al. For solid II, neutron diffraction measurements were made at 4.2 K. Despite the improved quality of their measurements, they too encountered difficulties in the structural refinement, concluding that the lattice was orthorhombic in the Acam space group, but with a less likely second possibility of it belonging to the Aba2 space group. The difficulty in the structural refinement resulted in a follow-up publication where the authors attempted

further refinements to their neutron data. This process included a retreatment of anisotropic thermal terms and addition of an asymmetry peak factor to the refinement. Ultimately, they were able to achieve a significant agreement between the refined structure and the observed data with the orthorhombic Acam lattice. Disadvantageously, this study did not take readings near the reported transitions temperature and made no contribution to settling the discrepancy in the two previously reported values. Another study was made in 1979 that, despite very high-quality measurements, was not able to refine a structure for phase I cubic acetylene that was without any major discrepancies.

The most recent work on these two solid phases was published in 1992 by McMullan and Kvick¹⁹⁴. This study was able to improve upon the previous studies as the authors successfully solved the issues of single crystal measurements of phase II and used single crystal neutron diffraction to study both phases, including structural data of the transition process itself, for both C_2H_2 and C_2D_2 . The quality of data obtained was also much higher and found a slight disagreement with the 133 K transition point, with their value reported at 127 K for regular acetylene and 139 K for deuterated acetylene. The only significant differences that would be expected between the two forms of acetylene are changes in lattice frequencies as a result of the mass change. The 12 K discrepancy between deuterated versus non-deuterated acetylene suggests that the solid-solid transition may be coupled to a phonon in the crystal lattice.

4.3 – Previous Computational Efforts

The past efforts of researchers to develop accurate potentials for acetylene that pertain to the work of this dissertation are delineated into three types of systems, the most extensive of such being the modeling of the bulk properties of acetylene^{52, 95, 201, 206, 209}. This, of course, represents the most common and easiest system of acetylene to study empirically. The second, and next most common, are studies on the formation and stability of acetylene clusters ranging from two molecules to tens of molecules^{200, 202, 204, 206}. This has received a lot of interesting attention in computational studies, and some, although limited, empirical data does exist. The third is the most directly relevant here, being the study of the adsorption of acetylene. Despite this, only two studies have ever dealt with the system of acetylene on graphite^{107, 216}, and only a single study could be found for acetylene adsorbed on MgO ²¹¹.

It is not practical here to summarize all of the past works in these areas, but some of the more significant efforts will be discussed. For the simulations of bulk acetylene, probably the first major study was conducted by Hirshfeld and Mirsky⁵². Multiple representations of the electrostatic distribution were tested, including a single point quadrupole, atomic point charges, and a distribution of point charges, dipoles, and quadrupoles placed on each atom, all fit to a quadrupole strength of 7.188 D Å. Van der Waals forces were described using a Buckingham potential. Their model failed to accurately describe the orthorhombic phase but performed well in the description of the cubic phase. Next, Filippini et al⁹⁵. performed a large-scale study exploring the use and adaptation of many general sets of parameters to fit to the acetylene system. Despite examining various electrostatic and van der Waals treatments, similar issues arose in their systems as occurred with previous study and the quadrupole strength that was used in their final models was one-third of the values used by Hirschfeld and Mirsky. Klein and McDonald²⁰¹ furthered previous studies in an attempt to include a description of the liquid phase by extending potentials already studied in the previous two studies. Their results were significant for their inclusion of the liquid phase in their studies, but because they were exploring potentials already studied, their work added nothing new to the description of the orthorhombic phase. Gamba and Bonadeo²⁰³ used a double dipole arrangement that was fit to the quadrupole and hexadecapole of acetylene obtained from ab initio calculations and a Buckingham van der Waals potential. Their model encountered similar problems to these others, but in the end, they were able to describe properties of both phases, with a discrepancy in the sublimation energy of the orthorhombic phase.

A more recent investigation by Garrison and Sandler⁹⁴ attempted to solve the same issues with a completely new approach from the older methods. Using a combination of Monte Carlo simulations and refinement of potentials from experimental data, they derived a set of potentials of a completely different form from the previous studies. This used the damped Morse oscillator potential described in equation 1.54 along with a similar damping modification of the electrostatic interactions. The van der Waals potentials also included a dummy atom potential at the molecule's center of mass and atomic point charges fit to a quadrupole strength of 6.17 D Å. Despite this attempt being more recent than the others, and with the benefit of more

powerful and accurate computation, they only refined their potentials based on the liquid phase data and did not make any attempts to model their model to the solid phase at all.

The development and form of potentials for dimers and clusters of acetylene have proceeded along the same general lines as those for the bulk acetylene. The main difference is that more specific attention was focused on the interactions of very few molecules, and these investigations were aimed at parameter development from direct inquiries into the intermolecular interactions and not structure and thermodynamics of bulk condensed phases. With less data available for comparison in regards to small clusters, and no validation against the bulk phase properties, the accuracy of these methods are more difficult to assess. One important piece of evidence is the energy barrier associated with the transposition of molecular orientations in acetylene dimers²⁰⁰. Some experimental evidence has measured this transition to be very close to 1 cm^{-1} . This number is suspiciously low based on intuitive understanding of the preferred orientations of quadrupoles. It is not a surprise that there should be a saddle point in between the two equivalent T-shaped orientations of a dimer pair. Furthermore, it would be unlikely that this saddle point should pass through a completely parallel configuration, as this is electrostatically unfavorable. The surprise is that this reorientational barrier should be so small for such a strong quadrupole. If accurate, it would suggest that the van der Waals forces are of similar strength to the quadrupole moment. Under this assumption, the development of these refinement models based on the molecule's microscopic behavior, rather than bulk behavior, represent an alternative methodology, though less validated, that could, potentially provide a better description of the intermolecular interactions in two-dimensional films.

Two studies have been aimed at the determination of atomic potentials that directly describe the observed film behavior of acetylene on graphite. The first of these was performed by Thorel et al.²¹⁶ in an attempt to describe powder neutron data collected for these films. While they were able to refine potentials that capable of describing the observed diffraction pattern, the actual results were not in keeping with the intuitive results expected of a two-dimensional system of quadrupoles. A second study was conducted by Peters and Klein¹⁰⁷ that brought in thermodynamic results obtained from isotherm measurements. They were able to produce physically reasonable results that describe thermodynamic data and the two reported solid phases. Their data is close, though not perfectly in keeping with the finding more recently

obtained and reported in the previous chapter of this dissertation. The main issue based on this new data is that the structure corresponding to the S_1 solid phase is a square lattice, but the T-shape of the molecules is skewed by several degrees. Furthermore, a major part of the thermodynamics analysis, the Henry's law constant, was 7% lower than those obtained in the new data, though this may in fact not be an issue as their value was based on isotherms in a significantly higher temperature range and the assumption of no molecule-molecule interactions may have more validity under such conditions. Indeed, the shift in the Henry's law adsorption energy observed at 133 K corresponds to a transition in the first monolayer, and may indicate that even before the first monolayer step, the molecules exist as a cluster gas rather than individual molecules.

The third major aspect lacking from their data is the so called S_{12} phase, reported by Thorel et al. to be a coexistence of both other solid phases, and more recently assigned by Trabelsi et al.²¹⁵ to the same identification. The possibility of an approximately equal two-phase coexistence region is not physically consistent with the available isotherm data. The alternative proposed in the previous chapter is a third solid phase, related the S_2 solid phase, but with an oblique, rather than rectangular, lattice. For consistency in comparison with the previous work, however, this phase will still be referred to as the S_{12} phase even though it would not seem to be an accurate description of the phase.

4.4 – Significant Experimental Results

The primary aspect which the force field adjustments were refined against were the observed densities of sub-step features that may correspond to transitions in the isotherm data. Furthermore, perhaps the most important requirement, was to produce results that were consistent with the observed T-shaped phase at coverages corresponded to the A-step of the isotherm data, as well as the disordered rectangular phase, while providing details consistent with the continuous melting transition that was observed.

Consideration was also given to the results of the previous neutron works at higher coverages not covered by this new study. This includes the results obtained by Thorel et al.²¹⁶ and Trabelsi et al.²¹⁵. The second of these publications provided significantly more data to work from than the first; however, there were significant discrepancies in the comparison of their data to the finding of Thorel et al., as well as the data presented in this work. A telling example of this

regards a disagreement in the peak positions and their spacings from one another for the low density square-T phase. The data reported herein involved the collection of diffraction data from three different experiments at two different facilities over a time space of decades that were all in agreement with each other and the findings reported by Thorel et al. The data reported by Trabelsi et al. in the locations of the diffraction peaks were shifted to higher Q values, and the spacing between the peaks was also different. Their data could not be fit to a square-T lattice, but rather fit best to a rectangular lattice, which is a substantially higher density. This casts doubt on the assumptions that might be made from their diffraction peaks as a similar inconsistency was identified in the S_2 phase in comparison to the work of Thorel et al.

If assumed that the distortion of the higher density phases is identical to the distortion present in the diffraction from the S_1 phase, it is possible to make some further assumptions of the structure of the two higher density phases. Though precise accuracy is not possible from the considerations being made, a reasonable proposal for the S_2 phase is that it represents a rectangular herringbone structure with two molecules per unit cell that is 4.45 Å by 7.38 Å, the molecules being rotated with respect to the shorter lattice vector by 40° and -55° and an out of plane tilt of between 20° and 25°, and an area per molecule of 16.43 Å², consistent with the observed isotherm density. Noting that the proposed structure is uniaxially commensurate with the $\sqrt{3} \times \sqrt{3}R30^\circ$ surface registry, this creates an interesting possibility, but this is only an approximation of the structure from the data available and may or may not be the case. Furthermore, this structure brings to light a unique relation to the quadrupole interaction and the low density bond-ordered liquid phase. The orientation of the molecules along the diagonal of the unit cell matches the preferred T-shaped dimer spacing between 4.3 Å and 4.4 Å, and the molecular angles place the molecules in a nearly T-shaped configuration along one of the diagonal directions, but not in the other. If accurate, this would suggest that the molecules will attempt to maintain the quadrupole alignment even as the unit cell must distort under higher densities. The uncertainty of describing the S_{12} phase is more substantial due to the coupling of the lattice vectors, cell angle, and molecular orientations in their effects on the structure factor. Despite this, the lattice can be assigned approximately as an oblique herringbone lattice with 1 to 2 degree skew away from rectangular, approximate cell dimensions of 4.5 Å x 7.5 Å with the molecules rotated away from the short axis of the unit cell by 35° to 40° and -55° to -60°, and out

of plane tilting of approximately 20°. Structures with this range also bare similar properties to the liquid and S₂ phase in the approximate T-shaped alignment of the molecules along only one axis. Based on the reported data available, it is not clear, however, if the S₁₂ phase occurs immediately after the completion of the C substep below 133 K, or if the film transitions continuously towards this structure from a rectangular phase first.

4.5 – Results from Standard COMPASS Parameters

In the initial study of the acetylene on graphite system, simulations were run using the default assignments made by the COMPASS force field in Materials Studio (Figure 4.1). Unfortunately, these results were clearly not consistent with the data available. The films only practically demonstrated a single incommensurate rectangular herringbone lattice that was independent of surface coverage. These results indicated a clear deviation from the experimental results and were the driving force behind further exploration of alternative force field variations to describe the system.

4.6 – Examination of Alternative Potentials

The creation of a new force field files for use in Materials Studio, and subsequent simulations series, at a range of coverages for the many options available in the literature is a computationally inefficient task when there is no certainty of their being any more accurate than COMPASS. In fact, there are reasons to doubt the accuracy of all of the available alternatives. Instead, simple models were constructed to create a comparison of the force fields within certain identical constraints.

The first model was a simple determination of the surface corrugation by calculating the interactions between a single molecule and the surface as a function of position, height, and molecular orientation. Only one investigation in the literature evaluated reasonable parameters to define the molecule-surface interaction, that being the work of Peters and Klein¹⁰⁷, whose set of potentials yielded results closest in nature to those being used here to describe the system and were utilized to generate these maps of the surface potential. These results were within the range of those that have been calculated for other small linear molecules like oxygen and carbon dioxide and are shown in Figure 4.2. One discrepancy, however, is that the optimized height from the surface obtained in this model was different from that reported by Peters and Klein, but only

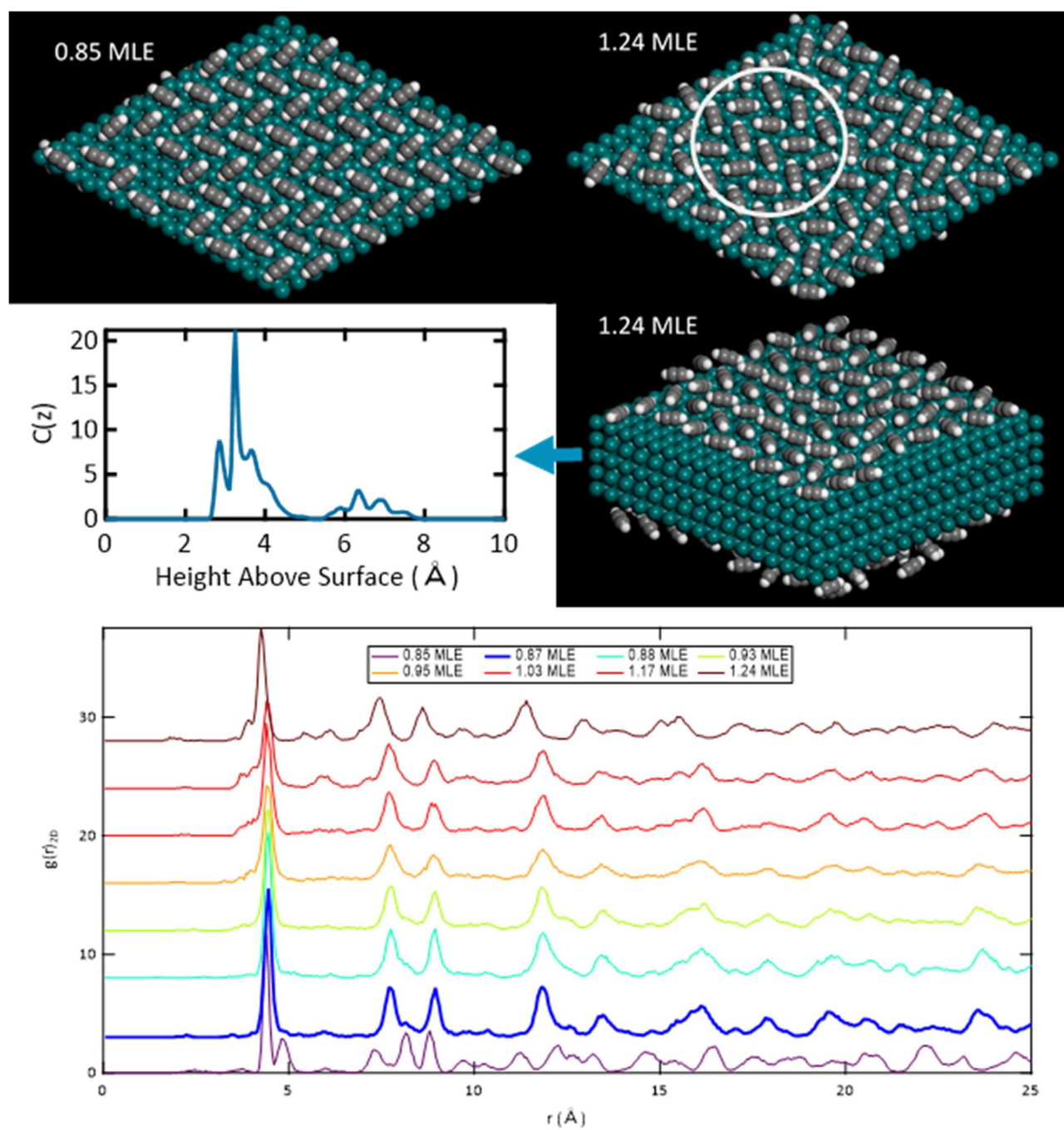


Figure 4.1: Simulation results for acetylene on graphite using default compass parameters

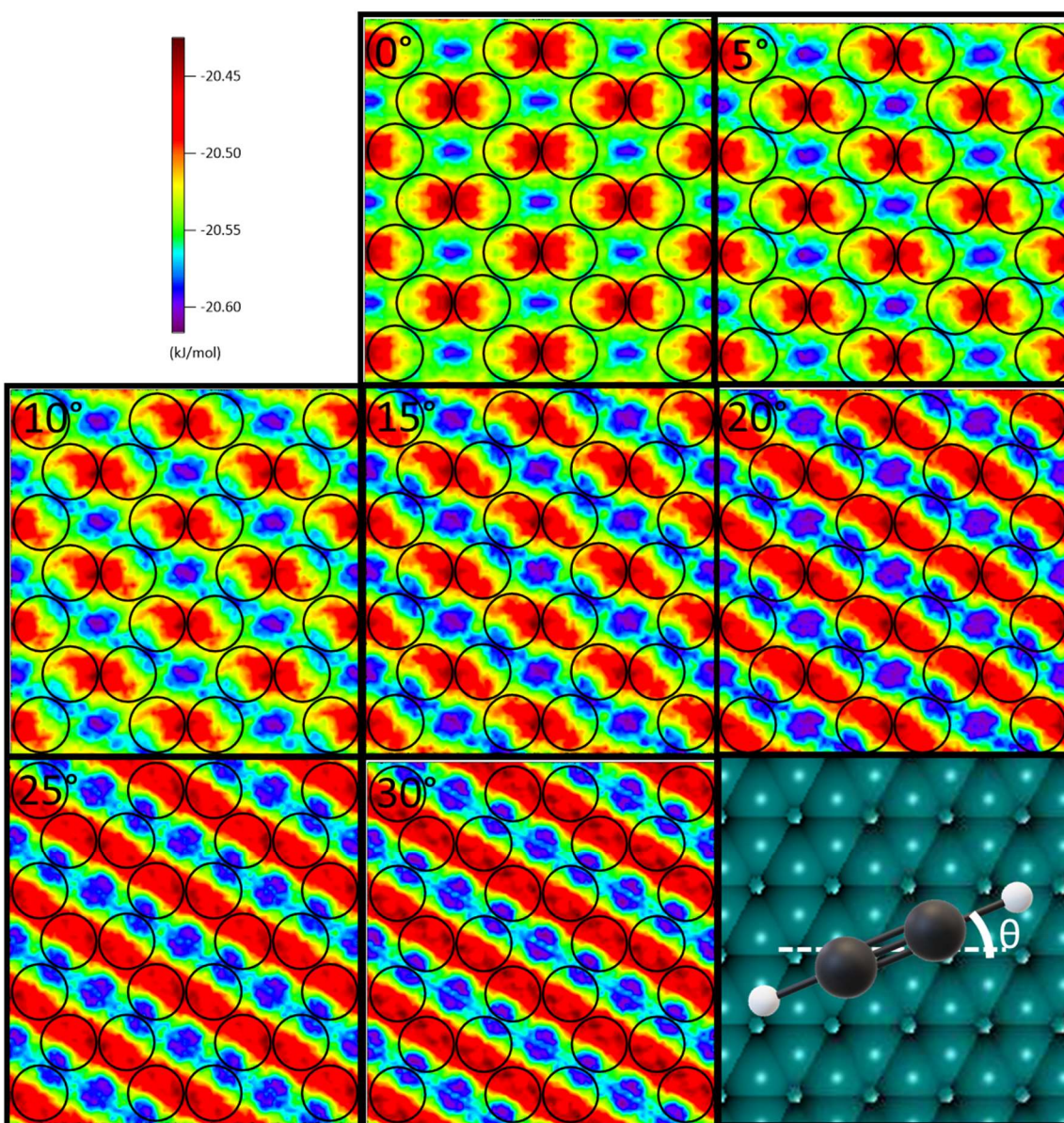


Figure 4.2: Calculated surface corrugations for acetylene and graphite

marginally. The reason for this discrepancy is not clear, but it is possible that further considerations were made in their work that were not specifically mentioned in the publication.

The second round of investigations into the applications of other literature-derived potentials for acetylene to two-dimensional films consisted of two forms of calculations being made using codes programmed in Wavemetric's Igor Pro 8.0 in order to analyze two important aspects of the two-dimensional system for several permutations of alternative force fields. The first of these were simple potential energy calculations based on the orientation of molecules within a two-molecule unit cell that was specified as an input. These calculations determined the potential energy for all orientations of each of the two unique molecules and created a contour plot of these data. These calculations only considered the molecule-molecule interactions and did not include any effect of surface corrugation. Insufficient information was available to include any anisotropic effects of surface images from substrate induction effects.

In general, the van der Waals potentials behaved similarly for all models attempted except in the case of the damped, which resulted in significantly higher attractive energies and a flatter potential energy surface. The first effect of note can be seen by looking at the angular energy dependence of the dimers. Figure 4.3 shows contour maps of these dimers as a function of the two molecular angles, which are representative of the cases examined. The angles are rotated by -45° to match angle convention that will be used for calculations of the whole unit cell. All use a 10^{-4} Lennard Jones potential "WL2¹⁰⁷" and examine several different quadrupole approximations for the same quadrupole moment (7.2 D Å). The 5-point charge distribution represents the inclusion of the hexadecapole moment calculated from SCF calculations. The most striking feature of these calculations was that none of them place a minimum exactly at perpendicular angles for the free dimers, which is not in keeping with experimental observations. As this represents the upper limit of reported quadrupole values for the molecule, this demonstrates a potential weakness in these models.

Tests were also done to examine the molecular angles when confined in the expected unit cells. For these trials, the electrostatic moment was treated using 4 point charges in all cases, since this the only possibility that could be employed for use in Materials Studio. The results for the square-T cell using the WL2 van der Waals parameters are shown in figure 4.4. When using

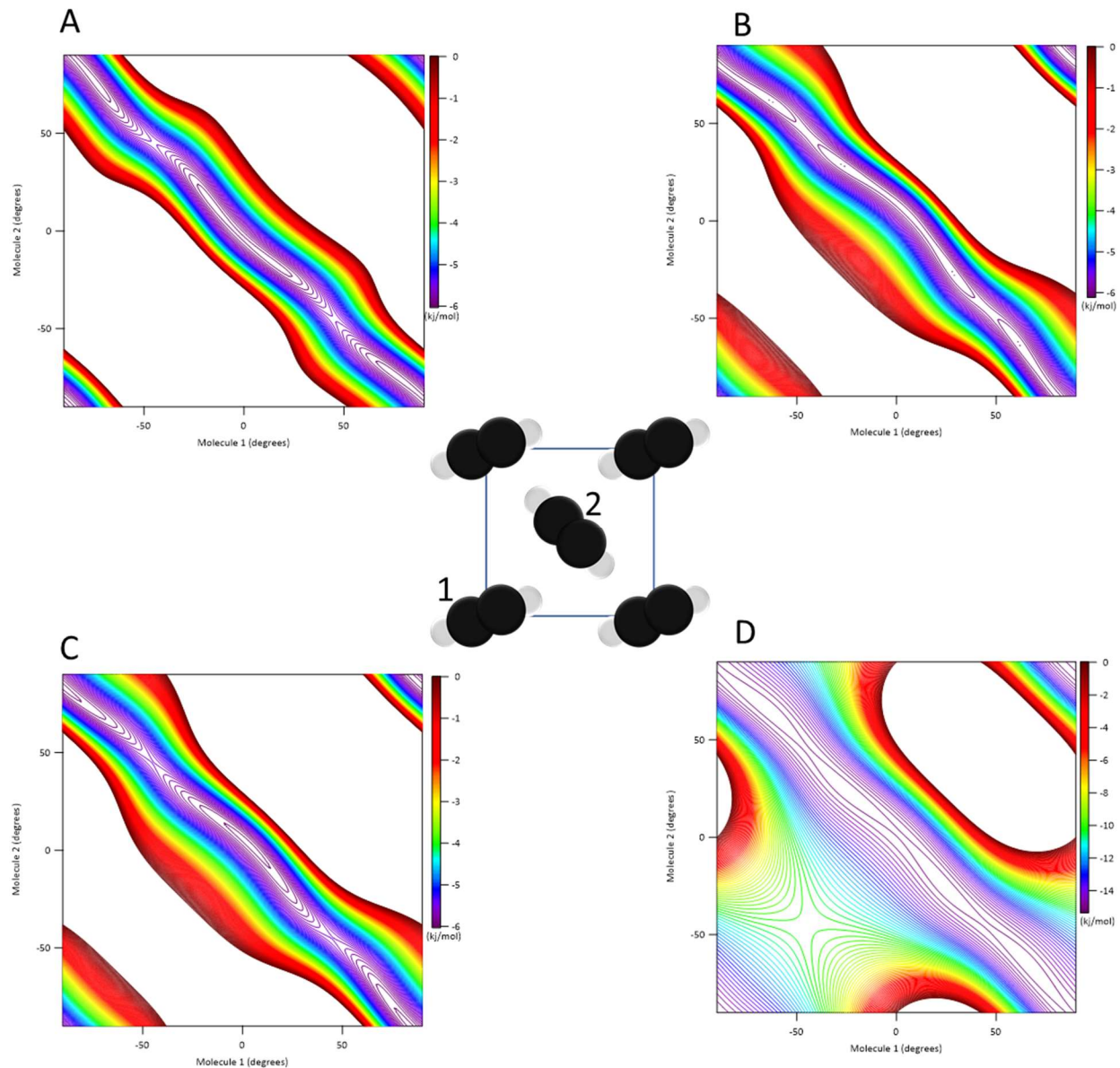


Figure 4.3: Potential Energy of dimer pair in a square-T lattice

A) Point quadrupole

B) Four point charges

C) Five Point charges

D) Damped Morse oscillator

Middle: Lattice considered for these calculations, specifying molecule numbers. Angles were defined by rotation away from the direction of the horizontal lattice vector

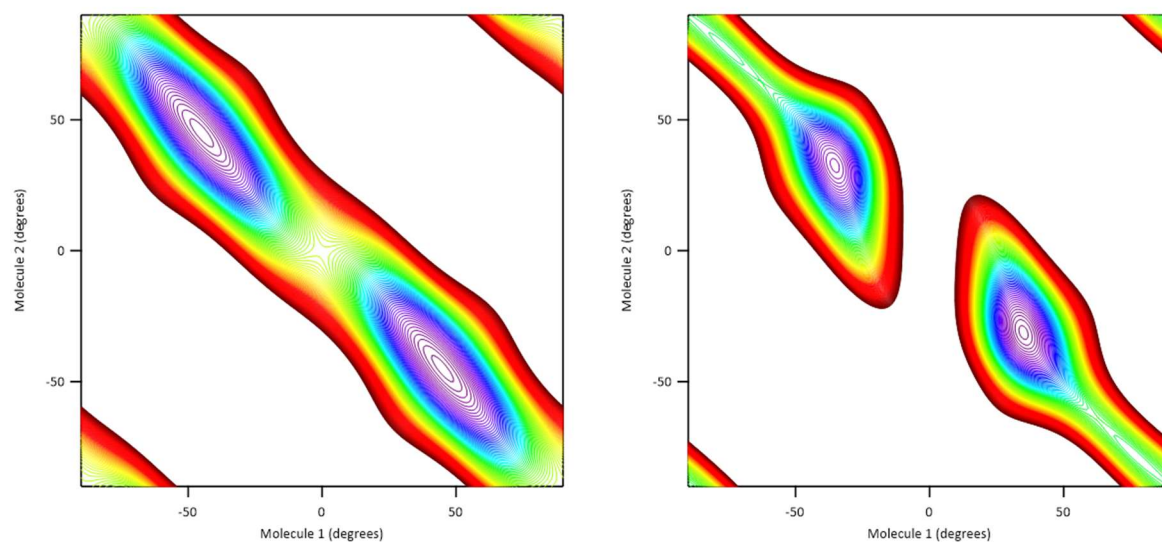


Figure 4.4: Orientational potential energy calculations for (left) square-T and (right) rectangular liquid phase

the default point charges assigned by COMPASS, instead of a single minimum at perpendicular angles along the diagonal to the unit cell, two minima occur for angle pairing on either side with a saddle point where the minimum should occur. This feature persisted with increased point charges until finally merging into the T-shaped minimum at a charge of 0.280 e^- . For the bond-ordered liquid unit cell, and the tentative assignments of the other unit cells, further difficulties arose. With point charges used of 0.298 e^- and 0.312 e^- , results were produced for the minima within a few degrees of each other. Unfortunately, the molecular angles were predicted between 30° and 40° and were symmetric (i.e. the same magnitude but opposite sign for the two distinct molecule types) for all rectangular and oblique unit cells (Figure 4.4). These angles did not produce fits that were in agreement with the neutron diffraction data available, which predicted asymmetric molecule angles, having magnitudes of $\sim 30^\circ$ for one molecule and $\sim 60^\circ$ for the other. The asymmetry of angles is a surprising result that could be attributable to the competition of the molecule-molecule and molecule-surface interactions which were not taken into account with these calculations. It is important to note that the angles suggested from the neutron data do show attempts to maintain the perpendicular orientations of the quadrupoles, indicating that it may be the molecule-molecule interactions themselves are the ailment of these calculations.

4.7 – Modifications to COMPASS Parameters

The results from the simple modeling studies all showed similar results based on the van der Waals potentials, but despite variations in quadrupole approximation and strength used, results proved inconsistent with the experimental data. These simple models were incomplete, however, and testing of force field variations in true molecular dynamics simulations was required. It was decided that COMPASS force field would continue to be used since the quadrupole behavior was the primary concern and, in general, the COMPASS potentials are good representations of hydrocarbon interactions. Three modifications were examined in these simulation trials: the first two were to increase the point charge assignments from their default setting of 0.223 e^- to 0.298 e^- and 0.312 e^- , and the third was based on the similarity of sp hybridized carbon's electronegativities to that of nitrogen's, and experimental evidence for weak hydrogen bonding present in condensed acetylene. For this modification, the atom type for the hydrogens was changed from "h1" (non-polar hydrogen) to "h1n" (polar hydrogen bonding to nitrogen/chlorine) and the partial charges were kept at the default 0.223 e^- . COMPASS does not

use an explicit hydrogen bond potential, however, and hydrogen bond effects were made by adjustments to the Lennard-Jones parameters. All bonding parameters for these two atom types are identical in the force field, and only the non-bond interactions were different.

The first trials were run for each variant at approximately 0.7 MLE coverage. Following completion of the temperature series for each pair, the structural results were compared. All three variants successfully produced the square-T unit cell at low temperatures, demonstrating immediate improvement over the force field default settings. However, the “h1n” type simulations produced a nearest neighbor distance of 4.21 Å, representing a significant error compared to the experimental range, 4.35 Å to 4.40 Å. The two modified quadrupole simulations were more consistent with this molecule spacing and were used moving forward with simulations at other coverages, while the “h1n” type modification was abandoned from further study.

From these two remaining modified systems, the results were not in either case a completely perfect fit for the experimental data. Regardless, when these results were examined holistically in combination with the default force field results, clear patterns emerged as a function of the quadrupole strength. The increase in quadrupole strength leads to the formation of a square-T solid phase at lower coverages and a herringbone phase at higher coverages. An oblique phase was observable as well, but the coverage this occurred with amplified with increasing quadrupole strength. For analogous coverages between the completion of C-step and the oblique coverage level, the system showed the rectangular herringbone phase. After islands began to form in the second layer, the oblique lattice was destroyed, and a reentrant rectangular phase was observed. The RDF analysis showed a nearest neighbor distance of 4.26 Å for high coverage solids and, in fact, a commensurate lattice for the rectangular phase. For low coverages, the square-T lattice had significant disorder that increased with quadrupole strength. The primary disordered components were bound 3-5 dislocations that would be consistent with KTHNY predictions for lattices with four coordinate bond orders, though the relative concentration at both quadrupole strengths was too high such that the ordered phase coherence length only extended a distance of several unit cells (even at 5 K). At higher temperatures, the films became floating and mobile while retaining the square bond order and coherence length, which eventually faded at another 30 to 40 K higher. The system maintained its ordered coherence length until the 100 K to 130 K range, where it transitioned into a disordered phase.

This phase did not show signs of the uniaxial commensurability of the experimental data; however, RDFs showed that while most ordered features were lost, the higher-order peaks corresponding to multiples of the square-T nearest neighbor distances were more pronounced at longer distances than any others. Transitory examples of one or two unit cells of a rectangular structure very close to the dimensions of the liquid phase structure from the neutron diffraction data were occasionally visible in the trajectories as well. A square-T phase with twisted molecule orientations and a low-density rectangular phase were also observed in coverage ranges near the lower half of the C-step, though this region contains no available experimental data for comparison. For relevant figures pertaining to these results, see the supplementals of the previous chapter.

4.8 – Conclusions

Though these simulations did not individually perform well to describe the experimental data, the corollaries that can be drawn from the trends discussed help provide some possible microscopic explanations of the film behaviors.

First, a low coverage square-T was observed that contained bound dislocation pairs. This phase melted within a 10 K window, and retention of the higher-order peaks of the square-T spacing and trajectories visualization demonstrate a tendency for quadrupolar ordering even in a disordered phase.

Oblique and rectangular structures were observed in ranges that were approximately in keeping with experimental ranges. Though the observed commensurability may not be in keeping with the available neutron data for such ranges, given the concerns of the quality of these data, it is possible that this is real, but equally possible to be an artifact of the simulations which also have quality issues. The formation of second layer islands and reentrance of the rectangular phases is consistent with the S_2 phase observation above the D sub-step coverages in the isotherms.

The full commensurability of the rectangular phase allows speculation of the mechanism driving the conversion to the oblique phase, which is uniaxially commensurate in the simulations. The lost surface registry and the quadrupole dependence on the observed coverage of this feature suggest that it is driven by the quadrupole interactions of the molecules, and would, therefore, demonstrate the frustration between the surface and the adfilm that persists in the

higher density phases. The formation of the rectangular phase before the oblique phase is uncertain due to the narrow coverage span between these two points and the lack of specific enough experimental data. Despite this, its commensurability and reentrant behavior with a second monolayer growth may suggest that the breakdown of the two-dimensionality of the quadrupole-quadrupole interactions brought about by the second layer result in less competitive molecule-molecule to molecule-surface interactions.

While it has not been possible to make any significant improvements in the correction of force fields to describe acetylene than any past attempts, the simple models employed did show the possibility for the failure in the approximations of the quadrupole moments. More sophisticated multipole expansion methods have been in some of the potential models found in the literature using distributions of point charges, dipoles, quadrupoles, and octupoles. Since the main focus was on a 4-point charge system that could be imported into Materials Studio, many of these were not tested except a single-point quadrupole and a 5-point charge distribution. Of note, these more complicated models have, in the past, encountered the same difficulties with bulk acetylene as many simple models. Therefore, it would have likely been no more reliable to use these models on the two-dimensional phases. It is hoped that in the future, an accurate and simple set of potentials may be developed that can be used to more accurately describe acetylene. The findings of this chapter showed that, while the force fields may not be perfect, looking at the behavior of the systems in the series of modified potentials still allows for connections to be drawn towards experimentally observed behavior.

Chapter 5 Chapter 5: Adsorption of Acetylene on MgO (100)

5.1 – Introduction

This chapter concerns the adsorption behavior for acetylene on the (100) surface of magnesium oxide powders. In contrast to the six-fold symmetry of the previous substrate, this surface is an archetype of a four-fold symmetric surface. Furthermore, the ionic nature of the substrate leads to a strong modulation of the surface potential. These symmetry and electrostatic effects lead to a surface that is well-suited for the quadrupole interactions of small molecules. In particular, the 2x2 is comprised of square lattices of alternating charges with lattice spacing of 5.96 Å. In the acetylene on graphite study, it was shown that the preferred spacing between molecular centers of mass had a spacing of 4.39 Å between nearest neighbors, consistent also with computational studies of acetylene dimers. Therefore, on MgO, the surface corrugation would create a spacing about 4% too small for the perfect square-T configuration to develop without strain. Two options would alleviate this strain: either the molecules being rotated somewhat relative to the molecular plane, or being rotated out of the plane. An incommensurate film would also be a possibility, but would not be reasonable to expect with the high electrostatic corrugation of the surface and the strong and similarly dimensioned quadrupole of acetylene.

Two previous studies in the literature examined this system. The first comprises LEED studies performed on films up to monolayer coverage below 90 K. This study identified a diffraction pattern consistent with a 2x2 commensurate film structure, but the data obtained could not be used to determine the molecular orientations. This same study also reported potential energy calculations for the adsorption behavior and reported a herringbone structure with the molecules rotated by approximately 20 degrees away from their perpendicular configuration. A separate study reported on neutron diffraction data taken from both monolayer and bilayer coverages. The investigators identified two diffraction peaks consistent with a square-T lattice for the monolayer film. The bilayer films showed similar diffraction behavior, with large diffraction peak broadening being indicative of an increase in disorder with second layer formation. This study only included two imprecise isotherm measurements, and leaves a large gap in the study of this system in the literature. The thermodynamics and phase behavior of the system have not been properly characterized outside of the LEED study, which were limited to temperature ranges too low for melting or critical transitions to be observable.

5.2 – Experimental

Isotherms were collected following the basic instrumentation and procedure outlined in Chapter 2. Isotherms were collected in a nominal range from 120 K to 200 K based on the pressure limitations of the instrument with acetylene. A 100 torr manometer was used for nearly all isotherms, which limited the upper reach in temperature obtainable. Below 128 K, a 1 torr manometer was used.

Computational studies were conducted on this system using the standard parameters of the COMPASS force field following the procedure outlined in Chapter 2. Force field variations were examined as well, in response to the poor performance with graphite. In this case, a magnification of the quadrupole-surface interactions resulted that were not physically realistic in nature. The single molecule energy minimizations were conducted using a 12.63 Å x 12.36 Å surface that was five atoms thick, with a vertical simulation space of 58.42 Å. Molecular dynamics simulations were run in three coverage regimes check. The simulated surface was 42.11 Å x 42.11 Å with a five-atom thickness and a vertical height of 108.42 Å.

Previously collected neutron diffraction data for use in this study were collected at both the HFBR and HFIR facilities. Unfortunately, quality of data for both sets was poor due to subtraction issues of the substrate backgrounds. A proper analysis of these diffraction data was discontinued for this system.

5.3 – Results and Discussion

The following results track the thermodynamic and computational studies for acetylene on MgO. The behavior is, as expected, starkly different to that of the graphite substrate and, in appearance, seems far simpler. Nonetheless, these data do show adsorption characteristics that are interesting, if not entirely unusual for adsorbed systems. Recorded isotherms show all three types of wetting present across a wide range of temperatures and a complete lack of asymptotic behavior before reaching the saturated vapor pressure. Molecular dynamics simulations support the 2x2 commensurate square-T structure on the first layer, with a more disordered film structure in the second monolayer. A comparison to the system of acetylene on graphite will be discussed and a tentative phase diagram is suggested shortly to follow.

5.3.1- Thermodynamics Results

A total of 45 Isotherms were analyzed in a range of $121.26\text{ K} < T(\text{K}) < 201.58\text{ K}$. Raw isotherm data were collected and adjusted for dead space volume, which were then interpolated to obtain smooth fits of the isotherm profiles. The general appearance of the isotherms remained constant over the entire temperature range and consisted of a sharp, well-defined first monolayer step at low pressures, a broad second-layer step occurring around 85% of saturated vapor pressure, followed with the isotherm reaching a plateau and remaining nearly flat until the saturated vapor pressure was achieved, and further where the isotherm displayed a sharp verticality (Figure 5.1). Within the data resolution of the instrument, this last transition was not preceded by any asymptotic behavior or upward curvature. The transition between the two-dimensional and three-dimensional phases appears to happen all at once, rather than in a discrete step-wise fashion or gradual convergence typically seen in isotherms. In a single isotherm, therefore, there is generally complete wetting of the first layer, incomplete wetting of the second layer, and non-wetting bulk condensation.

This unusual behavior of the system at the saturated vapor pressure warranted further investigation to eliminate the possibility of this being an artifact of instrument configuration. If indeed this were a false behavior, the most likely culprit would be a cold spot in the sample cell or capillary. This would cause abrupt condensation of gas on the metal wall and lead to bulk condensation before the completion of the isotherm. The isotherms were conducted on two different isotherm stations, using three different displaces with more than one heater configuration for one of these, employing multiple MgO samples, and including the replacement of a steel inlet capillary. While some of these changes were made due to instrument breakdowns, and not directly as part of investigating cold spots, the sheer number of these variations would seem to rule out the possibility of the isotherm profile being an artifact of the configuration.

A more detailed image of the full range of isotherm behavior can be seen in Figure 5.2. At 127 K and below, the first monolayer step is noticeably broader than at higher temperatures, with less definition at both the bottom and top of the isotherm step. The plateau region that follows is also notably less level, demonstrating that some degree of incomplete wetting occurs below this temperature. The characteristics of the second layer step are not distinguishably different from those at higher temperature, however, it is important to note that for the

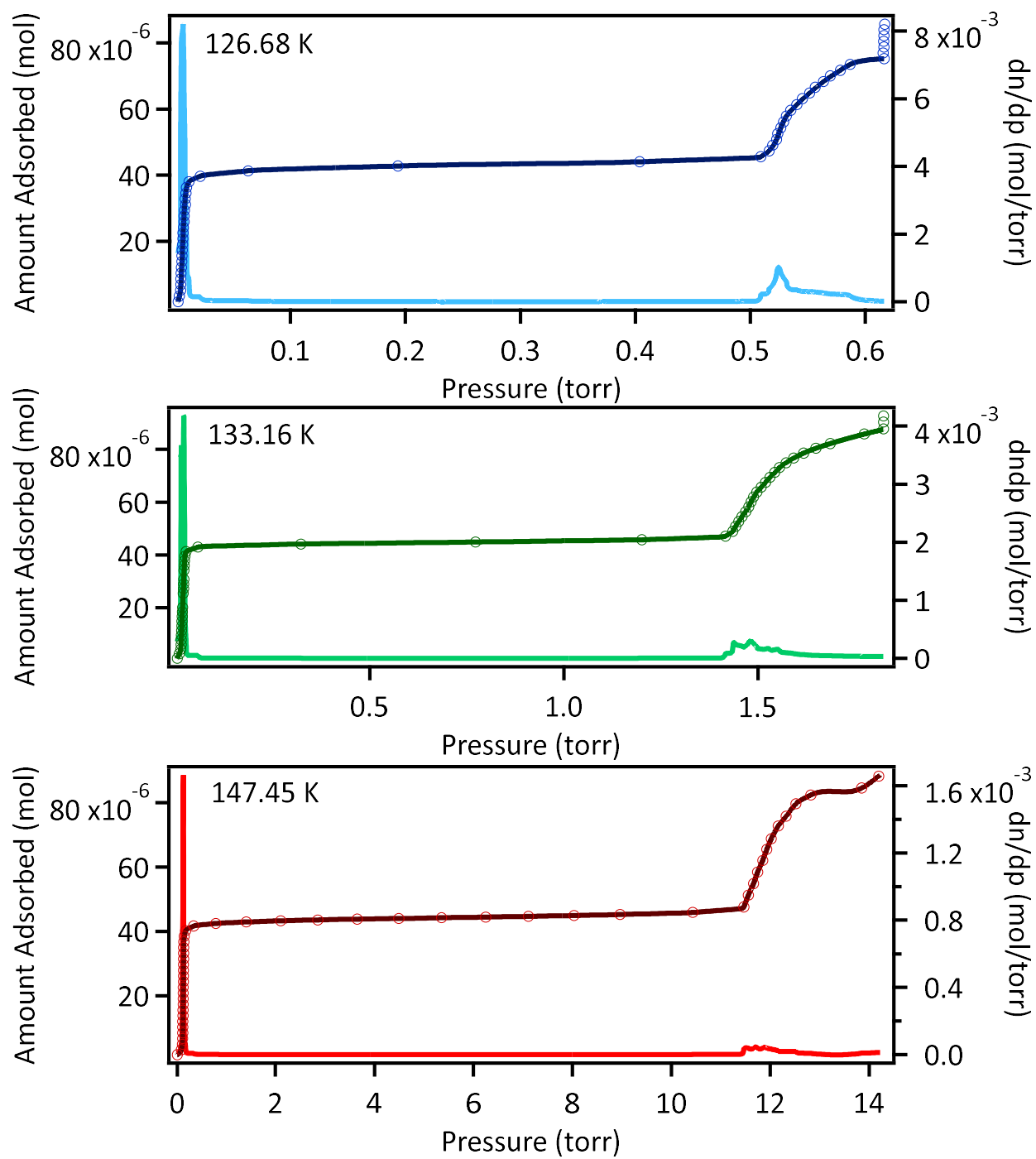


Figure 5.1: Selected Isotherms for acetylene on MgO

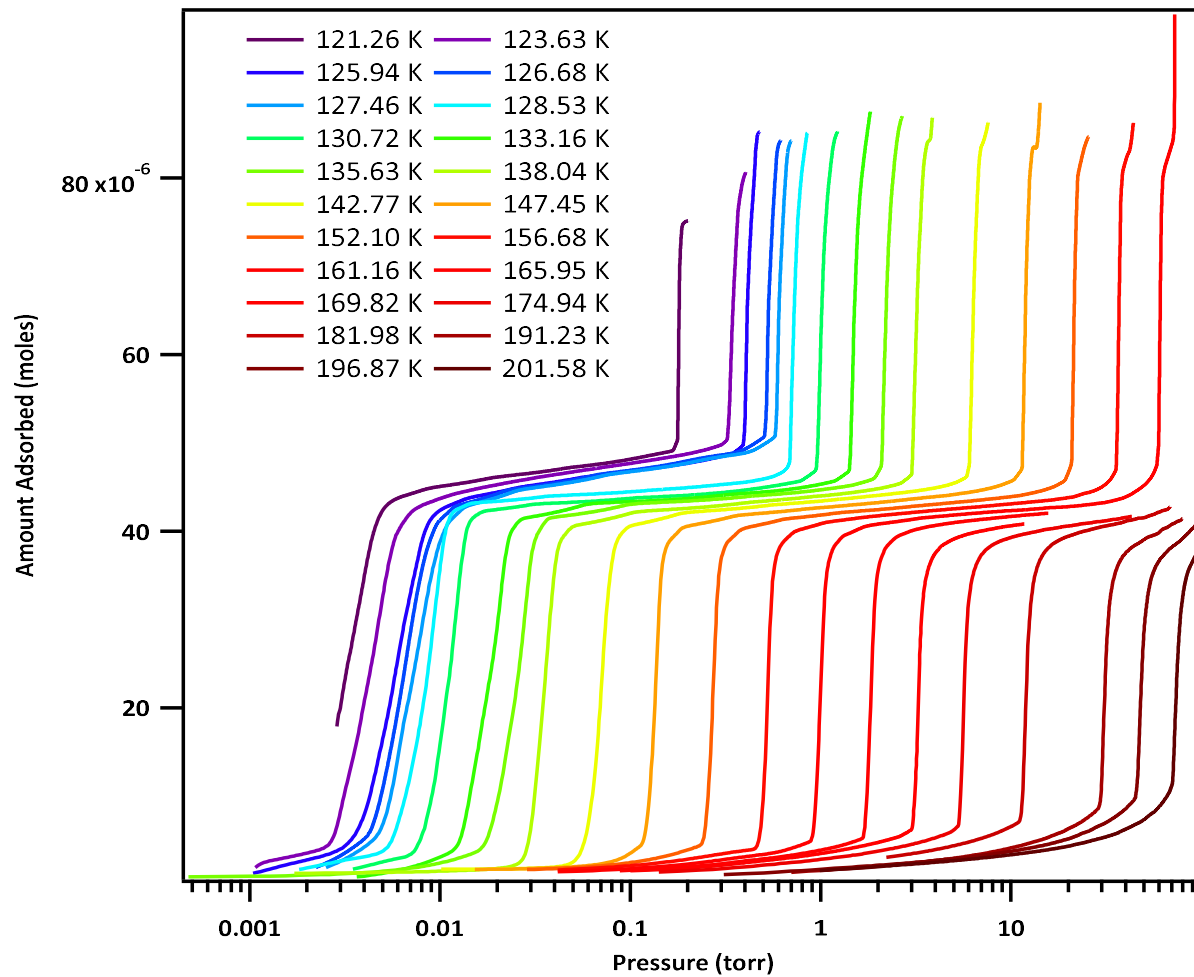


Figure 5.2: Full range of isotherms for acetylene on MgO

measurement process, the equilibrium of the second layering transition was very unstable, and in most instances prematurely converted to bulk condensation before the monolayer step was completed. The entirety of the feature could only be obtained if very small gas doses were applied and very strict convergence tolerances were used to determine equilibrium. At these temperatures, equilibration times were distinctly longer than those at higher temperatures.

At 128 K and above, the upper limits of the first step are much more distinctly defined and the levelness that follows indicates a noticeable change in the wetting behavior. The lower half of the first monolayer still lacks clear definition. The second layer appears the same as before, but the kinetics of its equilibration are significantly more stable. A change in the isotherm behavior occurs at 147 K, where the definition of the phase boundary at the lower-half of the first layer becomes much clearer. The trend that these phase boundaries follow from this point onward are suggestive of a liquid phase present in this range.

The thermodynamics of the adsorption process were obtained using the Clausius-Clapeyron analysis shown in Figure 5.3 and which are compiled in table 5.1. This table also contains the average areas per molecule for each phase and distinct region obtained using a point B analysis in comparison to methane isotherms conducted at 77 K. In the figure, the slopes of the data points in the first monolayer are distinctly divided into two regions. The intersection point of these lines occurs at 140 K. The positive sign of the differential enthalpy and small heat of adsorption in the low temperature region indicate that the formation of the monolayer is not enthalpically favorable and is instead driven by the large associated entropy. This suggests the film may have a high degree of disorder structure. For higher temperatures, this inverts, and the differential enthalpy becomes highly favorable, with a significant decrease in the differential entropy. This would lead one to the conclusion that the system undergoes a transition from a low temperature phase of disorder to a higher temperature, more ordered phase. Such a conclusion is against expectations, but without more detailed structural data than is available, it is not possible to draw any definitive answers as to the exact origins of these observations. The second phase is noteworthy in its thermodynamic similarities to the bulk condensed phase. This may provide part of the explanation for the difficulties in equilibration of the second layering step at low temperatures.

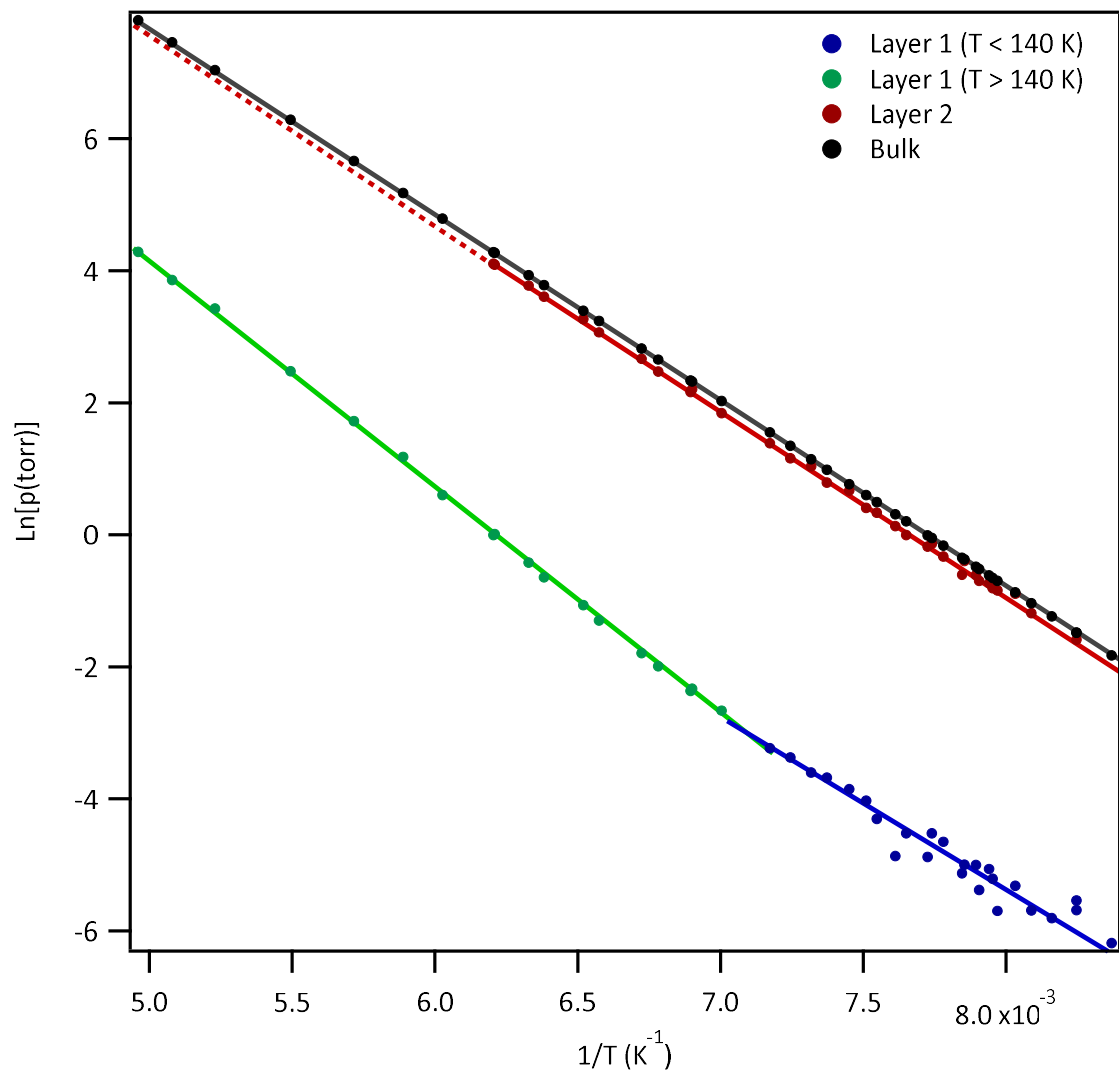


Figure 5.3: Clausius-Clapeyron plot for acetylene on MgO

Table 5.1: Thermodynamic results for acetylene on MgO

layer	APM $\text{\AA}^2$	$A^{(n)}$	$B^{(n)}$	ΔH kJ mol^{-1}	ΔS $\text{J mol}^{-1} \text{K}^{-1}$	Q_{ads} $\text{J mol}^{-1} \text{K}^{-1}$
1 (low Temp)	17.96	2433.4	14.136	3.239134	63.7185	20.23129
1 (high Temp)	18.54	3442.8	21.382	-5.15302	3.475252	28.62344
2	9.59	2801.2	21.488	0.181245	2.593968	23.28918
bulk		2823	21.8			23.47042

Figure 5.4 shows selected isotherms plotted as a function of the chemical potential. There is a noticeable evolution in the free energy of the adsorption process that occurs at low temperature up to approximately 140 K, following which the process halts and the chemical potential remains relatively constant as the temperature further increases. This reflects the behavior witnessed in the Clausius-Clapeyron analysis. The free energy becomes more negative with increasing temperature, showing that for the low temperature region, the monolayer formation becomes gradually more favorable until it reaches the transition temperature.

The Isosteric heats of adsorption were calculated from the isotherms for two temperatures, 134.39 K and 146.25 K (Figure 5.5). These calculated isosteres are an approximation of the true quantity, and calculated by two isotherms closely spaced in temperature. This thermodynamic relationship is an expression of the energy requirement for a molecule to move into the adsorbed phase from the vapor phase at constant coverage, convention however has it defined in such a way that the heats of adsorption are positive values, even though adsorption is exothermic. In another sense it might be alternatively defined as the isosteric heat of desorption, as from this reversed frame of reference, the sign convention is more consistent with the name. Through interpolation, isotherms can be used to calculate this quantity as a function of the amount adsorbed, rather than simply for the single fixed point that defines the layer transition used to calculate the previous energies. This provides indications of the thermodynamic evolution of a layering process as it progresses. It also is useful as a gauge to identify completed layering transitions and possible points of phase transitions in the film. The focus of the analysis was around the possible transition points noted earlier. It was not possible to obtain meaningful data from isosteres below 128 K however, the low pressures of the first layer step, and the instability of the second layer in this region introduced too much variance in closely spaced isotherms for viable analysis. The temperatures obtained however do fall on either side of the thermodynamic discontinuity observed in the first layer in the Clausius-Clapeyron. Of note in the behavior of the isosteres presented is the divergent behavior approaching zero coverage, and for the 146.25 K isostere, the strange drop and jump between the two layers. These are artifacts of the interpolation process required to enforce the constant coverage criteria. The former issue is caused by the sensitivity of the approximation in the so

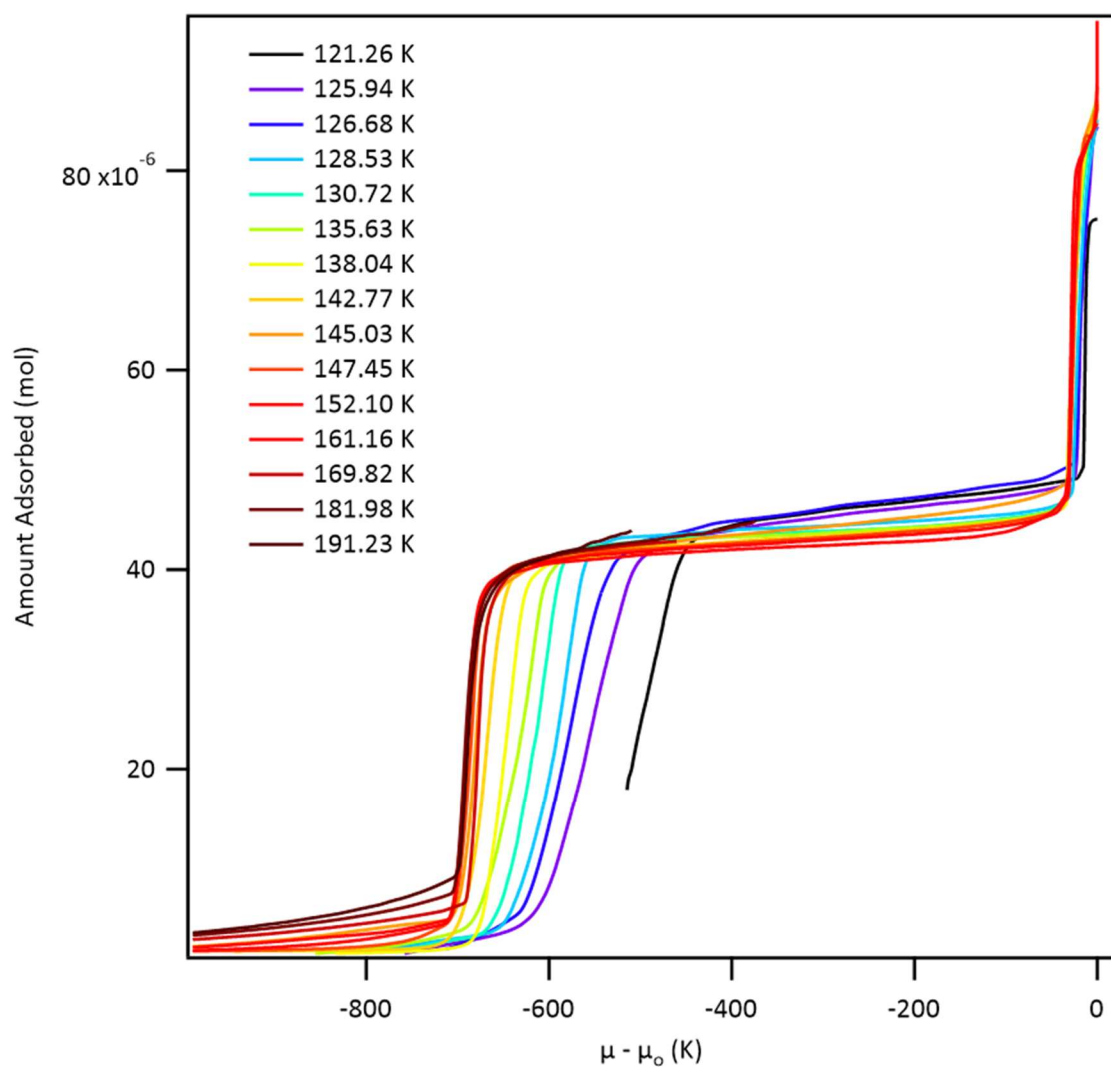


Figure 5.4: Isotherms plotted vs chemical potential for acetylene on MgO

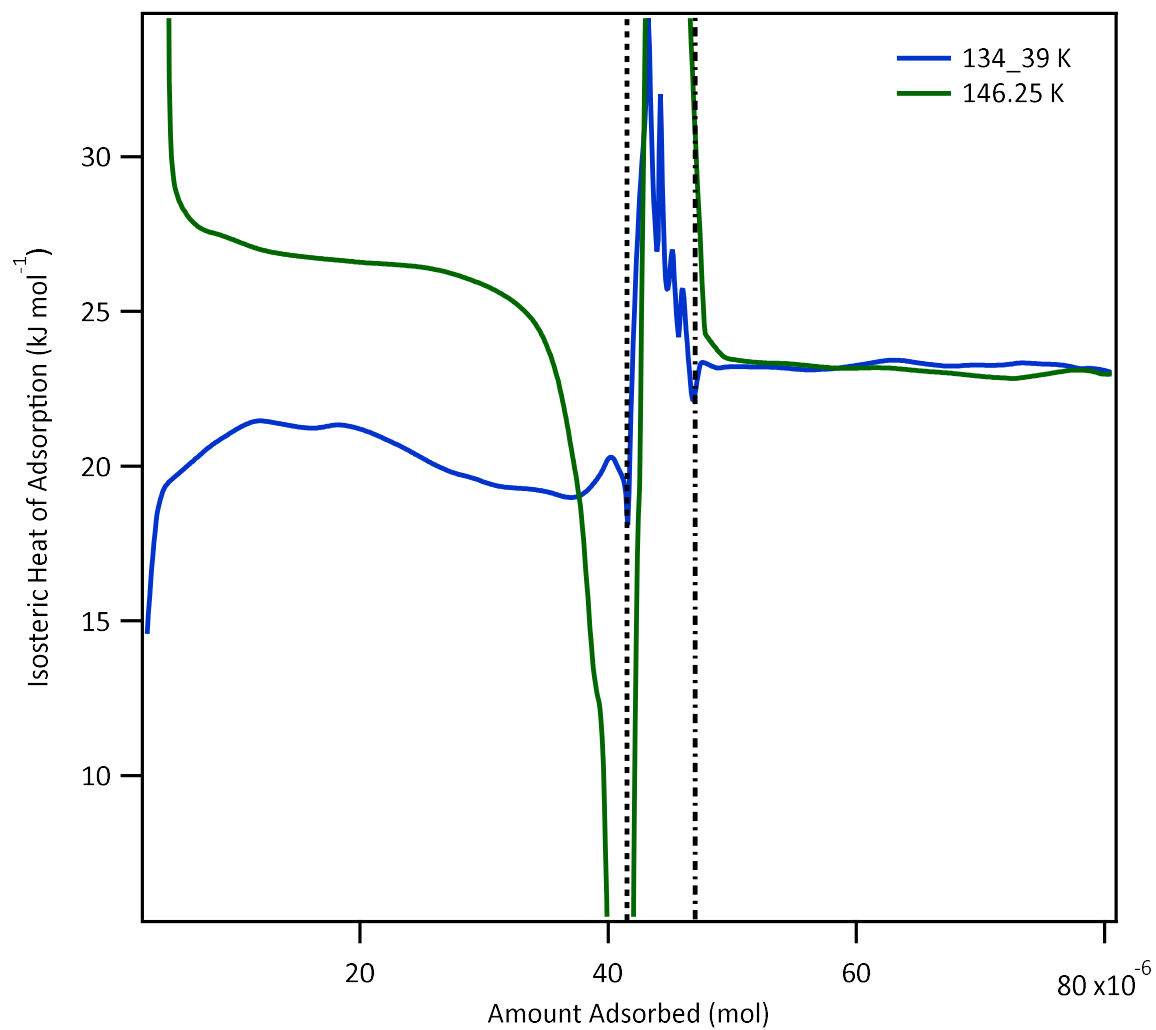


Figure 5.5: Isosteric heats of adsorption for selected temperatures of acetylene on MgO

called Henry's law regime to relatively small errors in measurement. The Henry's law constant discussed below is in effect the isotheric heat in the limit of zero coverage, so information in this region is still obtained. The latter case however was the result of small deviations in two consecutive isotherm points at the beginning of the first layering plateau. The regions corresponding to the formations of the first and second layers was reliably fit for both isosteres. The first layer shows the most significant differences in behavior, with an average value of approximately 20 kJ mol^{-1} at 136 K and 27.5 kJ mol^{-1} at 146 K. This is consistent with the changes in heats of adsorption observed in the Clausius-Clapeyron analysis. While both of these show a stark difference from the bulk heat of condensation of $\sim 23 \text{ kJ mol}^{-1}$, the second layer shows consistency at both temperatures and is consistent with the bulk value.

The Henry's law heat of adsorption was determined to be $26.367 \text{ kJ mol}^{-1}$ from the slopes of the isotherm data in the linear (horizontal) region preceding the first step (Figure 5.6). This analysis assumes both a lack of molecule-molecule interactions and that only normal physical adsorption forces are present in the limit of low pressure. The first of these assumptions is generally valid, though clustering is possible even at low coverages, but the second assumption precludes the possibility of binding to defect sites on the surface. The MgO used in this study is known for its high surface quality, and samples from more than one synthesis batch were used. The variance in the data reported is the result of the few number of data points recordable in the Henry's law region and showed no dependence on substrate sample. No discernable difference was evident in the trends between substrate samples. It is therefore likely that surface defects were not a major component of this data, though the possibility cannot be eliminated. Furthermore, clustering would not be expected with the influence of such a strong and heavily corrugated surface potential.

To probe and quantify the apparent transitions of the system more thoroughly, the evolution of derivative peak widths was used as a function of temperature. The widths of the two-dimensional compressibility is generally the more proper choice to use; however, for this system, the monolayer step occurred at very low pressure, making the compressibility very sensitive to the noise in the pressure and the amount adsorbed at very low coverages ($K_{2D} \propto (p/n^2)(dn/dp)$). A well-behaved, representative temperature selection of two-dimensional compressibilities as a function of chemical potential is given in Figure 5.7. The trend clearly shows

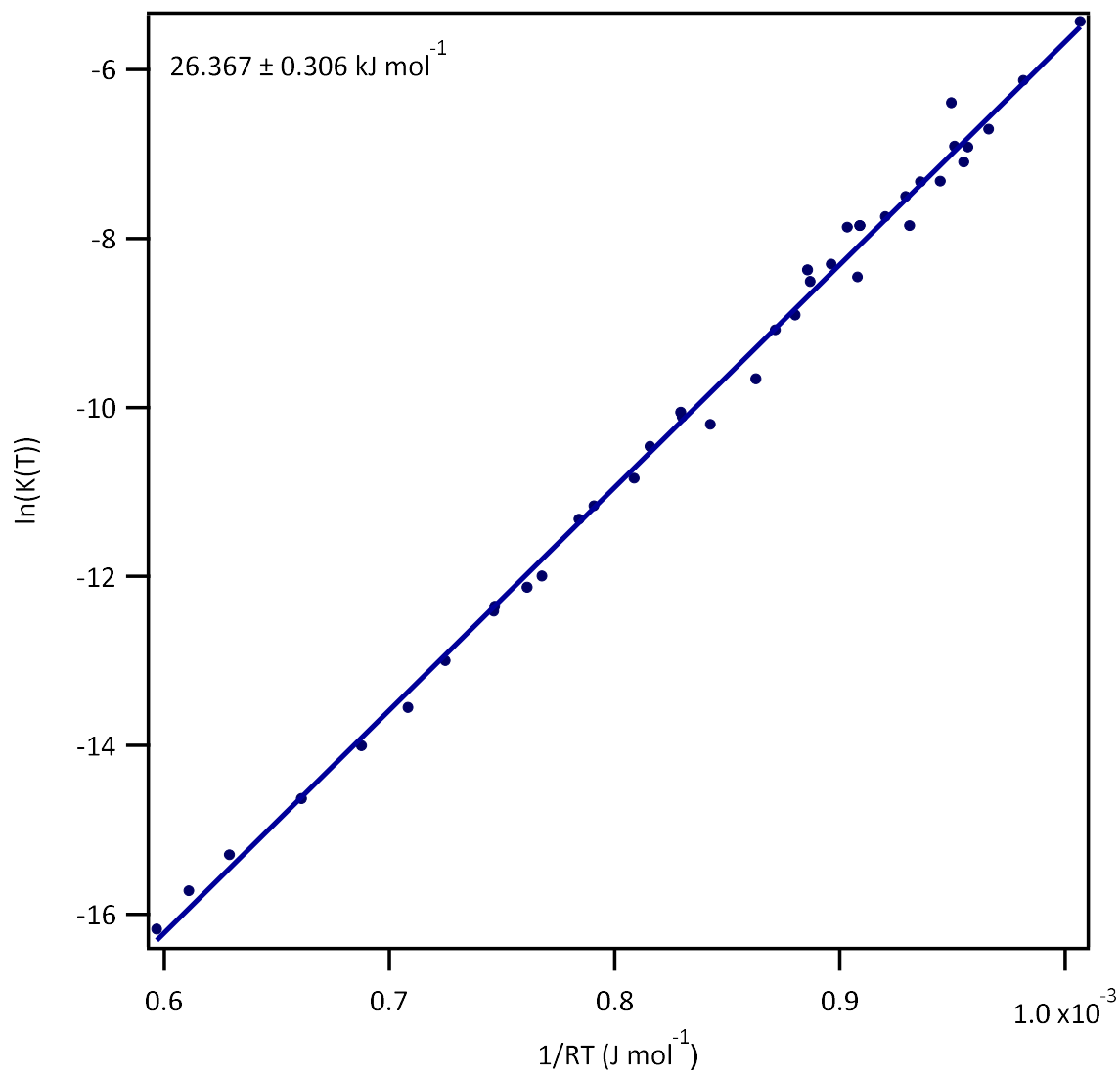


Figure 5.6: Henry's Law plot for acetylene on MgO

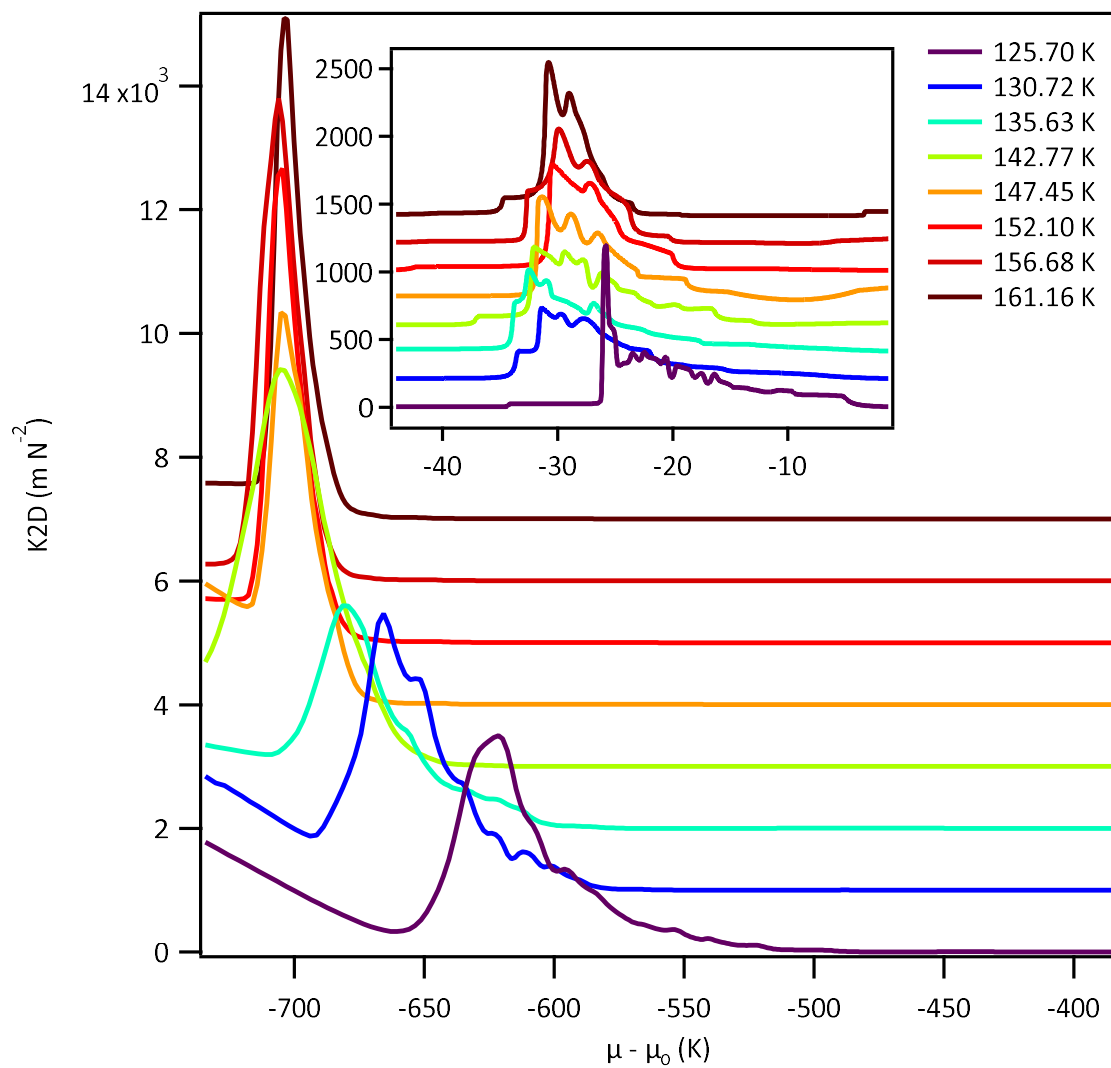


Figure 5.7: Isothermal compressibilities for selected temperatures of acetylene on MgO

a gradual narrowing of width and rise of intensity up until 142 K, followed by a mostly static behavior thereafter. Of the 45 isotherms analyzed, unfortunately, most of the ones below 147 K were unusable for analysis. Instead, the peak widths of the derivatives as a function of the equilibrium pressure were associated with the shape of the compressibility function given by the mentioned proportionality. The derivatives for the same temperature series of isotherms as depicted in Figure 5.7 (for consistency) is given in Figure 5.8. Here, the derivatives are plotted versus the reduced pressure so the trend is more easily followed. The last point to highlight on both of the previous two figures is the behavior of the second monolayer at 125 K. Its shift in position compared with the rest was generally observable below 130 K, but is more likely owing to the previously mentioned instability in this transition and cannot be considered as significant

Figure 5.9 show the peak widths of the derivatives as a function of temperature for layers one and two, respectively. The trendlines isolate two points where these data suggest changes occur for the first layer, being at 133 K and 147 K. The second of these points aligns very well to the observations made earlier regarding the shapes of the isotherms' steps. The point at 133 K, though, does not align with the very obvious change in wetting behavior at 128 K. It is likely that analysis of the isotherms below this point were limited by the instrument resolution, and detectable changes below 133 K would not be possible. The clarity of the wetting transition in the isotherm data, however, justifies the temperature of 127 K as the transition point, and not 133 K. For the second layer, only one point, at 135 K, can be determined from the data.

5.3.2 – Computational Studies

The computational analysis of this system utilized the standard COMPASS force field parameters. Though the previous chapter showed that, for the system of graphite, these parameters were insufficient to correctly describe the observations of the molecular quadrupole-quadrupole interactions, trials were conducted with the same modifications that were more successful with graphite, but on MgO, these resulted in the molecules becoming bound and locked by the surface charges into solid phase at 300 K (~1.5 times the bulk triple point). While the modifications to the quadrupoles are most likely more accurate to describe the molecule-molecule interactions, as was seen on the smoothly corrugated surface of graphite, it seems in the case of MgO that they over-estimate the electrostatic molecule-surface interactions. This seems to be supported based on the assigned charges to the surface ions by COMPASS being

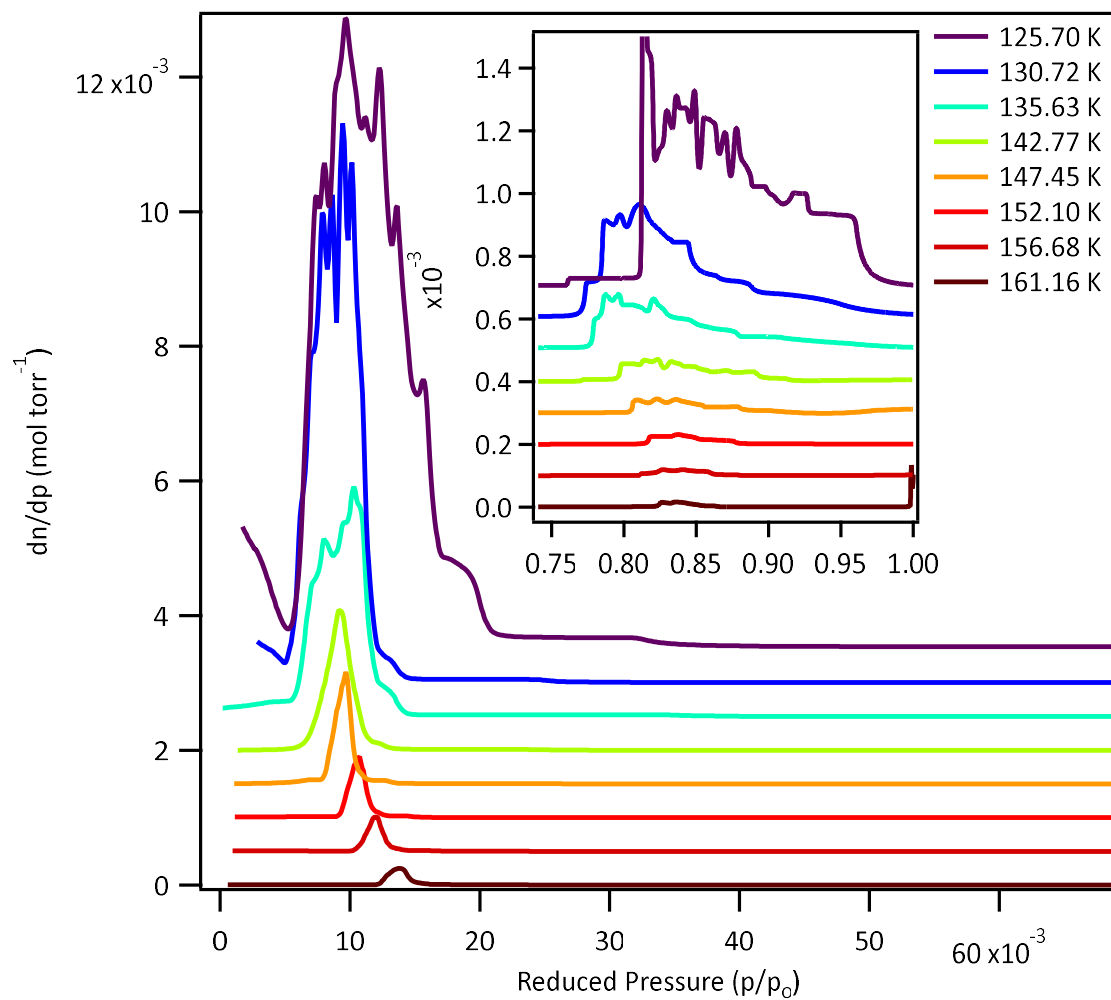


Figure 5.8: Figure 0.8: Plots of isotherm derivatives vs reduced pressure for selected temperature of acetylene on MgO

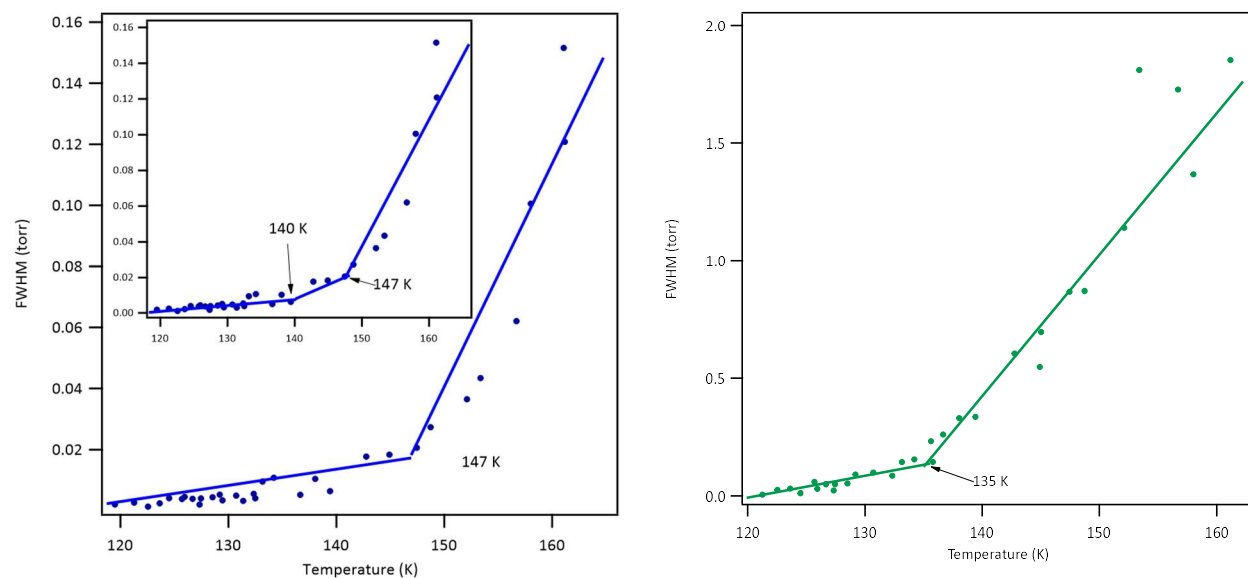


Figure 5.9: FWHM analysis for acetylene on MgO

left: FWHM for first layer step (note: the insert shows that lines fit to match the 140 K point observed in other data that may be possible, is not supported by the limits of these data)
right: FWHM for second layer step.

1.876 e^- . Previous theoretical work has estimated the effective ionic surface charge to be closer to 1.2 e^- . Time constraints prevented trials of adjusted quadrupole and surface charge parameters within this study. However, the standard force field assignments did produce reasonable behavior in the simulations conducted. It seems that the higher surface charge largely balanced out the weaker quadrupole interactions. The molecule-molecule interactions would still be an issue, however, as the molecule-molecule and molecule-surface interactions were cooperative for this system and the surface effect was significantly dominant, this would be less important than it was in the case with graphite.

5.3.2.1 – Energy Minimizations

The energy minimizations for single acetylene molecules were conducted in 5° rotation increments for all four high-symmetry sites of the surface. In all cases, the minimized configuration result was the same. The molecules displaced such that the centers of mass were positioned directly atop a magnesium atom center, with the molecules oriented to place the hydrogens over adjacent oxygen atoms (Figure 5.10). As was done with graphite, the substrate was removed and energy calculations were performed subsequently on solely the molecule in the absence of substrate. The resulting energy artifact from the 1-4 intramolecular interactions was then subtracted from the total non-bond energy from the original optimization output. The minimized binding energy was found to be -28.833 kJ mol⁻¹. This is 2 kJ mol⁻¹ larger than the results from the Henry's law analysis, and could be the result of the force field already discussed. The difficulty in determining intermolecular potentials accurately for any system though is always difficult, and these results are close the experimental values. The fact that all optimizations, irrespective of the original placement or relative orientations, converged to the same solution is not an unexpected outcome, but does serve to illustrate the strong potential gradient around this site and the depth of the surface corrugation.

5.3.2.2 – Molecular Dynamics Simulations

Molecular dynamics simulations were run at three different coverages corresponding to a sub monolayer film, monolayer film, and partial bilayer film. The monolayer structure for all three of these ranges was found to be the same regardless of the amount of molecules present,

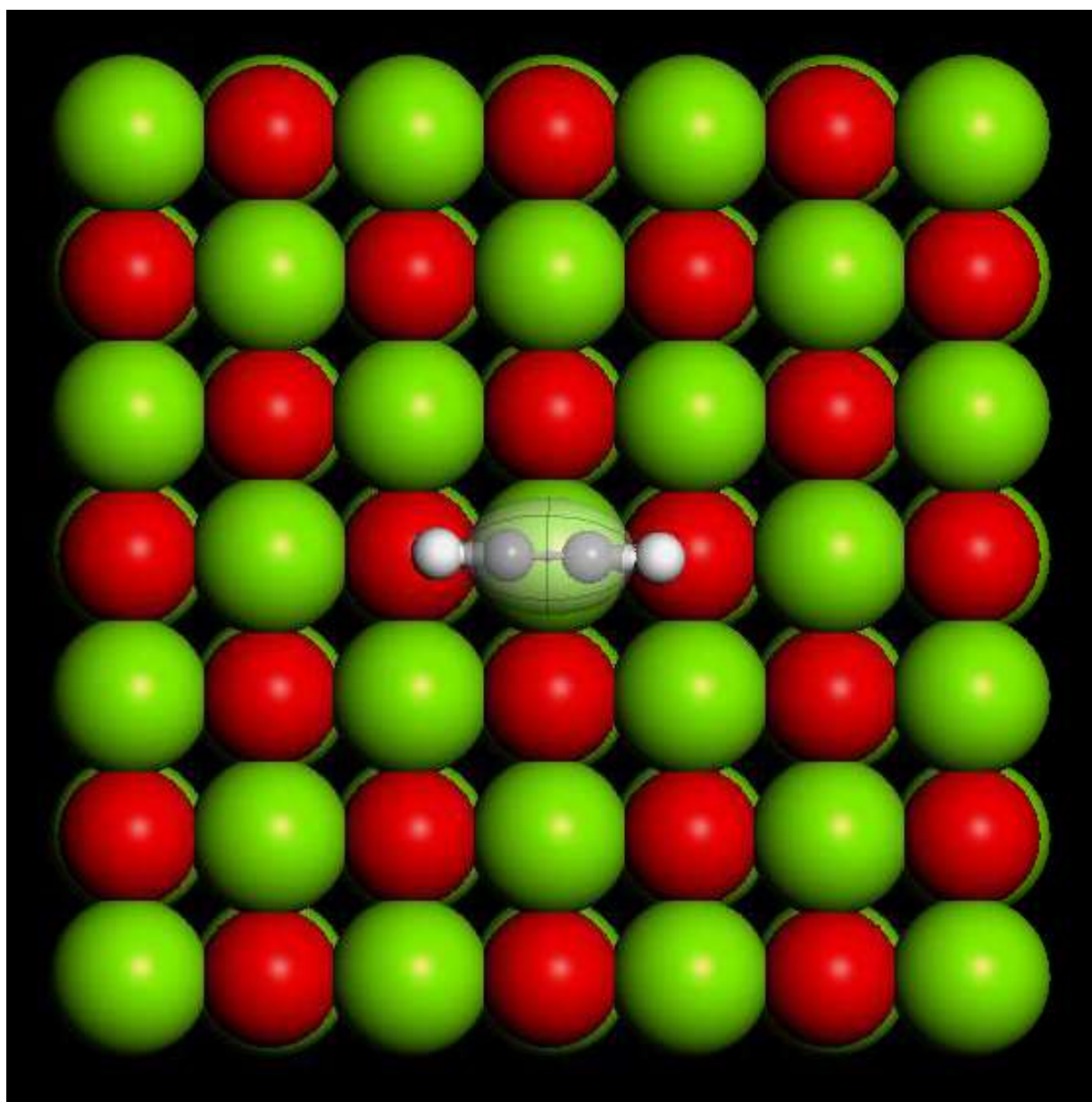


Figure 5.10: Minimum energy configuration for acetylene on MgO

which ultimately proved to be a 2x2 commensurate lattice in the square-T configuration. Figure 5.11 show trajectory snapshots for the three simulated coverages, each revealing the square-T arrangement. A fourth simulation result is also shown with the same number of molecules as the partial bilayer, but with the development of a striped phase instead. It is uncertain if this phase is the result of a false minimum from not allowing the simulations a long enough equilibration time at each temperature or if this is perhaps a real possibility for the system.

For all other simulations regardless of coverage, the 2x2 square-T phase with no significant in plane disorder was favored. The most significant aspect of the square-T phase is the out of plane disorder. In order to match the 2x2 registry with the surface, the molecules were required to tilt out of the plane approximately 10 to 15 degrees. This is most evident in the snapshots for the completed monolayer, it can be seen that along the vertical axis relative to the page, the tilt of the molecules are all aligned in the same direction, however along the perpendicular axis to this, the molecules in the same row tilt generally in the same direction, but there is not complete correlation of the tilt between rows.

The snapshot from the bilayer shows that the second layer of molecules contains a noticeably larger degree of disorder than the monolayer. The molecules in the second layer try to position themselves over the magnesium center that occupies the hollow site in the monolayer lattice. However, from this position there is not a way for the quadrupoles of molecules in the second layer to ever be fully optimized with those of the first. This leads to frustration of the lattice in the second layer, which is more weakly held in place by the surface, while the lattice of the first layer remains mostly unaffected.

Figures 5.12 and 5.13 show the temperature dependent radial distribution function and concentration profile normal to the surface. The radial distribution shows quite clearly that the long-range order of the system is maintained until the system is higher than 150 degrees. However, the disorder of the out of plane orientation decays much more rapidly with temperature, as seen in the concentration profiles. Furthermore, the most disordered of these peaks correspond to the atoms located farthest from the surface. The simulation results suggest that there is a stronger binding effect between the hydrogen atom proximal to the surface and the surface oxygen over which it sits. This atom therefore remains relatively fixed and acts as a pivot point for the out of plane libration. If the molecules reorient far enough, they will pivot

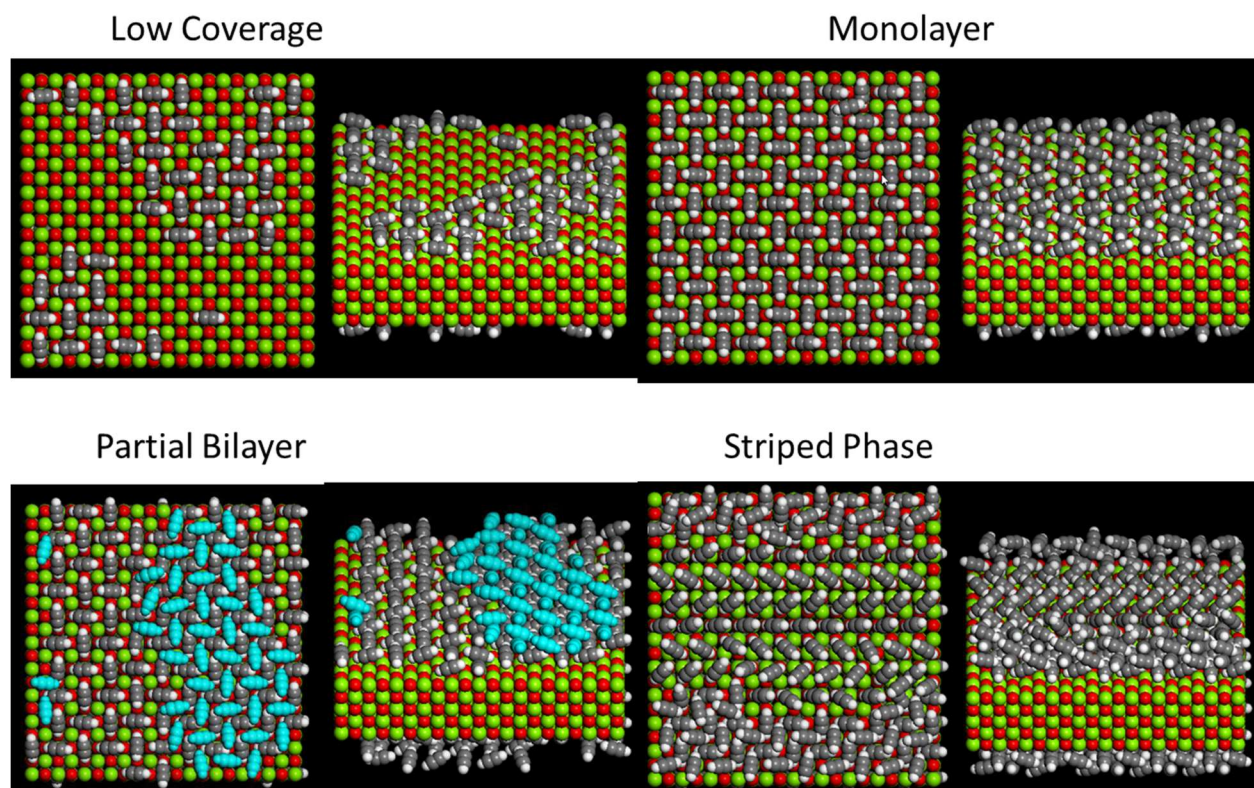


Figure 5.11: Simulation results for acetylene on MgO at varying coverages

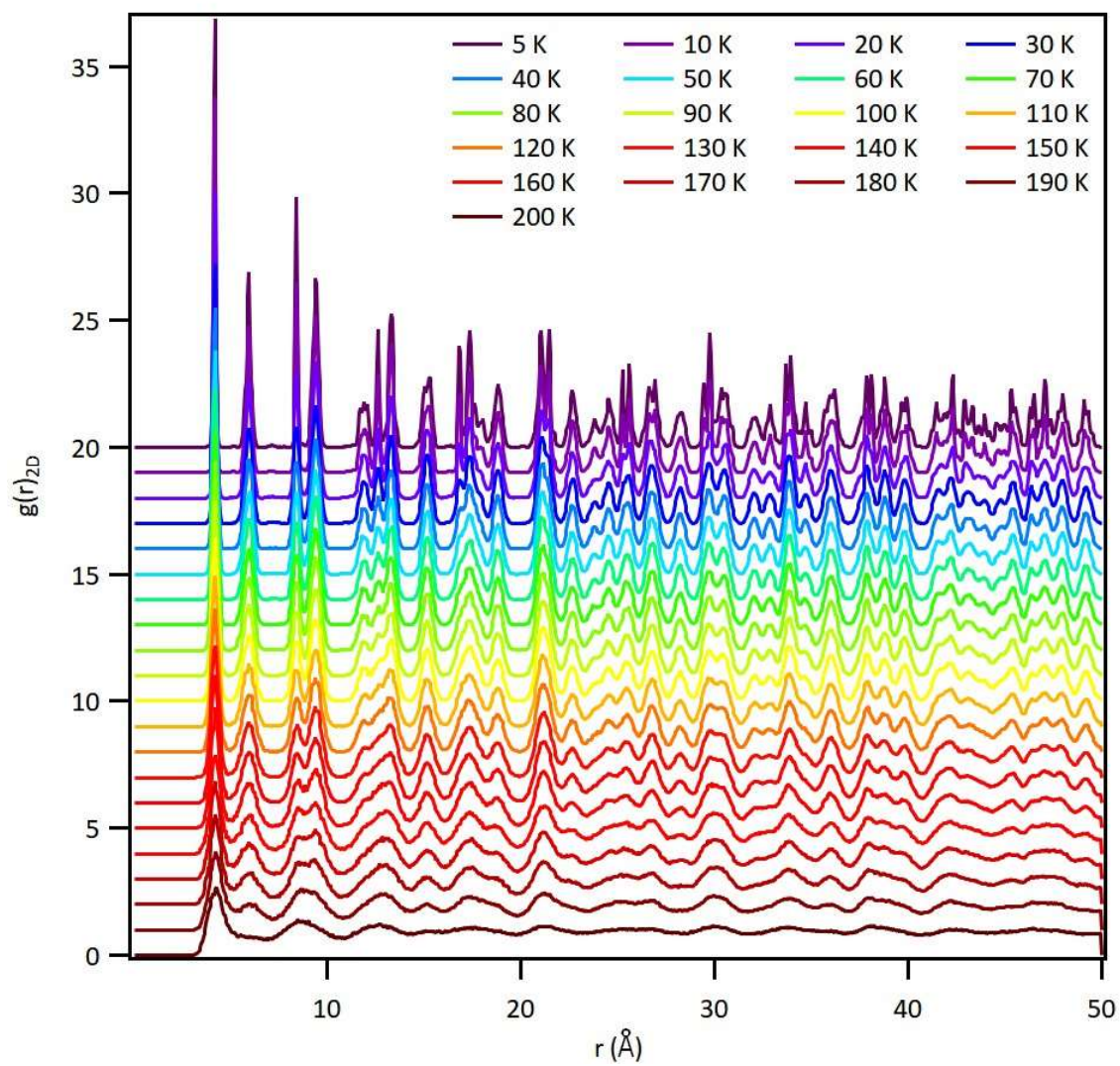


Figure 5.12: Radial distribution function for completed monolayer of acetylene on MgO

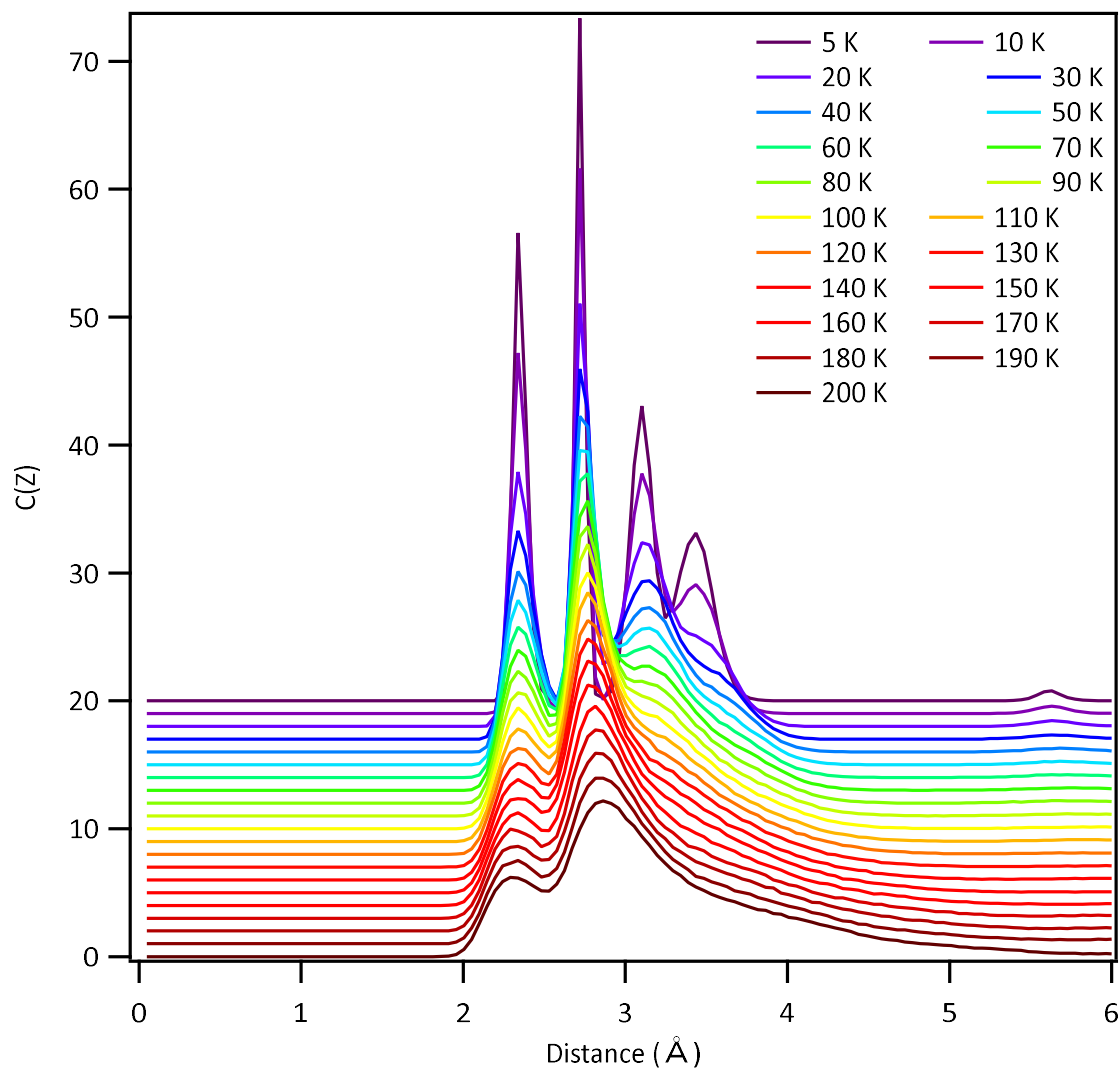


Figure 5.13: Concentration profiles for the completed monolayer of acetylene on MgO

around the center of mass, and the opposite hydrogen will quickly snap to the surface oxygen, rapidly reversing the molecular orientation.

Visual inspection of the snap shots over a range of temperatures show considerable in plane motion as well (Figure 5.14). This is a harmonic motion between the molecules of the lattice, and the molecules oscillated around their centers of mass, which remain relatively stationary. This motion is reminiscent of the those observed in model comprised of quadrupolar magnets fixed into a square lattice²²⁴. The fact the centers of mass remain stationary during this process demonstrates how strong the strong surface effect experienced by the molecules in these simulations

5.4 – Conclusions on the Adsorption of Acetylene on MgO

The (100) surface of MgO should be a nearly-perfect archetype for the optimization of a small, strong quadrupole, like acetylene. The simulation results support the relative ease with which the system rapidly and nearly universally adopts this arrangement. The out-of-plane “wagging” of the molecules around the hydrogen proximal to the surface show that out-of-plane disorder is more significant than the translational order of the monolayer lattice. Strong harmonic motions occur in the in-plane molecular orientations of the molecules, while the centers of mass remain stationary, as seen in the radial distribution functions for the centers of mass. The combination and amplitude of these motions do eventually overwhelm the lattice order with high enough temperatures, but the translational order can still be described as quasi-long range for a further 40° to 50° higher.

The behavior of the isotherms is even more surprising, with two potential continuous transitions identified for the first layer. Most surprisingly is that, in the low temperature isotherms where the surface corrugation and registry would be expected to bring about a highly ordered system, there seems to be highly enthalpically unfavorability and the behavior is driven by a large increase in entropy. The suggestion of significant disorder in the system at this point would seem to go against intuition. The lower of these two transitions appears to occur between 127 K to 128 K, placing it within one or two degrees of the observed lowest melting transition of acetylene on graphite, though if this is either a coincidence or implies a similar mechanism remains unclear. The higher temperature phase behaves much more as one would have expected, with a favorable enthalpy and a comparatively low entropy. Isotherms for the first

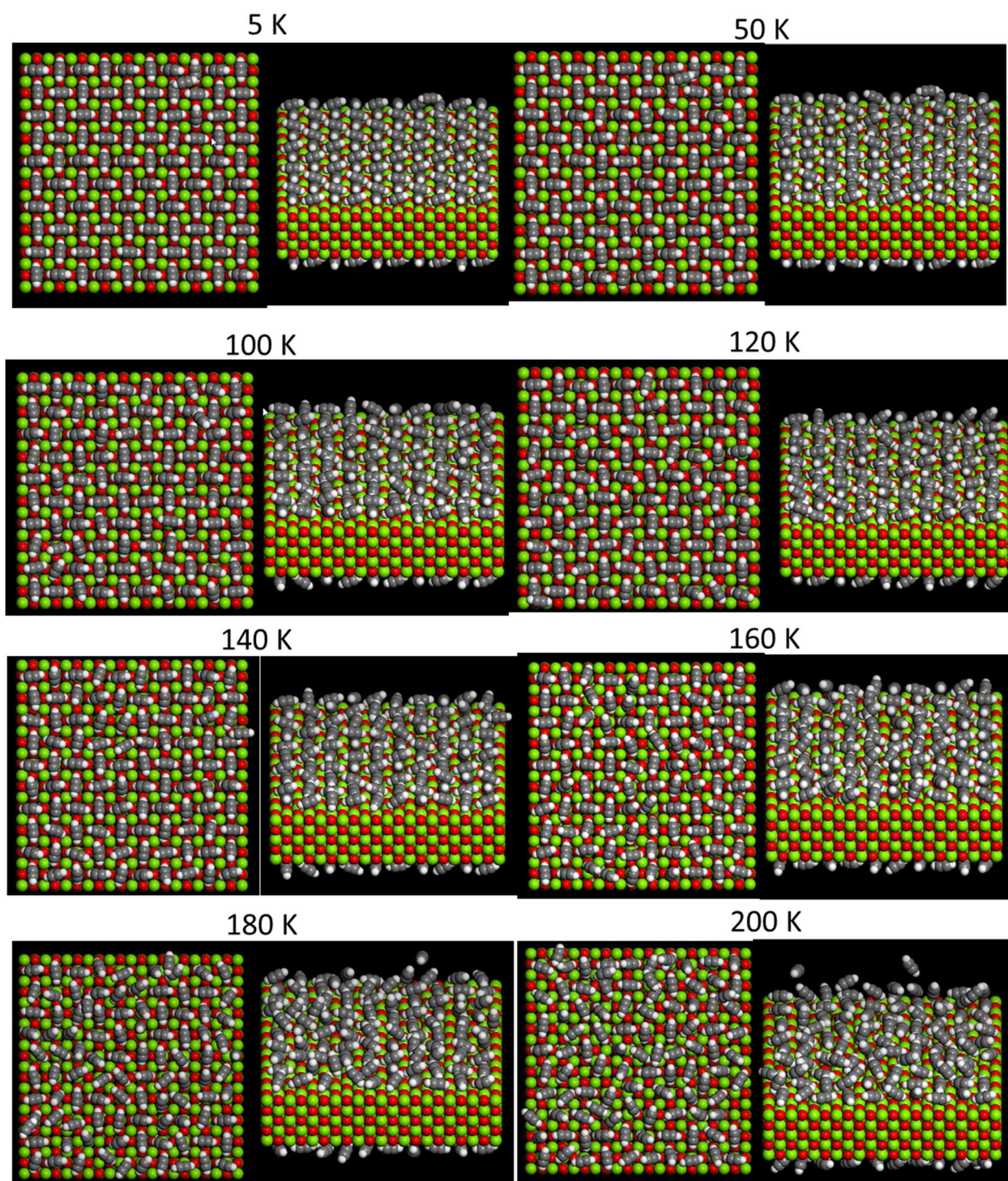


Figure 5.14: Simulation results for completed monolayer over a range of temperature

monolayer transition were run to approximately 10 degrees higher than the bulk triple point before reaching the pressure limits of the instrument, but qualitative inspection of the phase boundaries in the isotherm suggest the system had yet to reach its hypercritical point. This last aspect may not be too surprising with the presence of such a strong surface corrugation effect protecting the order of the system.

The neutron data collected for this study was, unfortunately, unusable for analysis. Previous LEED and neutron data support the 2x2 surface registry. The neutron data has, however, been unfortunately misquoted by other sources in the literature to indicate that the molecules adopt a square herringbone conformation, with molecules twisted 20° from the T-configuration. The lower pgg symmetry of such a herringbone structure would allow for three distinct diffraction peaks: $Q_{11} = 1.431$, $Q_{12} = 2.262$, and $Q_{22} = 2.862$. The diffraction data in this report contained only the (11) and (22) peaks. The (12) reflection is nearly extinct for the square-T symmetry, but is allowed for the square herringbone symmetry. The absence of this peak would clearly indicate that the system does indeed adopt the square-T lattice. Furthermore, it is easy to see that if the molecules were to be twisted in the plane by such a significant amount, this would push the hydrogen atoms to be situated over the oxygen-magnesium bond of the surface below, and such a structure optimizes neither the molecule-molecule, nor molecule surface, interactions.

This system seems to have defied the simplicity one might have expected for a molecule-substrate system that, on paper, would have seemed to be highly compatible. The data on this system at this moment is insufficient to support the proposal of a phase diagram, though several transitions are apparent in the isotherms. It is possible that these transitions relate to the out-of-plane molecular wagging in the film, and the in-plane harmonic motions may also play a role, but without more evidence this is merely speculative. A much more thorough structural and dynamic investigation will have to be conducted before any meaningful conclusions about the nature these transitions can be understood.

Chapter 6 – Adsorption of Allene on Graphite and MgO

6.1 – Introduction

This chapter outlines the experimentation and results of adsorption of allene on both graphite and MgO . Allene belongs to a symmetry point group not possessed by many small molecules, and as such presents a new opportunity to study the relationship between symmetry and adsorption. Not only do these systems afford a shift from the previous studies with acetylene in regards to both size and symmetry, but allene has a slightly weaker, though still substantial, quadrupole moment, a larger aspect ratio, and stronger van der Waal's interactions. This would lower the likelihood of its ability to adopt a pure square-T phase.

Allene has not received much interest in published research outside of catalytic studies and polymer chemistry. The physical properties of the molecule in the temperatures covered in the measurements of this chapter are not even well-studied. This issue added to the large number of difficulties encountered in handling this gas during experimentation. Fortunately, this also means that the data and properties reported will be novel.

6.2 – Experimental

Studying the adsorption of allene presented significant challenges due to the inherent instability of the molecule. Allene spontaneously converts to methylacetylene over time if not stabilized, is very reactive with many types of metals and rubbers, and will even undergo reactions with other allene molecules under the right conditions. The monolayer transition on graphite occurred at very low pressures, near the limits of the capacitance manometers, which meant it was especially susceptible to any slight gas impurity. The station had to be partially redesigned, and strict protocols had to be devised to generate stable and repeatable isotherms.

In addition to the normal process of isotherm measurements that have been defined and utilized in the previous chapters of this dissertation, some particular considerations that were touched on in Chapter 2 are also applicable in the handling of allene gas. The overall extra effort to control the isotherms warrants full clarity of the procedures followed. The largest issue that compromised the quality of the gas was the large number and high surface area of the rubber seals in the station's proportional valve. The exact nature of the incompatibility of allene and rubber could not be elucidated and, in fact, it was not listed as an incompatible material in most MSDS documents examined. Despite this, the relation of gas instability and the proportional valve was evident during the experimentation process. When the manifold was opened to the

vacuum pump and evacuated of all gas, if the valve connecting it to the proportional valve was opened, small but significant increases in pressure were observed. This occurred when both the gas intake manifold and the calibrated volume were completely evacuated of gas and continued for up to a week before off-gassing ceased. A helium leak checker determined the gas pressure was not the result of any leak from the air-tight seals of the valve. The behavior suggests that allene is able to permeate and adsorb into the rubber seals and was very slowly doing so during pumping.

The valve was exchanged for a new proportional valve that was considerably more compact, with far less surface area of rubber available. The two main rubber seals were O-rings, however, they were Viton instead of Buna, and the valve performance overall was significantly more stable.

The quality of the allene also seemed to degrade over the course of a week after being distilled with freeze-pump-thaw cycling, after which noticeable changes would appear during isotherm measurements. Only small aliquots were purified at a time, roughly enough to run one or two isotherms, and any remaining gas was discarded. During the isotherm measurements themselves, an excess of gas pressure was introduced during each gas dosing cycle, 10 to 20 times the target pressure. This means that most of the gas had to be evacuated by the vacuum pump in order to bring the pressure to the target range. This was not intentionally done as a precautionary measure; it was an effect of poorer dosing control with the new proportional valve. It did mean, however, that if there were any volatile impurities developing in the gas, they were purged from the calibrated volume with each cycle. It was never determined if this in any way helped, as controlled dosing was never obtained with the new system. It is mentioned here, though, as this may have helped to contribute to the enhanced stability of the new proportional valve system. Figure 6.1 shows the isotherm stability for the monolayer step of allene on graphite before and after implementation of the above considerations.

For computational studies of the allene systems, there is scant data in the literature. Only reactive force field investigations could be found from literature searches, and even the structure of solid allene is still unknown, with the only structural data based on IR measurements. Therefore, it is not possible to speculate on the accuracy of these simulations. In these studies, only the standard force field parameters were utilized in the calculations. The only exception

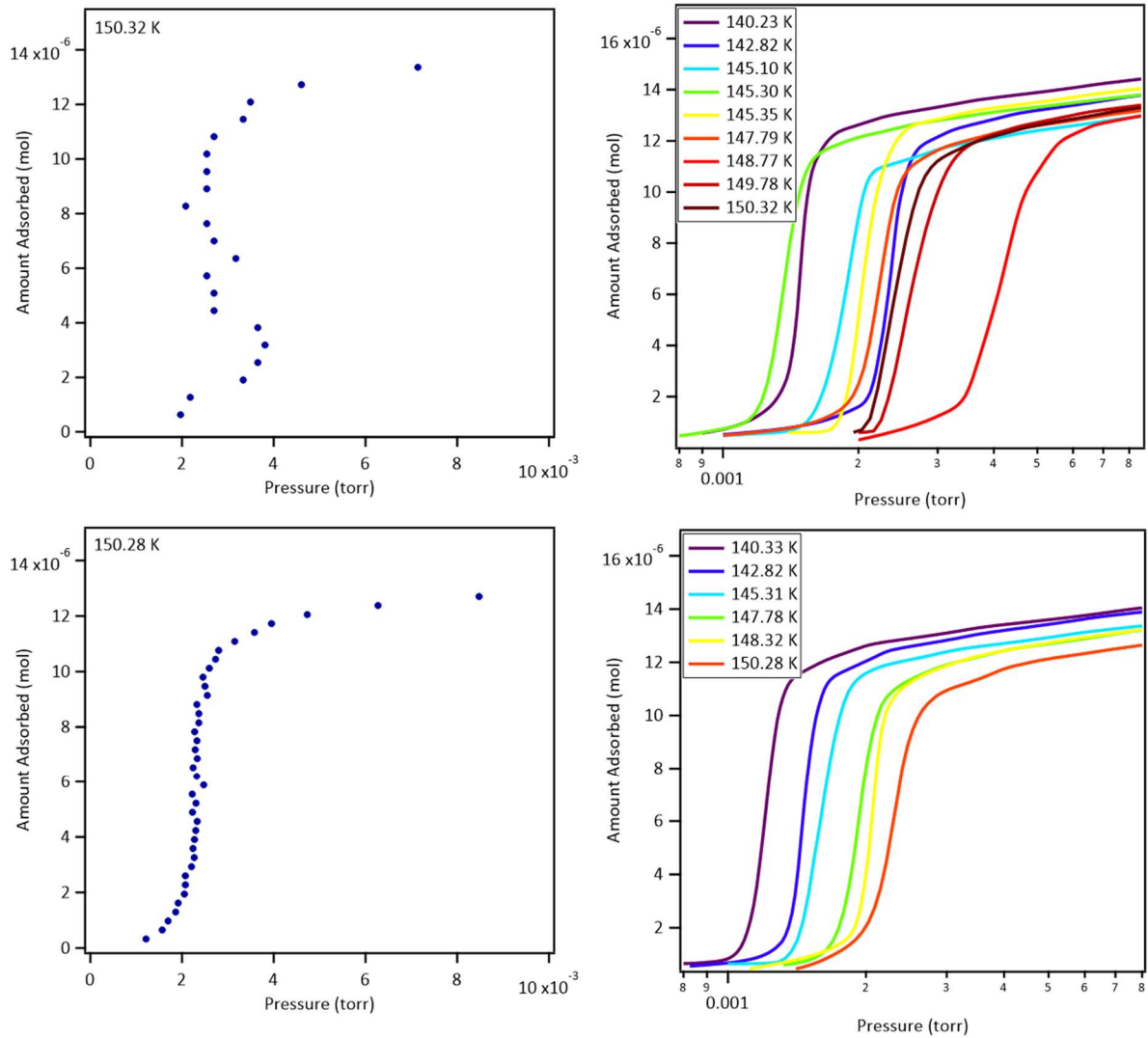


Figure 6.1: Isotherm results for allene on graphite with old proportional valve (top) and new proportional valve (bottom)

was the addition of a dihedral restraint on the orientations of the opposing hydrogen pairs of the molecule.

6.3 – Results and Discussion

The physical properties of allene prevent the ability to study the thermodynamics of any solid phase transitions. The bulk triple point for allene is 136 K, at which the saturated vapor pressure is less than 0.1 torr. Normal expectations of two-dimensional systems would see a melting point at around 70% of the triple point temperature (~95 K). Limitations on pressure measurements make this temperature range inaccessible to volumetric isotherm measurements. The critical point for allene occurs at 394 K. The rule-of-thumb for two-dimensional critical points is that they are expected in a range of 30-50% of the bulk critical temperature, being 120 K to 200 K for allene, therefore, any indications of phase transitions within the isotherm measurements presented here likely correspond to a hypercritical transition.

6.3.1 – Thermodynamics Results

A total of 38 and 24 isotherms were analyzed for allene on graphite and allene on MgO, respectively, over a nominal range of $140\text{ K} < T(\text{K}) < 201.58\text{ K}$. As with the previously discussed systems, isotherms were dead space-corrected and interpolated to obtain smooth data for the following analyses. The appearance of isotherms for both surfaces are similar in their general appearance, each possessing only two visible layering transitions and visible incomplete wetting (Figure 6.2). The step transitions on graphite occur at distinctly lower pressures than on MgO, indicating that film formation is more favorable on graphite. Also, on graphite a possible sub-step feature was noticed in some isotherms at lower temperatures (Figure 6.3). Sub-step features like this are common in isotherms and could correspond to the formation of a solid phase as the density of adsorbed molecules is increased. The feature, however, is subtle, inconsistent in coverage and behavior, and similar in magnitude to the uncertainty in measurement. Normally, such a small anomaly in the data would have been discarded, and was noted only for its quasi-consistent appearance in seven of the isotherms measured at low temperature. However, these isotherms all took place before system modifications were made to improve gas purity and the behavior was no longer observed afterwards. It was assumed that this feature, if it was not simply a coincidental pattern in the noise of several scans, was likely an artifact of gas purity issues.

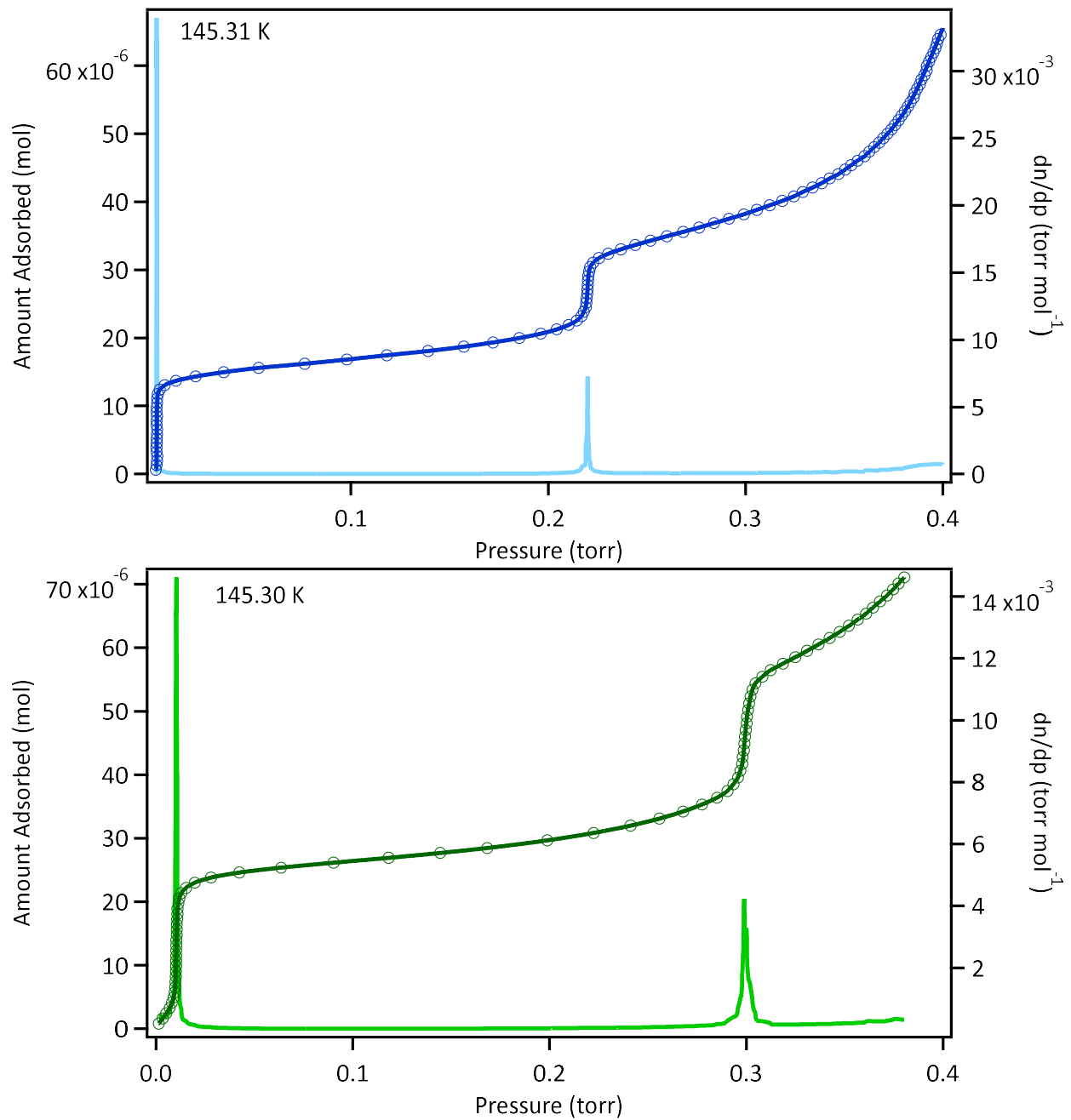


Figure 6.2: Example Isotherms of allene on graphite (top) and MgO (bottom)

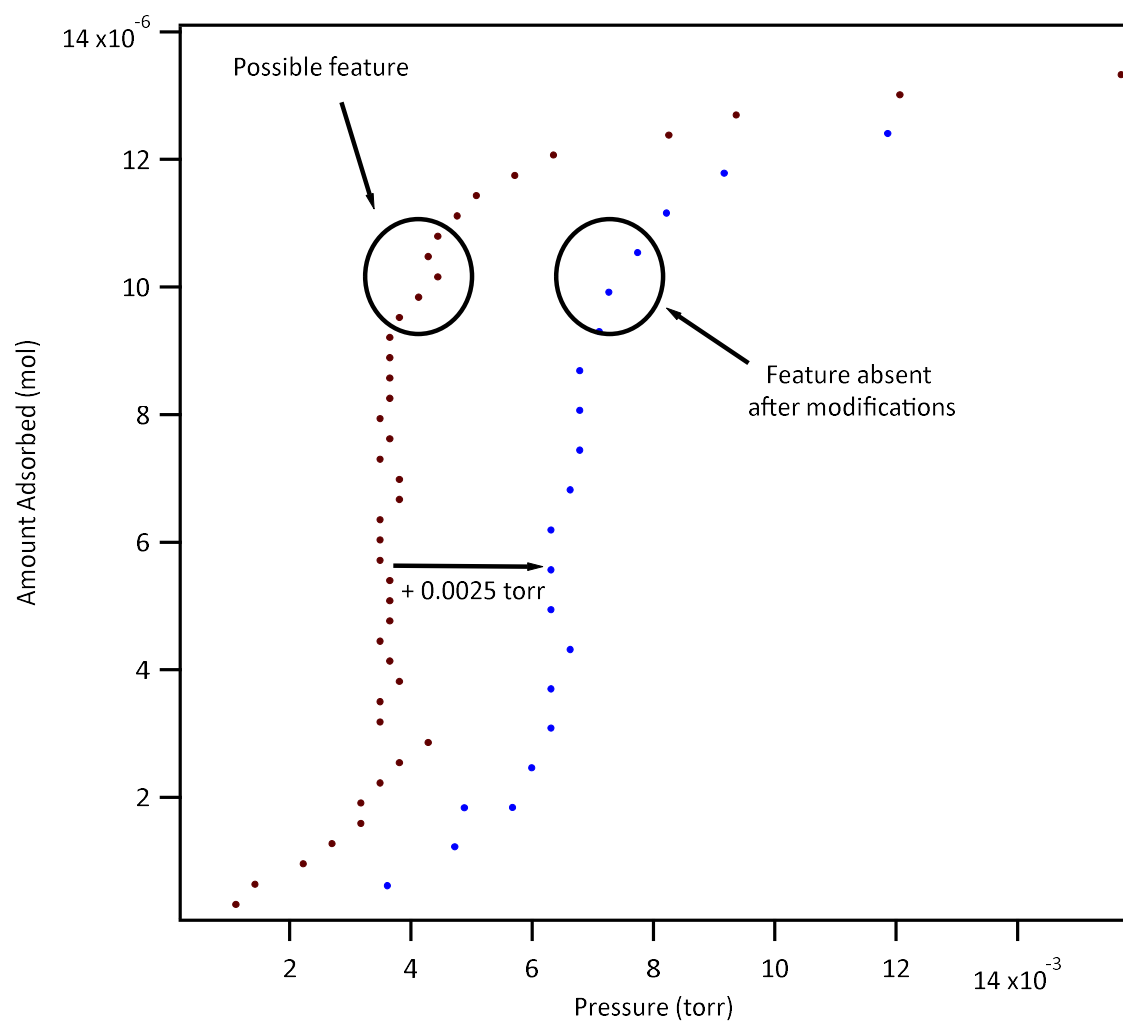


Figure 6.3: Possible feature on some isotherms for allene on graphite

Figure 6.4 shows selected isotherms for both systems over the temperature ranges measured. The similarity is even more apparent in these plots, but it is also worth noting that the much lower pressures of the first layer on graphite as compared with MgO. The loss of step verticality at higher temperatures is indicative of hypercritical behavior as well.

The thermodynamics were analyzed in the same manner as they were in the previous chapters using the Clausius-Clapeyron analysis. These results are shown in Figures 6.4 and 6.5 and are tabulated in Table 6.1. The results for MgO show only a single thermodynamic trend for all temperatures examined in both layering transitions. The monolayer formation is mildly enthalpically favored with a low but favorable entropy. The second layer is only marginally more favorable than the condensation of bulk allene. The case on graphite is more interesting. The first monolayer shows a distinct change in slope at 152 K. Below this point the monolayer formation is extremely enthalpically disfavored, with a heat of adsorption that is only 42% of the heat of condensation in the bulk phase. This is offset, however, by the even larger proportional entropy gain of the adsorption process.

Such a thermodynamic balance of entropy over enthalpy would not continue indefinitely. This can be seen in the isotherm plots of chemical potential in figures 6.7 and 6.8. The monolayer step is moving rapidly towards zero free energy as the isotherms go lower in temperature. The absolute limit for which this process would become unfavorable if no other phase transitions change the behavior before that point is 96 K. In contrast, the free energy for MgO for the first layering transition is comparatively constant with temperature.

The isosteric heats of adsorption are shown for two temperatures for each system (Figures 6.9 and 6.10). The isosteres for allene on graphite were subject to the limitations of the gas and the pressure limitations of the instrument that made reasonably reproducible results for this analysis difficult. Fifteen isotherm pairs were actually run in the hopes of measuring the isosteric heats for allene on graphite, and none of them were able to produce good isosteric heat measurements of the monolayer. Neither of the isosteres for that system are close to the bulk enthalpy of condensation following the second layering step; however, the isotherms very slowly asymptotically approach the saturated vapor pressure following this point, and it is likely that if the isosteric heats were calculated for coverages far beyond the second monolayer, they would eventually converge on the bulk phase. MgO continued to be the more behaved of these two

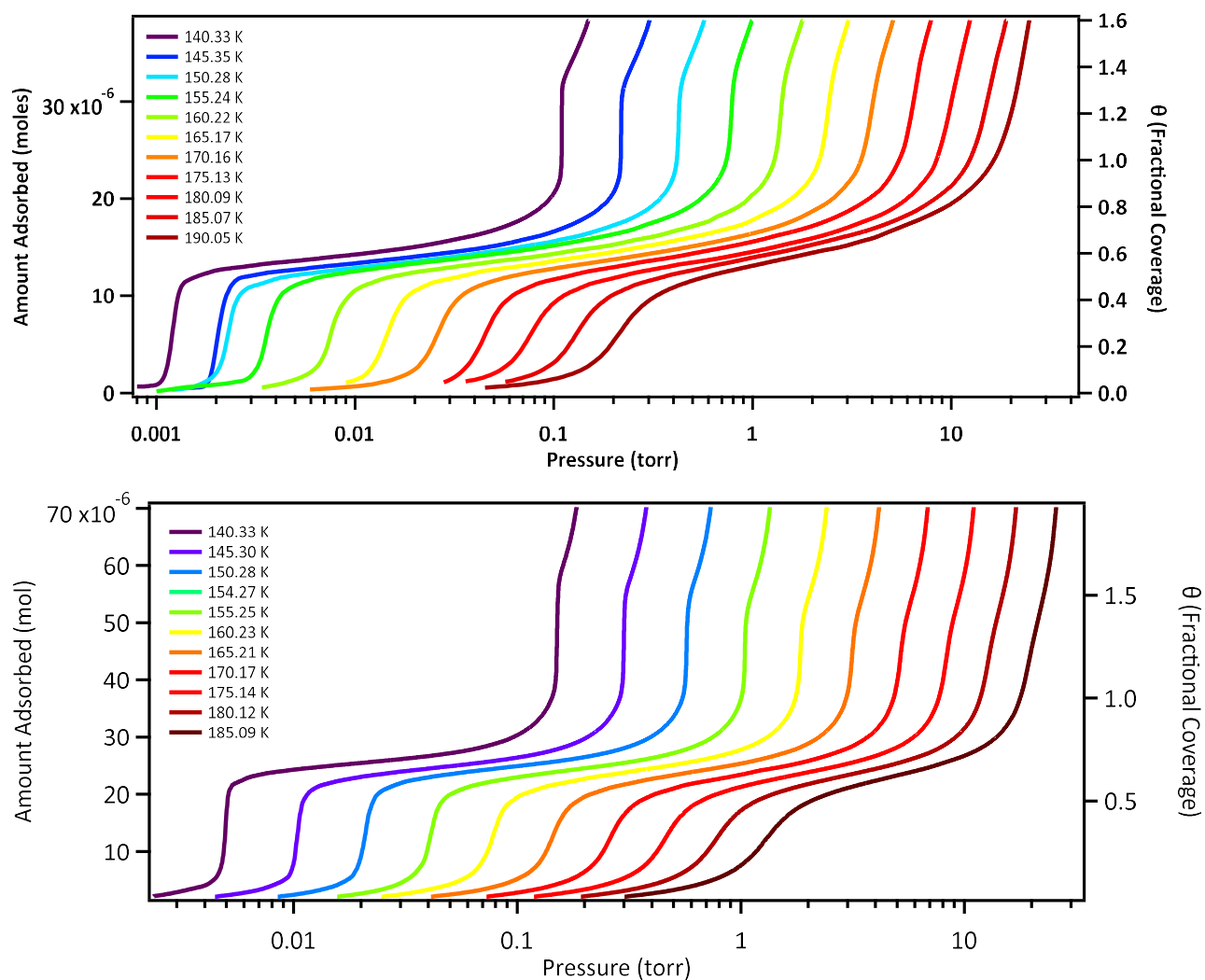


Figure 6.4: Range of isotherms for allene on graphite (top) and MgO (bottom)

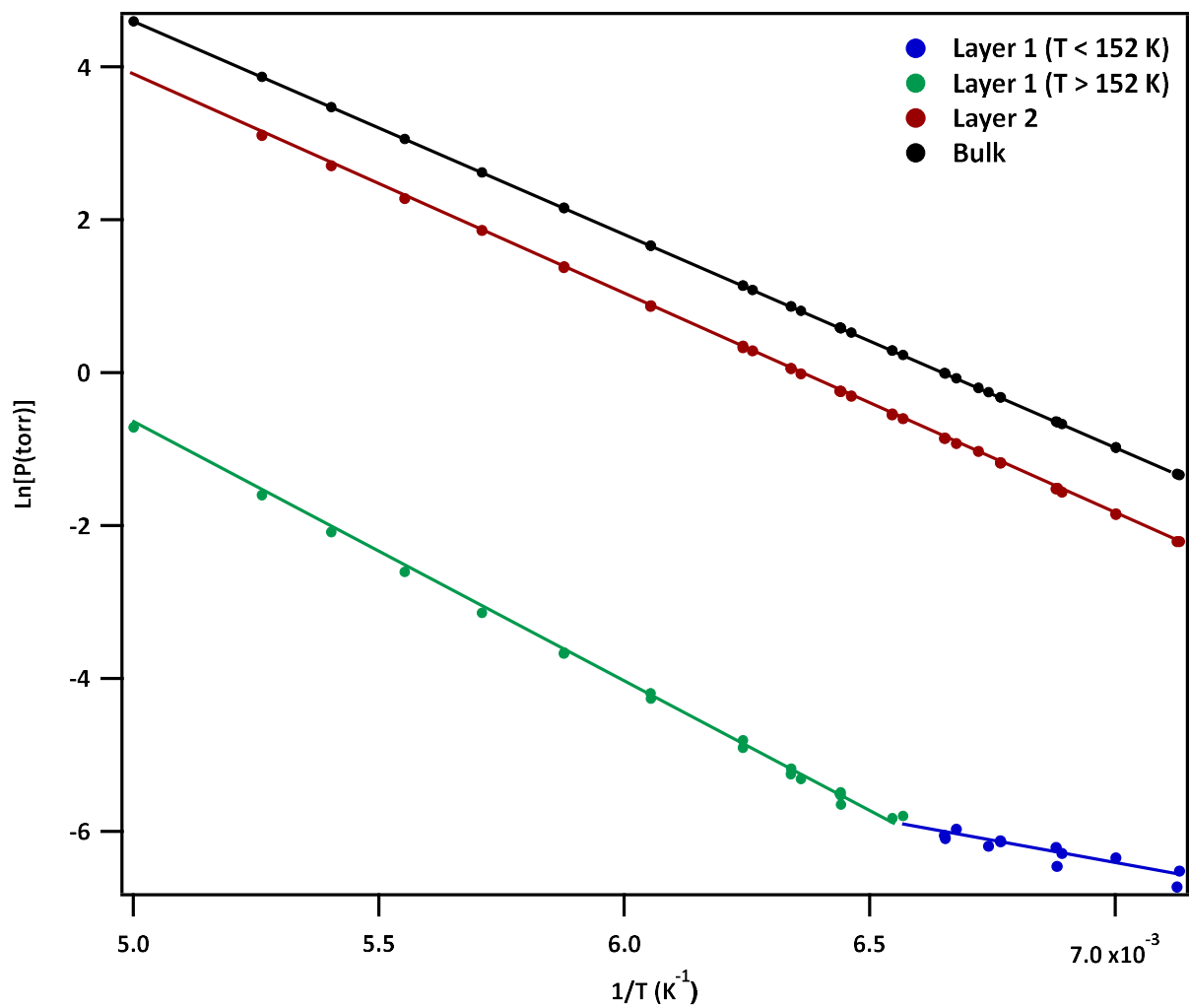


Figure 6.5: Clausius-Clapeyron analysis for allene on graphite

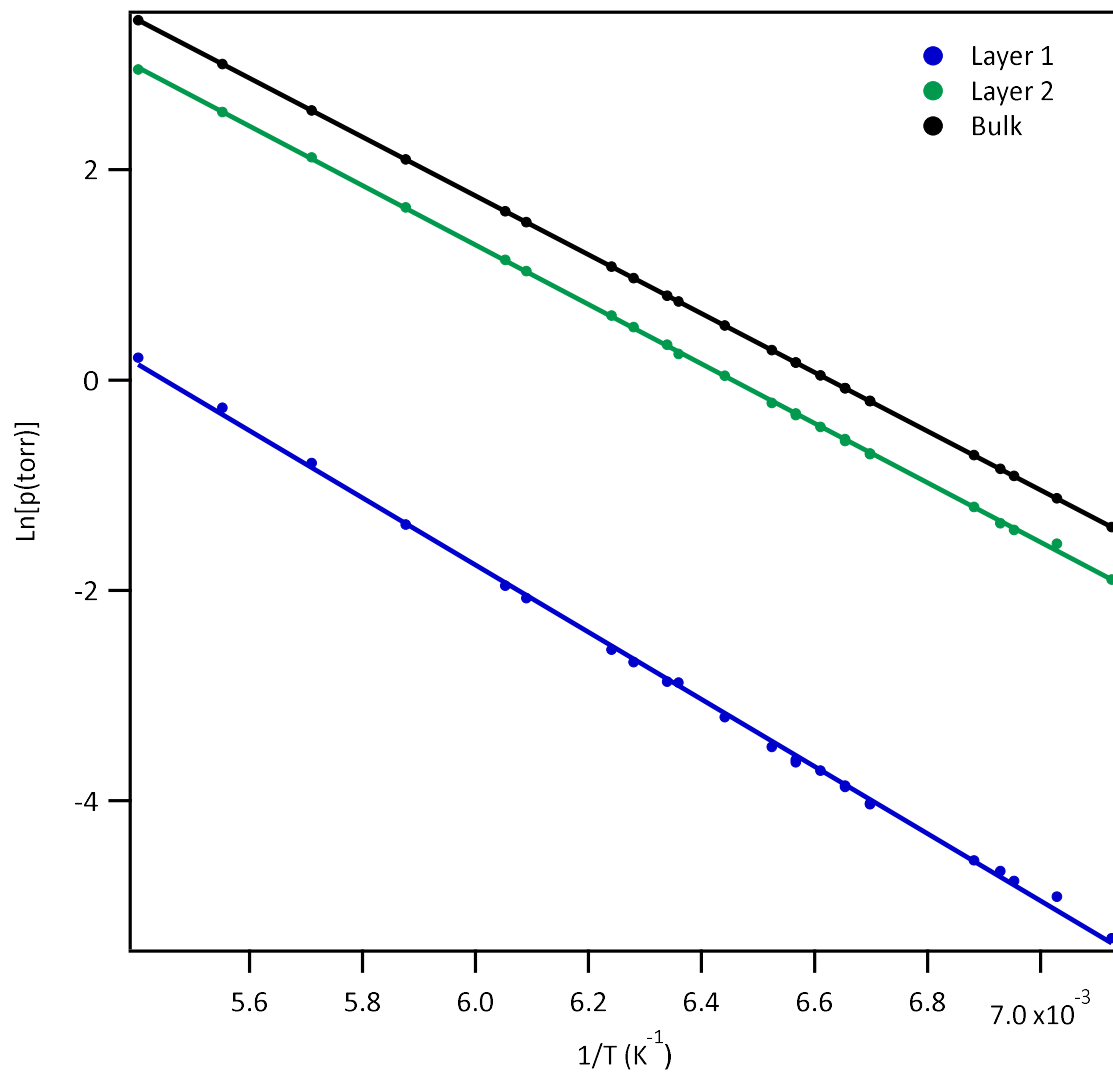


Figure 6.6: Clausius-Clapeyron analysis for allene on MgO

Table 6.1: Thermodynamic results for the adsorption of allene on graphite and MgO

Surface	Feature	APM (Å ²)	A	B	ΔH kJ mol ⁻¹	ΔS J mol ⁻¹ K ⁻¹	Q _{ads} kJ mol ⁻¹
Graphite	Layer 1 (T < 152 K)	26.10	1217	2.0487	13.116	136.87	10.118
	Layer 1 T > 152 K)		3274.7	15.594	-3.992	24.259	27.226
	Layer 2	11.02	2861.2	18.183	-0.554	2.7336	23.788
MgO	Layer 1	25.03	3191.4	17.39	-3.300	9.3782	26.533
	Layer 2	11.18	2823.3	18.222	-0.239	2.4609	23.473
	Bulk		2794.6	18.518			23.234

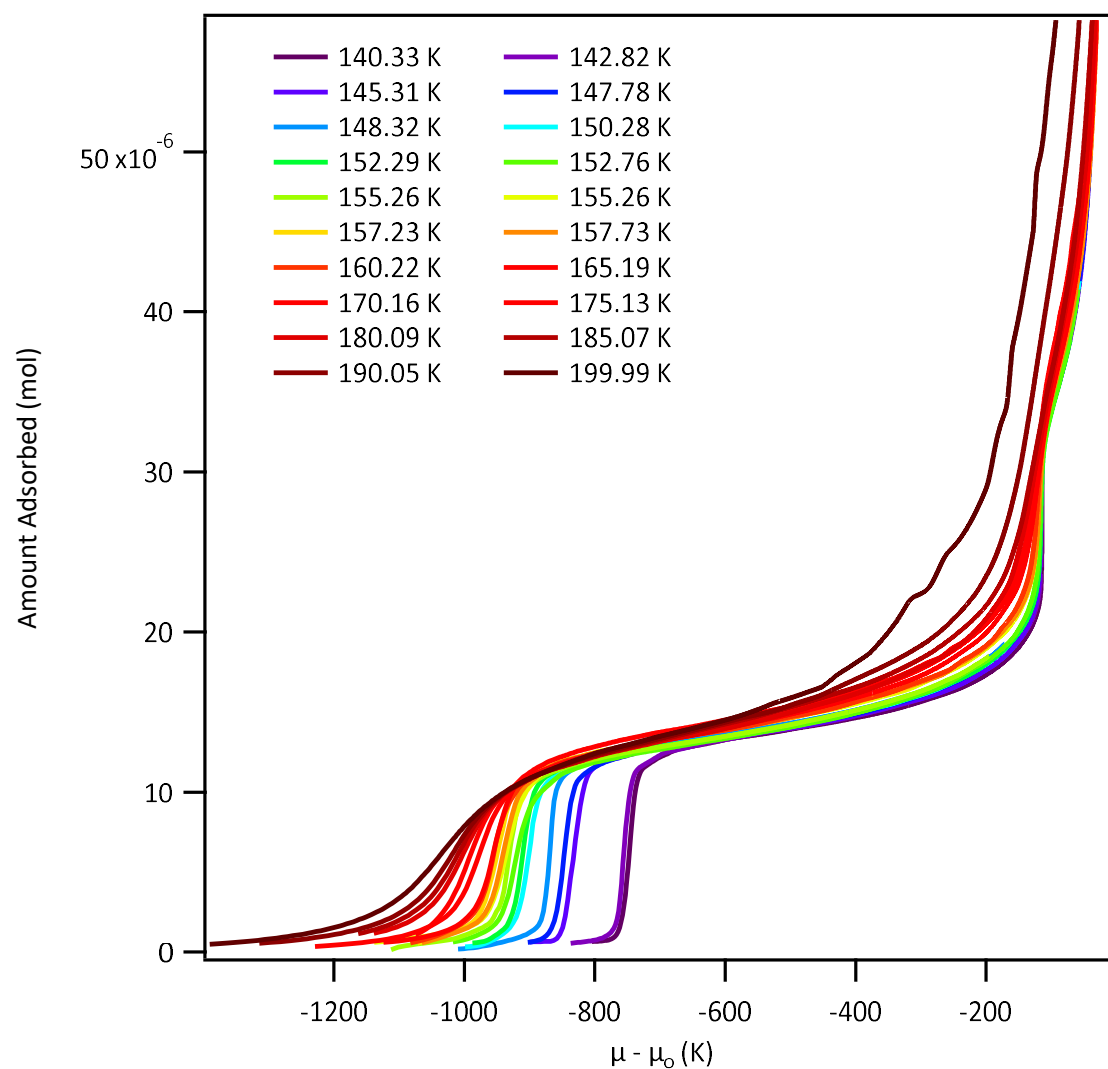


Figure 6.7: Isotherms plotted vs chemical potential for allene on graphite

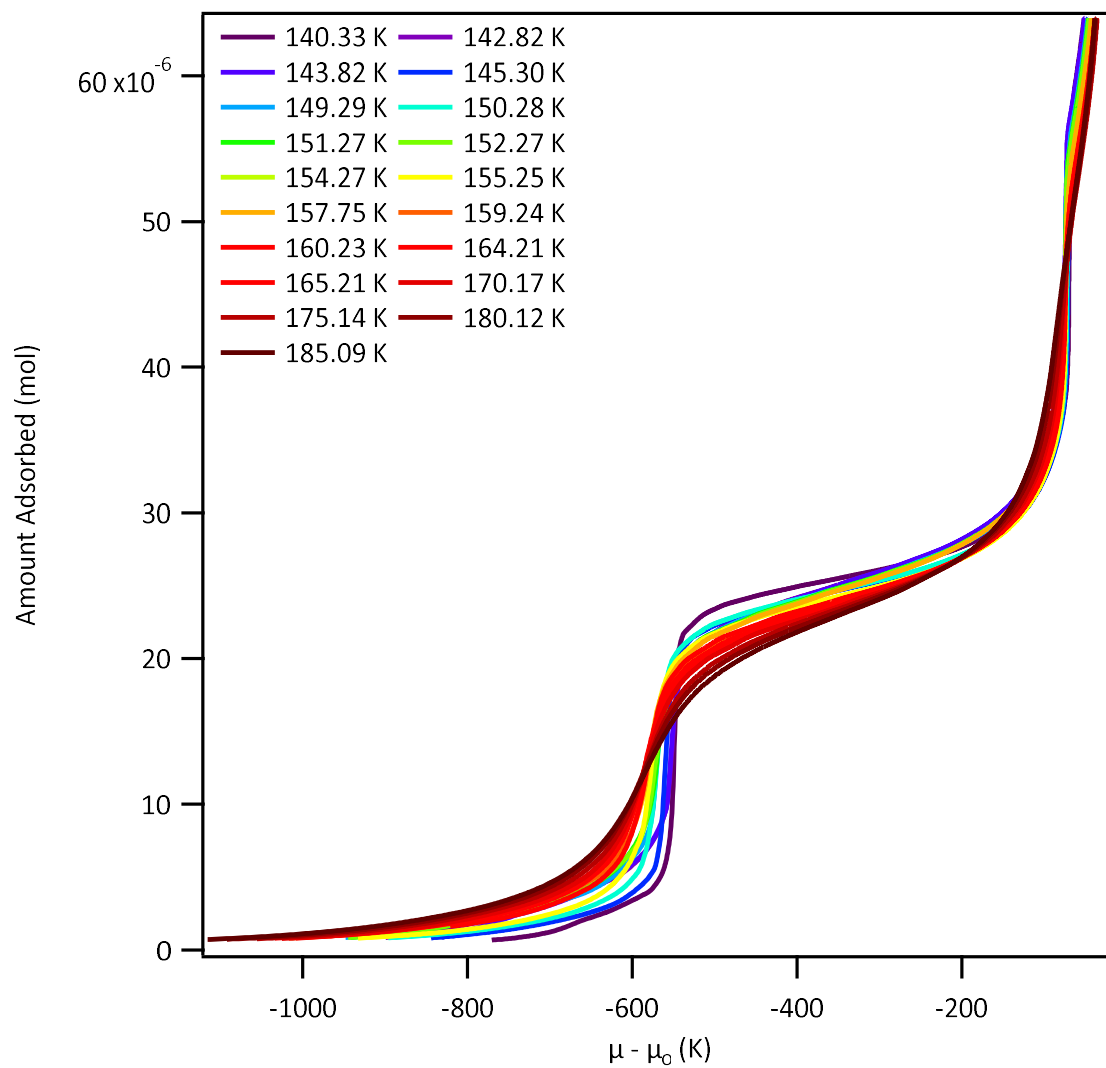


Figure 6.8: Isotherms plotted vs chemical potential for allene on MgO

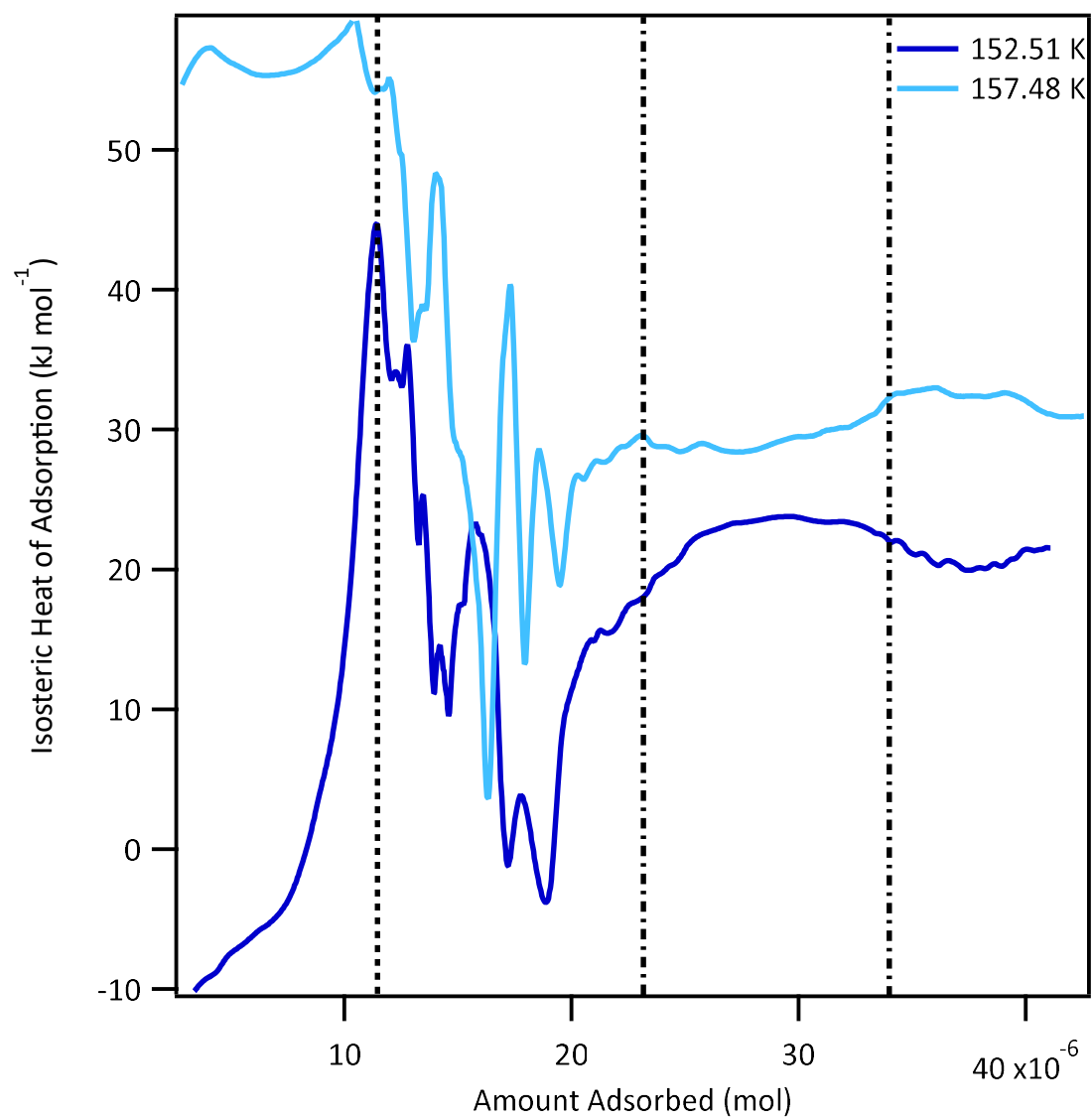


Figure 6.9: Isosteric heats of adsorption for allene on graphite

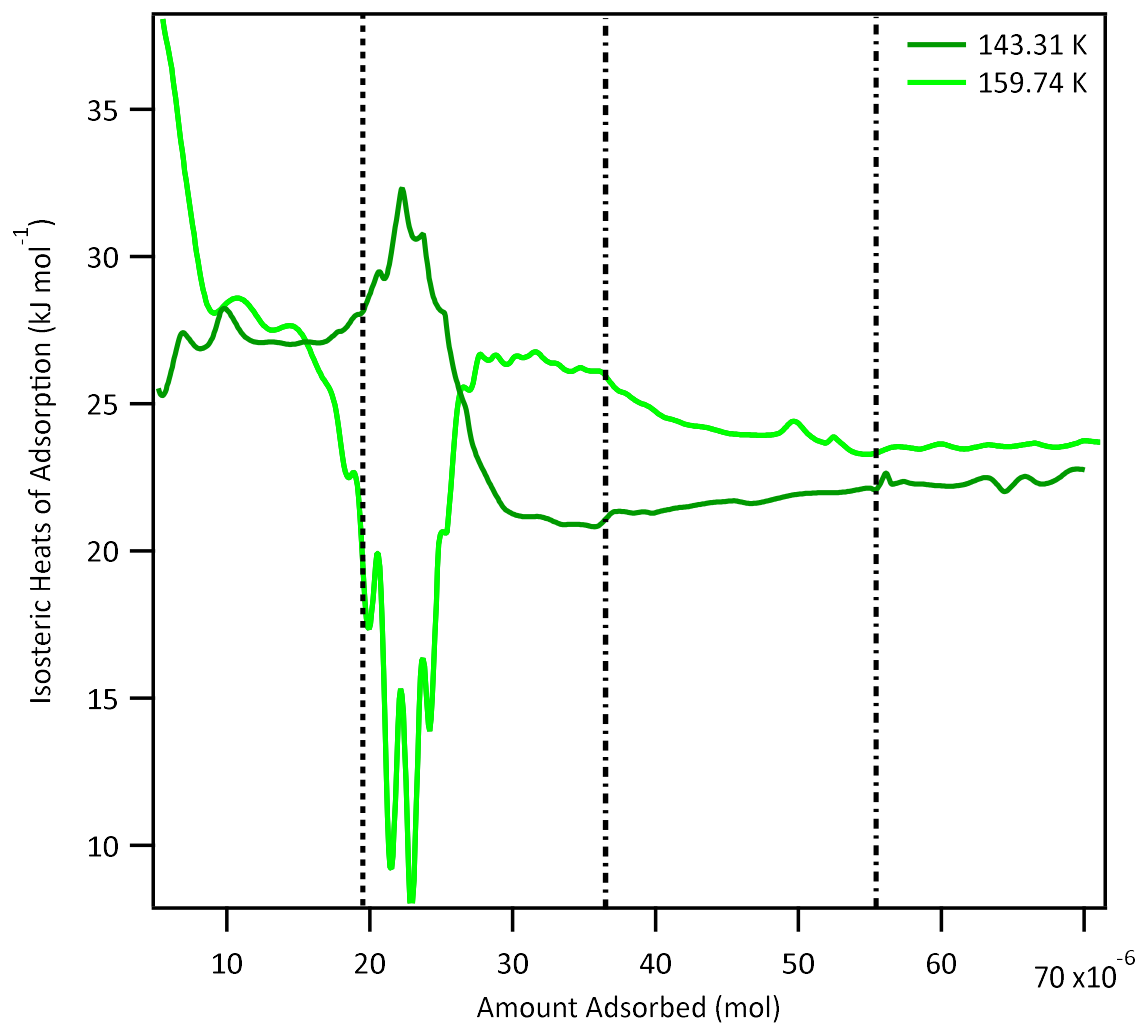


Figure 6.10: Isosteric heats of adsorption for allene on MgO

systems with well-defined and stable isosteric heats of adsorption in both monolayers. The average value for the monolayer is around 26-27 kJmol⁻¹ and the second layer values are converging around 23 kJ mol⁻¹. These are consistent with the Clausius-Clapeyron analysis and the bulk enthalpy of vaporization.

The Henry's law heats of adsorption were calculated from the linear region before the monolayer riser and are shown in Figure 6.11. This region in the graphite system did not produce reliable results for all but the highest temperatures. The region generally only corresponded to two or three recorded data points before the monolayer step began and reliable consistent fitting of the slopes of these isotherms was not possible. The analysis was only performed using the data taken from isotherms at and above 170 K. The value at 30.8 kJ mol⁻¹ is much higher than the bulk heat of condensation and would indicate the interaction between allene molecules and the surface is highly favorable, however, the overall difficulties for this system should limit the significance placed on this value. The data for the MgO system continued to be the easier of the two to analyze, with reasonable quality of fits across the entire temperature range and a Henry's law region very similar to the bulk phase. If both of these values are trusted, it would indicate a strong interaction of allene with graphite's surface, but a more average interaction with MgO. Contrasting this with acetylene, where the interactions were stronger with MgO, it could indicate that the van der Waals interactions are a much more significant part of this adsorption behavior than its large quadrupole moment. Alternatively, it could represent an issue with size compatibility between the size of the molecular quadrupole and the corrugation of the surface that prevents molecules from finding effective binding sites and lowering the adsorption energy through electrostatic repulsive forces. Of note, it must always be considered that the assumptions made with Henry's law will not work with all surfaces or gases, and may even feature differences between surface samples if the defect concentration is high enough.

The two-dimensional isothermal compressibility was used to locate possible phase transitions in these adsorbed systems. It should be noted that, despite the many difficulties the graphite surface presented in these studies, when it came to this analysis, the data was remarkably well-fit and consistent across temperatures. On graphite, these analyses show

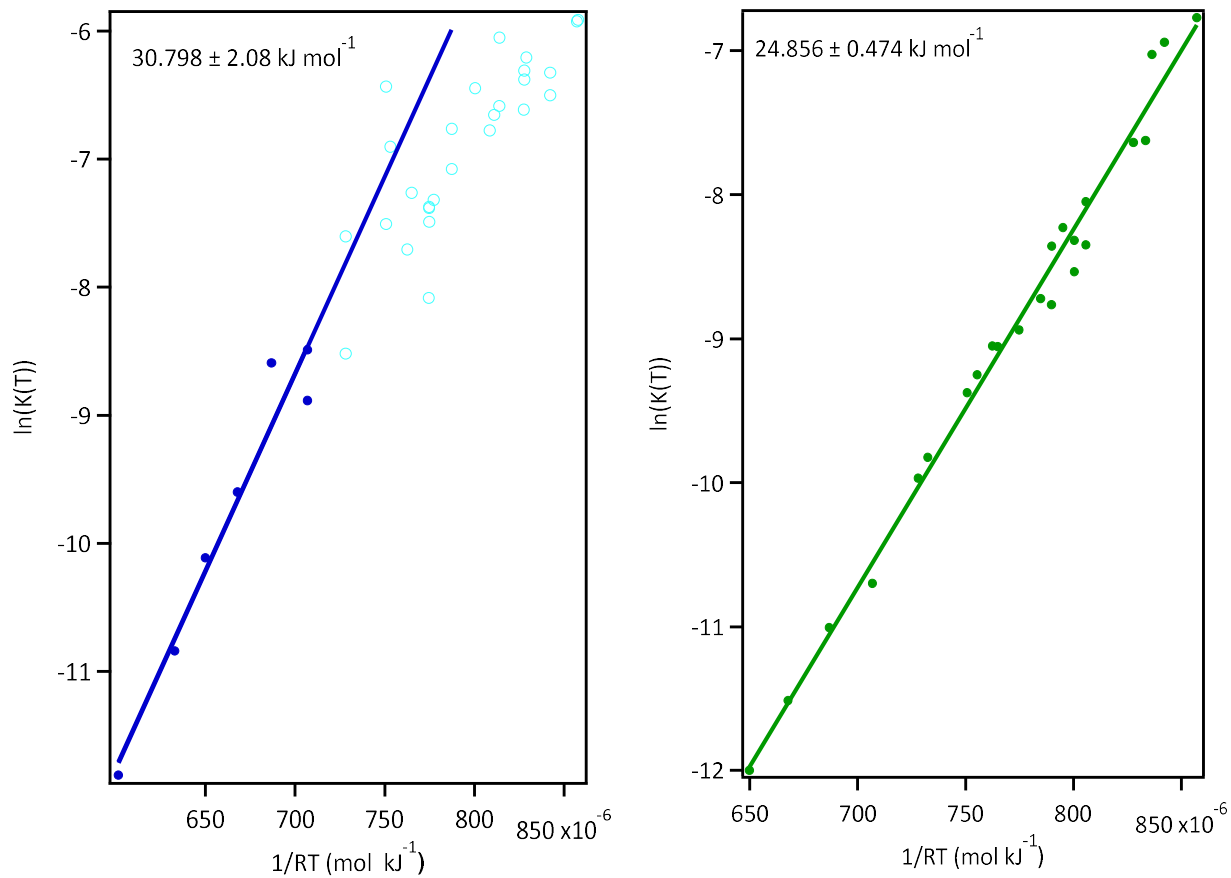


Figure 6.11: Henry's law plots for the adsorption of allene on graphite (left) and MgO (right)

Note: light blue open circles for graphite show data points from regions where pressures were too low for good statistics, these were disregarded from the line fit

potential transitions occurring at 150.5 K and 151.5 K for the first and second layer, respectively. For MgO, the same type of transition features were observed at marginally higher temperature: 155 K for the first layer, and 156 K for the second layer (Figure 6.12). Within the error margin of the analysis, the temperatures for both layers of both systems may actually be coincident. Based on where these fall relative to the bulk triple point would indicate that these features correspond to critical transitions in the film, a conclusion supported by the evolution of the isotherm steps before and after these points.

6.3.2 – Computational Studies

Computational analyses were made on these systems with molecular dynamics calculations using the standard COMPASS parameters. The validation of this force field for cumulated double bond systems is unclear, but the lack of any force field parameters to prevent the free rotation of the molecular bond around the central axis demonstrates the lack of development in this area. This issue was resolved by defining a restriction of this motion using a system restraint, but this is no guarantee of physically realistic behavior. Despite this, there does not seem to be any other force fields more tailored to the behavior of allene, and COMPASS has a significant library of validated results on other hydrocarbons and a long and successful utilization in the study of adsorbed systems.

6.3.2.1 - Energy Minimizations.

Following those same procedures already prescribed, the binding sites and associated energies for allene on these surfaces was examined through geometry optimization calculations for single molecules adsorbed on the surface (figure 6.13). On graphite, the molecules did not show preference for any particular surface location or orientation with respect to the surface, and the calculated binding energies were $28.76 \text{ kJ mol}^{-1}$, varying by 0.01 kJ mol^{-1} across the surface sites tested. One preference the molecules did seem to show is in the orientation of the opposing hydrogen pairs, with one pair level with the surface and the other perpendicular. On MgO, all starting points would converge on surface magnesium atoms with the molecule twisted at an angle relative to the surface lattice. The molecules on this surface oriented with the hydrogen pairs at 45° to the surface. The hydrogen proximal to the surface was situated over surface oxygen atoms. The interaction energy was calculated to be $34.52 \text{ kJ mol}^{-1}$, which is distinctly in disagreement with the observed Henry's law heat of adsorption. While this may

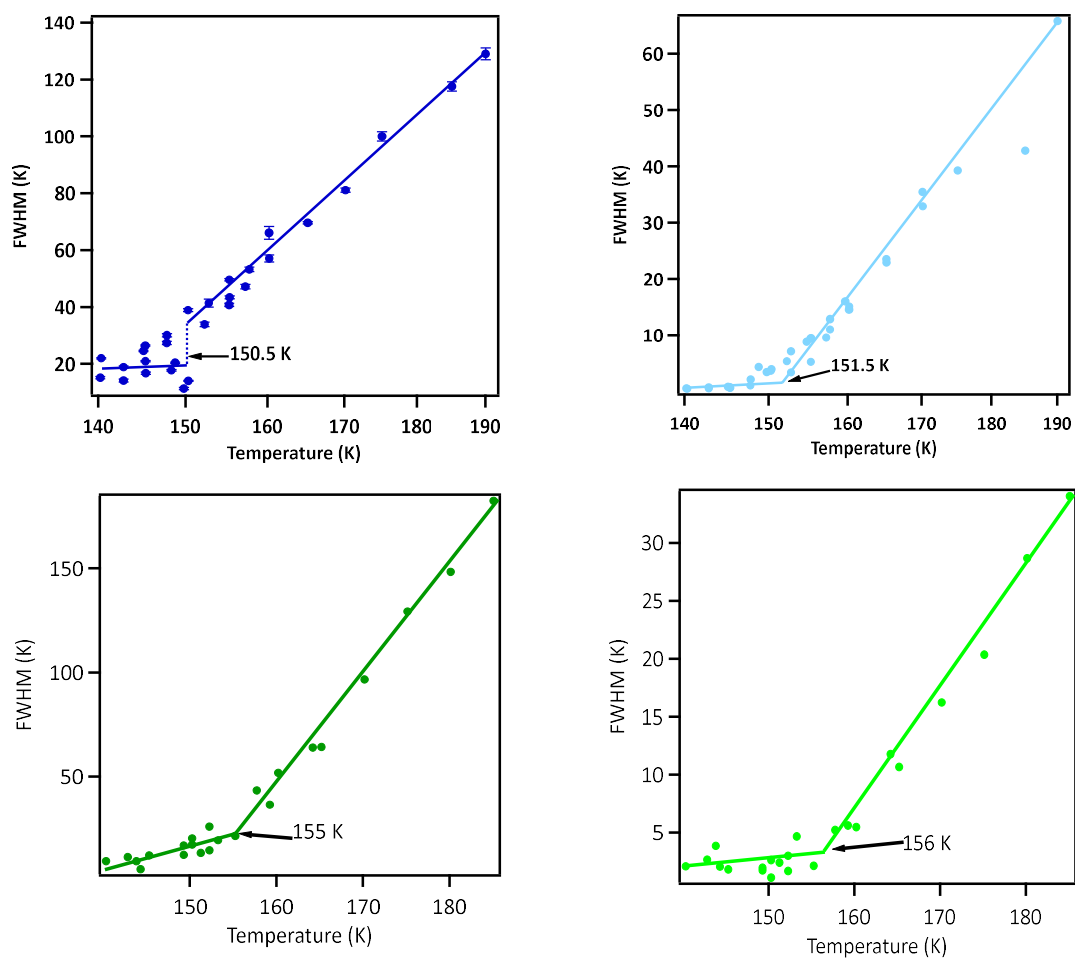


Figure 6.12: FWHM half max analysis for allene on graphite and MgO

Left: layer 1
 Right: layer 2
 Top: graphite
 Bottom: MgO

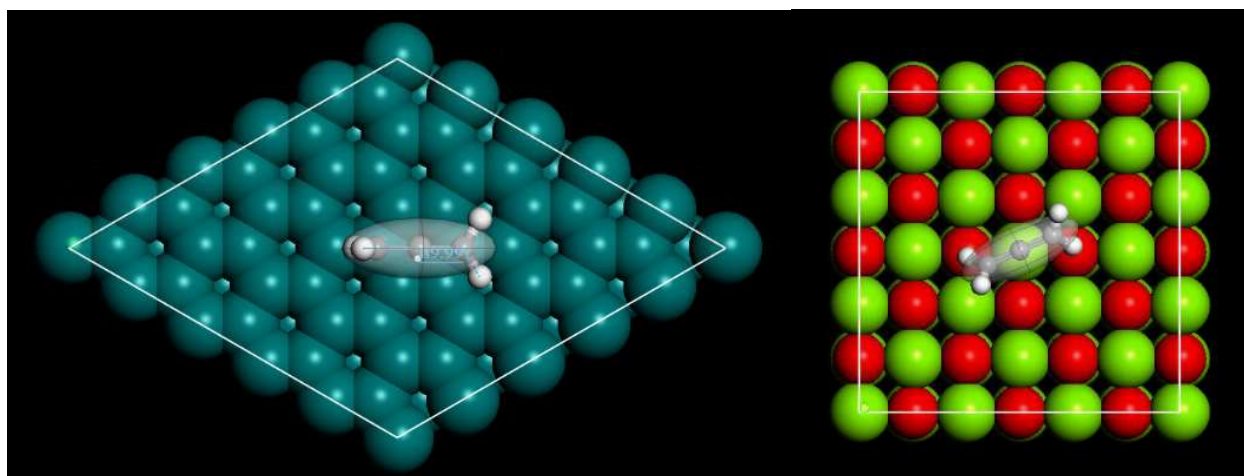


Figure 6.13: Energy minimization results for allene on graphite and MgO

Note: for graphite, no significant favorable position was observed, instead, this shows the preferring axial orientation of opposing hydrogen groups relative to the surface

indicate descriptive issues for this molecule in the force field, it may also be a failure of one or more of the Henry's law assumptions.

6.3.2.2 – Molecular Dynamics Simulations

As was done with the simulations of acetylene on MgO, simulations of these systems with allene were run with densities corresponding to sub-monolayer, completed monolayer, and bilayer coverages. During the course of these simulations, observations of the equilibration of the non-bond energies lead to a distinct point in both systems. When the systems reach 80 to 90 K, the equilibration time to reach minimum energy and the total change in energy from beginning to end of the simulations took considerably longer, up to 500 ps at the highest coverages. A similar point was also noticed only for the MgO surface at 130 K. A significant change in the non-bond energies of the molecules would be indicative of a structural relaxation in the film, and therefore signal a phase transition. The lower of these two temperatures observed for both surfaces did show signs of more ordering following this point, as seen in the radial distribution functions (Figure 6.16). This is also the region where the triple point would suggest that a possible melting/freezing point occurs. Identification of exactly what occurs at the 130 K shift was not as immediately apparent in the data, but may signal changes to the liquid state or the critical point in the simulated system.

A comparison of snap shots for the completed monolayers on both surfaces is shown in Figure 6.14. Most notably, a difference with allene compared to acetylene is the high degree of orientational disorder of the molecules. This was observed for all coverages examined and does not seem to be a result of insufficient simulation times to allow for equilibrium based on the energy outputs from the simulation results. The optimized structure of the single molecules with the surface shown in the previous subsection, and the regions of short-range ordering in the simulations may suggest an explanation for the disorder (Figure 6.15). Based on the size and orientation of the single molecule shown in its preferred binding site in the previous section, the steric constraints would only allow one configuration of surrounding molecules that is also similarly optimized. The molecules would have to stack in a “slipped” parallel arrangement along the diagonal lines of magnesium surface atoms with their centers over these atoms. This leads to regions with a commensurate 1x3 herringbone structure in parts of the simulated film. Configured in this way, the positive ends of the molecular quadrupoles are in close proximity,

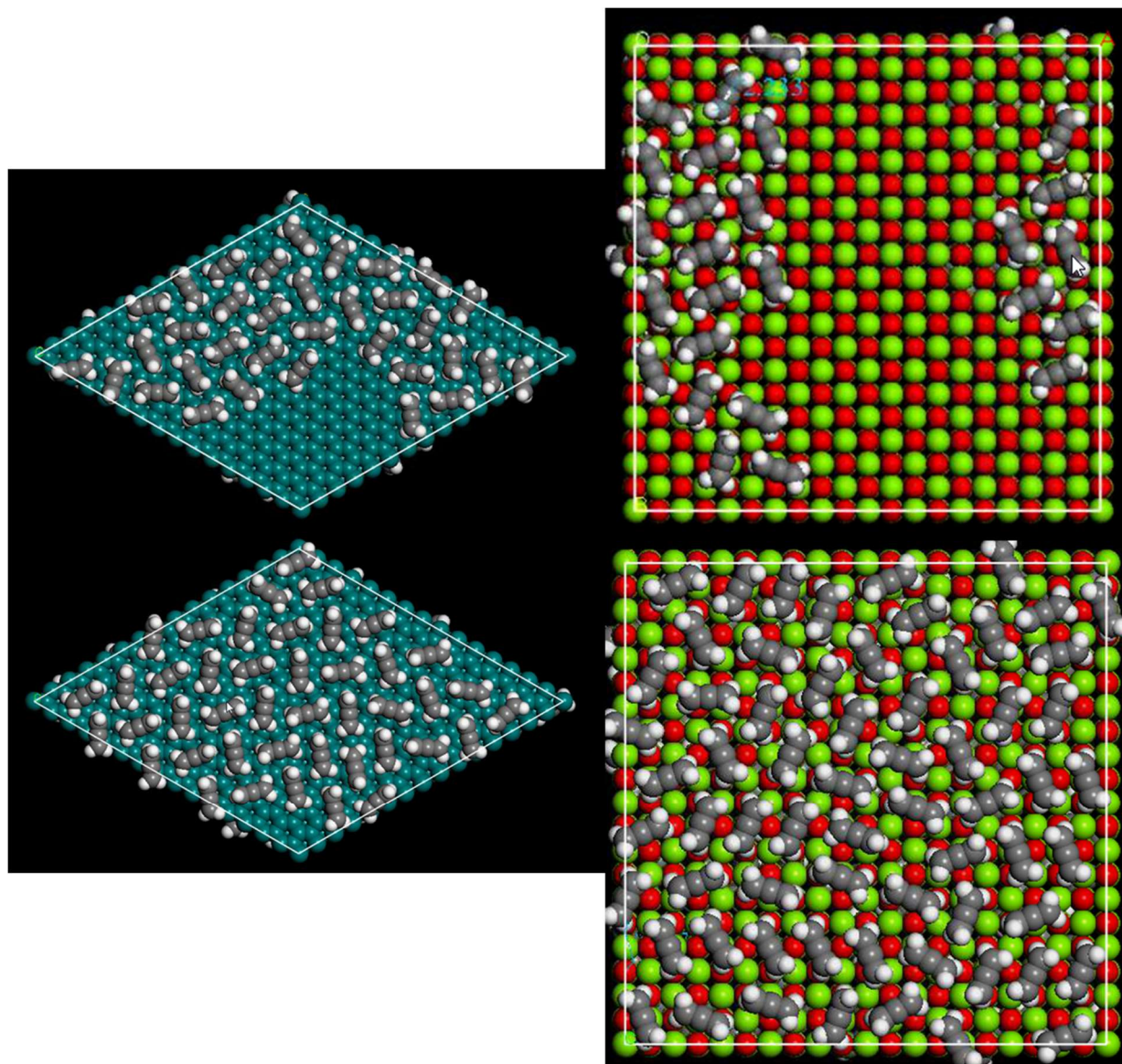


Figure 6.14: Simulation snap shots for allene on graphite and monolayer and sub monolayer coverages

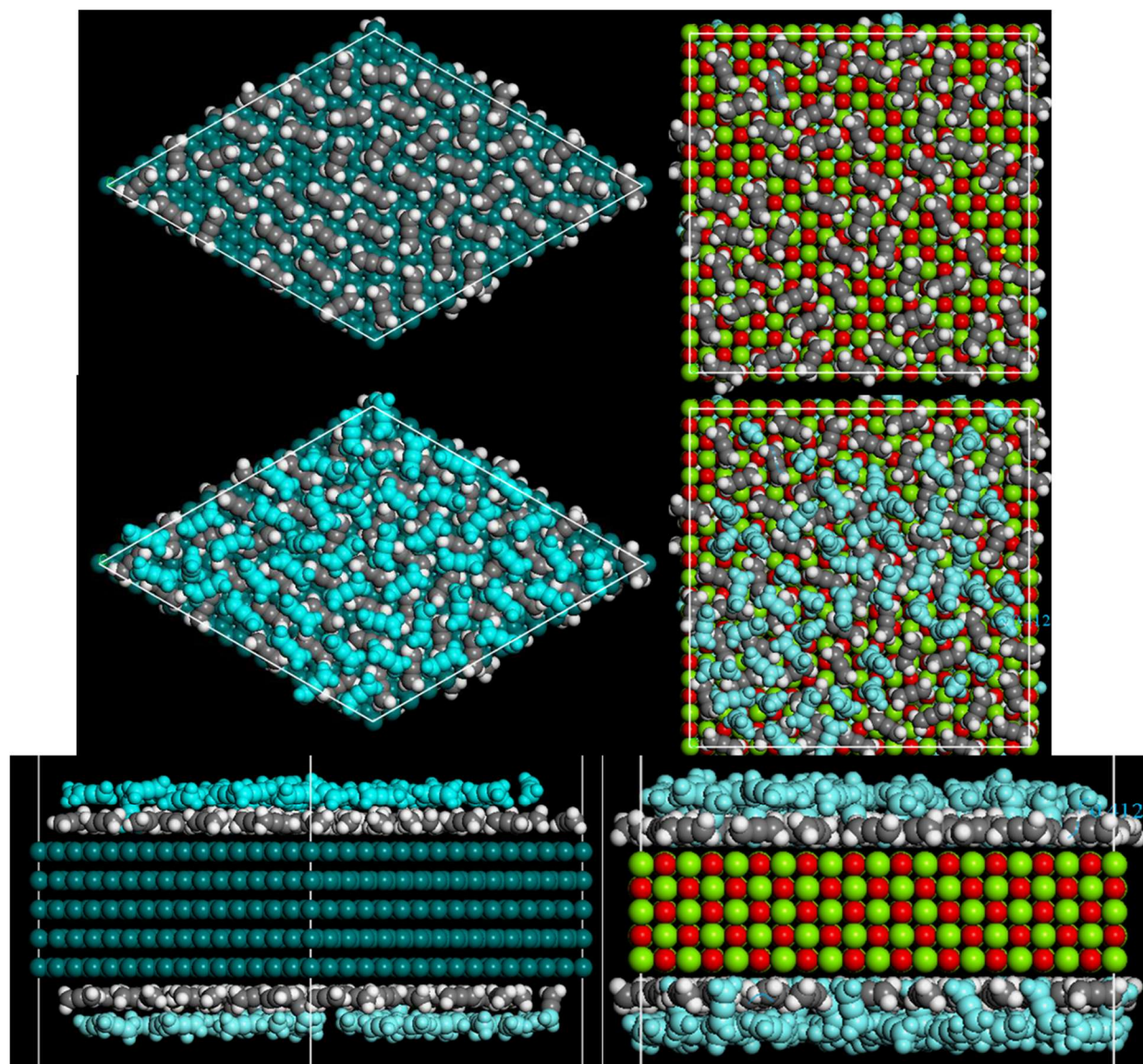


Figure 6.15: Simulation snap shots of bilayers of allene on graphite and MgO and 5K

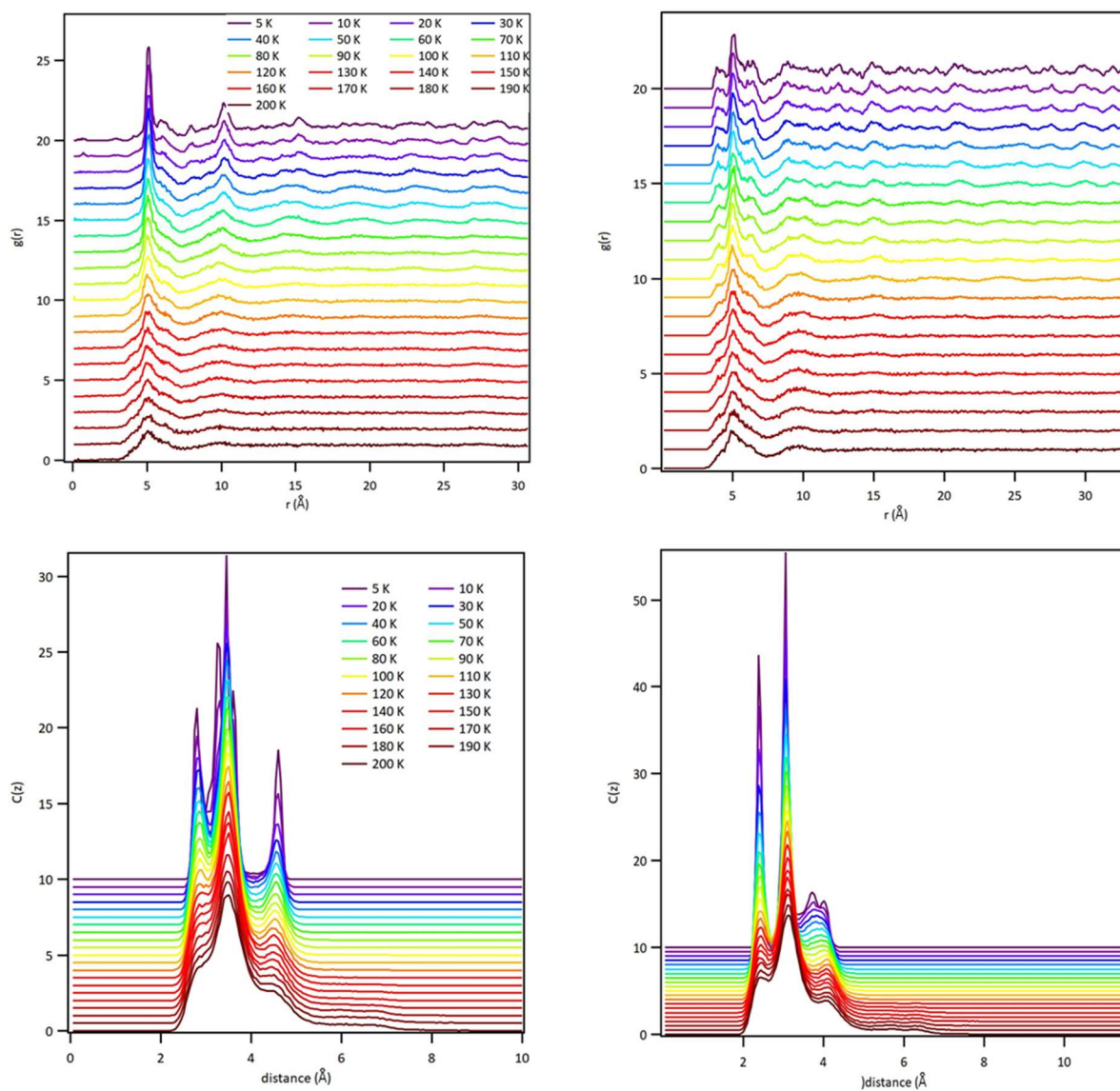


Figure 6.16: Radial distribution function and concentration profile analysis for allene monolayer on graphite (left) and MgO (right)

meaning there is optimization of the molecule-surface interactions with simultaneous frustration in the molecule-molecule interactions. Also observable is a region of a square bond pattern structure that appears to be incommensurate with the surface, and is an somewhat efficient way of minimizing the quadrupole-quadrupole energies in longer quadrupolar molecules alternatively to square-T and herringbone lattices. Though not quite as efficient as the square-T lattice, this orientation does optimize the van der Waals forces between molecules as well and is a reasonable structure for allene in two dimensions. In the bilayer regime, there are a considerable number of molecule perpendicular to the surface that act as members of both layers (Figure 6.15). In contrast with acetylene where the quadrupoles and surface corrugation are cooperative, these simulations suggest the possibility that there is competition between two differently orientation configurations that might be similarly optimized. It may also be possible that the hindered rotation of molecules by surrounding molecules and the strong modulation of the surface potential in competition with one another means the equilibration processes are too slow to be reached in these simulations.

Allene on graphite shows a much higher degree of ordering in its structure, adopting an incommensurate, centered rectangular herringbone lattice with the molecular orientations no more than 15 degrees from the perpendicular T-configuration. Small amounts of the slipped-parallel unit cell are observable, but the population of these occurrences is small and the boundaries of these two structures show very little signs of lattice strain. There are no signs of the bound dislocation pairs that were seen in the acetylene on graphite simulations with increased quadrupole strength. These simulations suggest that on graphite, the molecule-molecule interactions of allene dominate. Above 100 K, the films show a fair degree of isotropic disorder. It has been postulated that linear quadrupole interactions in two-dimensional systems can never become fully isotropic or disordered. The corollary to this is that they can become very close this point, but some bond and orientational ordering will survive. This does seem to be what is occurring in these higher temperature simulations. The ordering is very weak, and the disorder is very dynamic. The molecule-molecule interactions are extremely poorly optimized in such a phase. It would seem logical that the strong surface attraction of these molecules and the effect of thermal energy on their two-dimensional behavior create a system of high entropy, but low enthalpy, due to the way the molecules are forced to interact. Though not conclusive, such

a scenario would describe anomalously low enthalpy, extremely high entropy adsorption behavior as witnessed in the isotherms.

6.4 – Conclusions on the Adsorption of Allene

The adsorption isotherms and simulation studies of this current chapter represent novel work done on the study of the physical interactions of the smallest cumulene molecule, allene. Despite its unique differences from other molecules as a result of its stacked double bonds, and it being a rare example of a small, light, simple molecule with $D_{\infty h}$ symmetry, studies on the physical properties and behavior of this molecule are very limited. Most work is focused on catalysis and polymer applications.

The data presented in this chapter shows that allene was able to act against expectations and displayed some interesting adsorption properties. Though allene is a close cousin to acetylene in terms of its constituents, its size, and its quadrupole strength, small differences can lead to significant changes in the adsorption behavior. This is plainly evident in the isotherm and simulation studies presented in this chapter.

The thermodynamics of allene were studied on surfaces of graphite and MgO in a temperature range from 140 K to 200 K which correspond to a range above the triple point for the bulk phase. Two layering transitions were seen for each system, along with distinct incomplete wetting present following completion of the monolayers. The differential heats and entropies of adsorption displayed interesting and unexpected results for both systems. On graphite, the first monolayer displayed two thermodynamically distinct regions, with the divide at 152 K. The higher temperature region was one of moderate and favorable enthalpy and entropy. The lower region however possessed an massive, positive enthalpy value; the corresponding heat of adsorption was only 42 % of the bulk heat of condensation. Despite this decidedly thermodynamically unfavorable situation, the free energy for this transition is highly favorable, driven, against the enthalpy, by an even more startlingly large entropy. On MgO, the adsorption processes were moderately enthalpically favored, with a very small, but favorable entropy as well. Analysis showed each layering transition to be thermodynamically constant of the entire temperature range. Temperatures corresponding to potential phase transitions were identified using the two-dimensional compressibilities. On graphite, a determination of 150.5 K was made, with the second layer's point was to within a degree the same. Similarly, on MgO,

155 K was observed as a potential phase transition with the second layers corresponding value measured to be only 1 K higher in temperature and quite possibly occur at the same temperature as each other

Molecular dynamics simulations were conducted for a range of coverage densities with both substrates. On graphite, the films adopted an incommensurate centered rectangular structure of fairly high order. At warmer temperature though, the molecules become high disordered while trapped to the two-dimensional plane, leading to very poorly optimized molecule-molecule interactions, but pinned by a large but smooth molecule-surface interaction.

The physical properties of allene prevent the isotherm measurements from reaching a temperature where solid adsorbed phases might be observable. The molecular dynamics highlight some potentially interesting aspects of the system, but the extra restraints required by the force field indicate a lack of consideration for cumulenes in molecular dynamics. While comparisons were drawn between these simulations, the isotherm behaviors, and the interactions of quadrupolar molecule, these connections were speculative in nature. It is hoped that these studies will lead to structural and dynamic studies of allenes adsorption processes. In the regions outside of the isotherms reach. Empirical experimental data would also serve a test case to validate or invalidate the simulations results, and by extension, the quality of the forcefields abilities to model cumylene systems.

Chapter 7 – Conclusions

7.1 – Review of Objectives and Studies

The goal of this dissertation was to examine the adsorption behavior of two simple linear hydrocarbons that possess anomalously strong quadrupole interactions compared to similarly sized molecules. One of these, acetylene, has been well-studied in the literature and, despite a colossal effort, has resisted accurate computational modeling. The other, allene, represents the opposite side of the spectrum, as it has received very little attention from researchers and very little effort in the explorations of its properties outside of very specific applications. In short, neither molecule is well-understood, and each provides the test bed for exploration of unique and interesting behaviors in adsorbed systems.

Acetylene and allene present several different cases for the examination of ways systems of varying symmetries may interact. For example, the molecular size and quadrupole strength of acetylene creates a large preference towards a square-T lattice. The size and orientation of molecules within this lattice matches closely with the 2x2 commensurate registry of the MgO (100) surface. The preferred molecular spacing is only marginally larger than that of this surface registry, but the corrugation of the surface potential creates strong molecule-surface interactions. Conversely, graphite, with its hexagonal surface configuration, is incompatible with the square-T lattice preferred by the molecules. Other similarly sized but weaker quadrupolar molecules, such as nitrogen, tend to adopt hexagonally configured herringbone lattices that are a compromise between the molecule-molecule and molecule-surface interactions. Alternatively, the stronger quadrupole of acetylene allows for more frustration of forces to occur, and a complex phase behavior during adsorption results.

Physisorption studies provide an ideal method to refine and validate the development of intermolecular potentials. Simulations conducted using such potentials are invaluable in the microscopic picture they can provide to match the abstract quantities of empirical data. These potentials, when possible, are typically validated by their ability to describe bulk behavior. For example, in the instance of acetylene, it is clear that despite accurate information now available on three distinct condensed phases (two solids and a liquid), the ability to describe all three collectively with a single set of potentials, or even just for the two solid phases, has not been met with complete success. The adsorption of acetylene on graphite, with its many subtle transitions and interacting continuous and first order melting transitions, provides a much larger range of

behaviors that could help lead to the development of more accurate modeling for this molecule. Similarly, it appears that allene has hardly, if at all, been the subject of targeted modeling studies.

7.1.1 – Acetylene on Graphite Summary

Adsorption isotherms were examined between 119 K and 141 K. Computational studies were performed that included comparisons of previous force fields utilized in the literature, as well as energy minimizations to examine molecule-surface interactions and molecular dynamics simulations that were conducted for several forcefield variations for a wide range of coverages. Elastic neutron diffraction data was collected over a temperature range from 10 K to 165 K within the primary monolayer step with a primary focus on the melting region observed in the isotherms from 124 K to 138 K. Major highlights are succinctly summarized as follows:

- Adsorption Isotherms
 - Four distinct features were observable before the beginning of the second layering transition (labeled A through D).
 - A prominent transition present in all features, A through D, was observed at 132.5 K, and a much more subtle transition observed at 126 K for substeps A, B, and D.
 - The C substeps displayed a second possible transition around 134.5 K that is seemingly unique to this substep alone.
 - Clausius-Clapeyron analysis showed a general trend in mild or moderate enthalpic unfavourability in adsorption, with large and favorable differential enthalpies. The exceptions to this are the C'_1 and C_2 substeps, for which this trend is completely reversed.
- Computational Studies
 - Initial studies using the default COMPASS force-field parameters only showed a single ordered phase that was a commensurate herringbone structure inconsistent with other experimental results.
 - Examination of other published force fields suggested more accurate behavior may be obtained with stronger quadrupole strengths than the default COMPASS values.
 - Studies of several variations to the quadrupole interactions were conducted showing data more consistent with experimental results

- Three ordered phases consistent with previous studies, as well as this study, were observed: a low-coverage square-T structure, a high-coverage rectangular herringbone structure, and a high-coverage, obliquely distorted herringbone structure.
- In the square-T phase, dislocations and melting behavior nominally consistent with KTHNY theory for melting were observed.
- Neutron Diffraction
 - Diffraction profiles for the ordered low-coverage phase were fit to a square-T lattice with a diffuse disordered background present.
 - Diffraction profiles for a disordered phase occurring above 133 K were fit to a uniaxially commensurate centered rectangular structure.
 - Diffraction profiles from 127 K to 132 K showed distinct coexistence of the two aforementioned phases.
 - Two-phase refinement of diffraction profiles in the coexistence region showed melting behavior of the solid phase consistent with some predictions made by the KTHNY model:
 - Melting process began at 126 K
 - Melting was continuous until after 132 K, where it became first order
 - Notable deviations from this model:
 - the liquid phase was not isotropic
 - the melting ends in a first order transition
 - Data seems to describe a nearly uniaxial melting process that suggests strong influence of both the molecule-molecule and molecule-surface interactions

7.1.2 – Acetylene on MgO Summary

Adsorption isotherms were collected in a temperature range from 119 K to 201 K. Computational studies examined the adsorption behavior using the default COMPASS force-field parameters. Preliminary neutron data was also collected for the monolayer film at low coverages, however, issues with background subtraction data quality prevented meaningful analysis of film structure.

- Adsorption Isotherms
 - Isotherms consisted of two, well-defined layering transitions with non-wetting behavior after each.
 - Isotherms transitioned instantaneously between non-wetting to bulk condensation at the saturated vapor pressure.
 - At low temperature, mild incomplete wetting characteristics were observed in the first layering step, which evolved into two transitions at 128 K and 140 K, proceeding to a complete wetting behavior.
 - Clausius-Clapeyron analysis shows that, below 140 K, the adsorption is enthalpically unfavorable and is driven by a large entropy, and above 140 K, adsorption is favorable both enthalpically and entropically.
 - Apparent phase boundary behavior of the first layering step suggests that the film has not yet reached a critical point at the highest temperatures measured.
 - Monolayer APM values are consistent with a 2x2 commensurate registry.
- Computational Studies
 - Molecular dynamics show a highly-ordered square-T phase in a 2x2 commensurate registry with the surface.
 - Molecules are tilted slightly out of the plane to allow for the mismatch in size between the molecule and surface lattice.
 - As temperature increases, disorder in these out-of-plane orientations grows, while the in-plane ordering remains constant.
 - Harmonic oscillations within the film structure were observed to be consistent with simple models of a two-dimensional lattice of quadrupoles with fixed positions.
 - Simulations of partial second layer coverages still show a relatively high degree of positional order of the molecules, but the molecular orientations deviate from the ideal T-shaped configuration.

7.1.3 – Allene on Graphite Summary

Isotherms were collected over a temperature range from 140 K to 200 K. These were supplemented with computational studies of the molecule-surface interactions and molecular dynamics simulations at three coverages.

- Adsorption Isotherms
 - Two distinct layering steps were observed with obvious incomplete wetting behavior in the isotherm shape.
 - The free energy values of the first layering step show the adsorption to be highly favorable.
 - Clausius-Clapeyron analysis shows two thermodynamically distinct regions in the first layering step:
 - Below 152 K, the differential enthalpy is significantly unfavorable; however, this is offset by an even more significant, favorable entropy value.
 - Above 152 K, the adsorption is moderately enthalpically favorable, with less, though still substantial, entropic favorability.
 - FWHM analysis suggests a critical point occurs in both layers around 150 K.
- Computational Studies
 - Molecular dynamics trajectories show single, distinct, ordered structure and seems split between two motifs:
 - A bond (brick-laying) pattern
 - A rectangular herringbone structure with the molecules twisted about 15 degrees from the T-configuration
 - Molecules are oriented with one hydrogen pair parallel to the surface and the opposing pair perpendicular to the surface.
 - Quasi-long-range order begins to develop around 90 K.
 - The second layer is much more highly disordered than the first layer.

7.1.4 – Allene on MgO Summary

Isotherms were collected over a temperature range from 140 K to 185 K. These were supplemented with computational studies of the molecule-surface interactions and molecular dynamics simulations at three coverages.

- Adsorption Isotherms
 - Two distinct layering steps were observed with obvious incomplete wetting behavior in the isotherm shape.

- Clausius-Clapeyron analysis shows layering features are moderately enthalpically favored with moderately large entropic favorability.
- FWHM analysis suggests a critical point in both phases that occurs around 155 K.
- Computational Studies
 - Molecular dynamics trajectories show two distinct motifs with a high degree of disorder:
 - A bond (brick-laying) pattern
 - A herringbone lattice with a 3x1 commensurate registry
 - Molecules are oriented with the terminal hydrogen pairs of the molecules 45° from the surface.
 - Quasi-long-range order begins at 80 K.
 - Within the second layer, disorder is much higher, having multiple molecules perpendicular to the surface that penetrate both layers.

7.2 – Future Works

All systems studied in this dissertation would benefit from neutron diffraction or other similar structural measurements. Any ordering transitions present for allene on both substrates are far outside the temperature range obtainable with isotherm measurements. The extremely positive differential enthalpy and entropy below 152 K on graphite is especially unusual and warrants further investigation using different experimental probes in more detail in this temperature range and at lower temperatures. Acetylene on MgO presents seemingly contradictory behavior between the expected molecule-substrate compatibility. The region around the transitions at 128 K and 140 K will require a much more detailed experimental study, including structural analysis in order to understand the nature of these transitions. Acetylene on graphite needs a more detailed structural analysis of the higher coverage phases, including the transitions of the C substep in the isotherms, as well as the transitions from the S_{12} and S_2 phases.

These studies are meant to represent the two simplest examples in a homologous series of linear hydrocarbons with quadrupolar interactions. These studies can be further expanded in the future to include modifications of substrate symmetry, such as with the three-fold honeycomb lattice of hexagonal boron nitride. Explorations of other molecules could include methyl acetylene, with its broken axial symmetry, diacetylene, with a longer aspect ratio and higher

quadrupole moment, and substituted acetylenes or allenes, such as difluoro-acetylene, with a very similar size to acetylene but a smaller quadrupole moment.

7.3 – Closing Remarks

The cooperation, competition, and structural frustration observed in the systems of these studies, both real or computational, demonstrate just how interesting and complex these systems can be. An example of this is the general trend of enthalpic unfavorability and high entropic favorability present across all of these systems. Furthermore, even in a system where the sizes and symmetries of the molecules and surface are highly compatible, such as acetylene on MgO, the observed results display high entropies and two distinct transitions as revealed in the isotherm data. The complexity of these interactions drives behaviors that are atypical compared with many other adsorbed systems that have been studied in the literature.

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Appendices

A – Two-Dimensional Radial Distribution Function Script

The default calculation algorithm included in the Forcite analysis package was intended for analysis of three-dimensional systems however, and if used on two-dimensional systems resulted an artifact that drove the intensities towards zero at increasing distances. Though reasonable information about the first coordination shell could be obtained, the errors in intensities of each subsequent shell grew rapidly in magnitude. It was assumed at first that this was the result of the normalization of molecules in a two-dimensional plane over the volume of a spherical shell element for each radius bin in the generated histogram. Such an artifact would be easily corrected for, however applying such a correction did not remove the artifact, and only marginally improved the results. The exact reason for this issue was not determined, however it was suspected that it was the result of the combination of the volume element problem and the way the algorithm dealt with periodic boundary conditions in three dimensions vs two dimensions. While this latter issue should not seem to make a difference in theory, it was noted the calculations typically resulted in an extra odd feature at a distance correlated with the lengths of simulation box along in the surface plane, indicating a boundary artifact.

Materials Studio allows for the use of custom scripts written in Perl to enable additional analysis not directly possible with the tools native to the program. This following script enables the user to obtain the two-dimensional radial distribution functions from simulation trajectories in the form utilized in this dissertation.

A.1 – Perl Script for Calculation of Two-Dimensional Radial Distribution Function

The following text is the Perl code for the determination of two-dimensional radial distribution functions from molecular dynamics simulations in Materials Studio 6.0. Some lines of code had to be split over multiple lines to be formatted into this document. The end of individual command lines typically end in a semi-colon or right bracket symbol. It may require lines to be reparsed if imported from this document back into a Perl script file. The code is as follows:

```

#!/perl

use strict;
use Getopt::Long;
use MaterialsScript qw(:all);
use POSIX;
use Math::Trig;

#####
#Set Controllable Variables#####
#####

my %Args;
GetOptions(\%Args, "Document_Name=s", "Start_Frame=f",
"Number_of_Frames=f", "End_Frame=f", "R_max=f", "dr=f");

#####
#Dependent Parameters (DO NOT ALTER)#####
#####

#Import Arguments#####

my $docname = $Args{Document_Name};
my $start = $Args{Start_Frame}; #first frame of RDF calc
my $numframe = $Args{Number_of_Frames}; #total frames analyzed
my $endframe = $Args{End_Frame}; #last frame of RDF calc
my $rmax = $Args{R_max}; #maximum radius for rdf calculation
my $dr = $Args{dr}; #histrogram resolution
    #requires more frames for good statistics but takes longer
    #too many frames and system will run out of memory

#Set Files#####

my $trajectory = Documents -> ActiveDocument;
my $frame = Documents -> New("frame.xsd");
my $progress = Documents->New("progress.txt");

#Set Frame Intervals#####

$trajectory -> CurrentFrame = $trajectory -> EndFrame;
my $numframes = $trajectory -> NumFrames;
my $framestep = ceil(($endframe - $start)/$numframe);
my $startframe = $endframe - $framestep * $numframe;
    if ($startframe < 1){

        my $p = 1;

        until($startframe >= 1){

```

```

        $startframe = $endframe - $framestep * ($numframe
- $p);

        $p++

    }

}

```

```

my $numstep = ($endframe - $startframe)/$framestep;

```

```

#Cell Parameters and Indices#####

```

```

my $cell = $trajectory -> SymmetryDefinition;
my $lengthA = $cell -> LengthA;
my $lengthB = $cell -> LengthB;
my $lengthC = $cell -> LengthC;
my $thetadeg = $cell -> AngleGamma;
my $theta = $thetadeg * pi / 180;

```

```

my $xmax = $lengthA;
my $ymax = $lengthB * sin($theta);
my $zmax = $lengthC;
my $cellarea = $xmax * $ymax;
my $topmolenum;
my $botmolenum;

```

```

my $megaindex = int($rmax / $ymax + 0.5);
my $megashift = 2 * $megaindex + 1;

```

```

#Prepare Output Table#####

```

```

my $rdf = Documents -> New("$docname rdf.std");

```

```

$rdf -> ColumnHeading("A") = "r";
$rdf -> ColumnHeading("B") = "rdf top";
$rdf -> ColumnHeading("C") = "rdf bottom";
$rdf -> ColumnHeading("D") = "rdf combined";

```

```

my @radius;
my @Rrtop;
my @Rrbot;
my @Rrcombined;

```

```

for (my $w = 0; $w < $rmax/$dr ; $w++){

    my $radius = $dr * ($w + 1);
    my $Rr = 0;

    $rdf -> Cell($w , 0) = $radius;
    $rdf -> Cell($w , 1) = 0;

```

```

    $rdf -> Cell($w , 2) = 0;
    $rdf -> Cell($w , 3) = 0;

    push (@radius, $radius);
    push (@Rrtop , $Rr);
    push (@Rrbot , $Rr);
    push (@Rrcombined , $Rr);

#    $Documents{"progress.txt"}-> Append(sprintf "w = $w");
#    $progress -> UpdateViews;

}

#####
#Start RDF Calculation#####
#####
#####

#Select Frame#####

for (my $h = 0 ; $h < $numstep ; $h++){

    my $percent = 100 * $h / $numstep;

    print "h = $h";

    $Documents{"progress.txt"}-> Append(sprintf "$percent
%ln");
    $progress -> UpdateViews;

    my $framenum = $startframe + $h * $framestep;

    $trajectory -> Trajectory -> CurrentFrame = $framenum;
    $frame -> ClearContent;
    $frame -> Copyfrom($trajectory);

    $frame -> SymmetryDefinition -> LatticeOrigin = Point(X =>
0, Y => 0, Z => 0);
    $frame -> SymmetryDefinition -> OrientationConvention = "A
along X, B in XY plane";
    $frame -> ReorientToStandard;

#Initialize Arrays and Scalars#####

    my @xtop;
    my @xmegatop;
    my @ytop;
    my @ymegatop;
    my @ztop;
    my @zmegatop;

```

```

my @xbot;
my @xmegabot;
my @ybot;
my @ymegabot;
my @zbot;
my @zmegabot;

#Get Centroids#####

my $moleculestop = $frame -> UnitCell -> Sets("top") ->
Molecules;

foreach my $molecule (@$moleculestop){

    my $centroidtemp = $frame -> CreateCentroid($molecule
-> Atoms);

    my $coordinate = $centroidtemp -> CentroidXYZ;

    my $x = $coordinate -> X;
    my $y = $coordinate -> Y;
    my $z = $coordinate -> Z;

    until ($y >= 0){

        $y += $ymax;
        $x += $lengthB * cos($theta);

    }

    until ($y <= $ymax){

        $y -= $ymax;
        $x -= $lengthB * cos($theta);

    }

    until ($x >= $y * cos($theta) / sin($theta)){

        $x += $xmax;

    }

    until ($x <= $y * cos($theta) / sin($theta) + $xmax){

        $x -= $xmax;

    }

    until ($z >= 0){

        $z += $zmax;

    }

}

```

```

    }

    until ($z <= $zmax){

        $z -= $zmax;

    }

    push (@xtop, $x);
    push (@ytop, $y);
    push (@ztop, $z);

}

my $moleculesbot = $frame -> UnitCell -> Sets("bottom") ->
Molecules;

foreach my $molecule (@$moleculesbot){

    my $centroidtemp = $frame -> CreateCentroid($molecule
-> Atoms);

    my $coordinate = $centroidtemp -> CentroidXYZ;

    my $x = $coordinate -> X;
    my $y = $coordinate -> Y;
    my $z = $coordinate -> Z;

    until ($y >= 0){

        $y += $ymax;
        $x += $lengthB * cos($theta);

    }

    until ($y <= $ymax){

        $y -= $ymax;
        $x -= $lengthB * cos($theta);

    }

    until ($x >= $y * cos($theta) / sin($theta)){

        $x += $xmax;

    }

    until ($x <= $y * cos($theta) / sin($theta) + $xmax){

        $x -= $xmax;

    }

}

```

```

until ($z >= 0){
    $z += $zmax;
}

until ($z <= $zmax){
    $z -= $zmax;
}

push (@xbot, $x);
push (@ybot, $y);
push (@zbot, $z);
}

if ($h == 0){
    $topmolenum = scalar(@xtop);
    $botmolenum = scalar(@xbot);
}

#Create Megacell#####

my $scalar = scalar(@xtop);

for (my $j = 1; $j <= $scalar; $j++){

    my $xtemptop = $xtop[$j];
    my $ytemptop = $ytop[$j];
    my $ztemptop = $ztop[$j];

    for (my $k = -$megaindex; $k <= $megaindex ; $k++){

        for ( my $l = -$megaindex; $l <= $megaindex ;
$1++){

            my $xtemptop2 = $xtemptop + $l * $xmax;
            my $ytemptop2 = $ytemptop + $k * $ymax;
            my $ztemptop2 = $ztemptop;

            push (@xmegatop, $xtemptop2);
            push (@ymegatop, $ytemptop2);
            push (@zmegatop, $ztemptop2);

        }

    }

}

```

```

my $scalar = scalar(@xbot);
for (my $j = 1; $j <= $scalar; $j++){

    my $xtempbot = $xbot[$j];
    my $ytempbot = $ybot[$j];
    my $ztempbot = $zbot[$j];

    for (my $k = -$megaindex; $k <= $megaindex ; $k++){
        for ( my $l = -$megaindex; $l <= $megaindex ;
$1++){

            my $xtempbot2 = $xtempbot + $l * $xmax;
            my $ytempbot2 = $ytempbot + $k * $ymax;
            my $ztempbot2 = $ztempbot;

            push (@xmegabot, $xtempbot2);
            push (@ymegabot, $ytempbot2);
            push (@zmegabot, $ztempbot2);

        }

    }

}

#Calculate Distances#####

$scalar = scalar(@xtop);
my $scalarmega = scalar(@xmegatop);

for (my $n = 1 ; $n <= $scalar ; $n++){

    my @radiustemp = ();

    for (my $o = 1 ; $o <= $scalarmega ; $o++){

        my $radiustemp = sqrt(($xtop[$n] - $xmegatop[$o])
* ($xtop[$n] - $xmegatop[$o]) + ($ytop[$n] -
$ymegatop[$o])*( $ytop[$n] - $ymegatop[$o]) + ($ztop[$n] -
$zmegatop[$o])*( $ztop[$n] - $zmegatop[$o]));

        if ($radiustemp > 0 && $radiustemp <= $rmax){

```

```

        push (@radiustemp, $radiustemp);
    }
}

for(my $q = 0 ; $q < $rmax / $dr ; $q++){
    my $radius = $radius[$q];
    foreach my $radiustemp (@radiustemp) {
        if ($radiustemp >= $radius && $radiustemp <
$radius +$dr){
            $rdf -> Cell($q , 1) += 1;
        }
    }
}

}

$scalar = scalar(@xbot);
my $scalarmega = scalar(@xmegabot);
for (my $n = 1 ; $n <= $scalar ; $n++){

    my @radiustemp = ();

    for (my $o = 1 ; $o <= $scalarmega ; $o++){

        my $radiustemp = sqrt(($xbot[$n] -
$xmegabot[$o])*( $xbot[$n] - $xmegabot[$o]) + ($ybot[$n] -
$ymegabot[$o])*( $ybot[$n] - $ymegabot[$o]) + ($zbot[$n] -
$zmegabot[$o])*( $zbot[$n] - $zmegabot[$o]));

        if ($radiustemp > 0 && $radiustemp <= $rmax){
            push (@radiustemp, $radiustemp);
        }
    }
}

for(my $q = 0 ; $q < $rmax / $dr ; $q++){

```

```

        my $radius = $radius[$q];
        foreach my $radiustemp (@radiustemp) {
            if ($radiustemp >= $radius && $radiustemp <
$radius +$dr){
                $rdf -> Cell($q , 2) += 1;
            }
        }
    }
}

#Convert to RDF Values#####
for (my $u = 0; $u < $rmax/$dr ; $u++){
    my $radius = $dr * ($u + 1);
    my $Rrtop = $rdf -> Cell($u , 1);
    my $Rrbot = $rdf -> Cell($u , 2);
    my $Rrcombined = $Rrtop + $Rrbot;

    $rdf -> Cell($u , 1) = $Rrtop / ($numstep * $topmolenum * 2
* pi * $radius * $dr * $topmolenum / $cellarea);
    $rdf -> Cell($u , 2) = $Rrbot / ($numstep * $botmolenum * 2
* pi * $radius * $dr * $botmolenum / $cellarea);
    $rdf -> Cell($u , 3) = $Rrcombined / ($numstep *
($topmolenum + $botmolenum) * 2 * pi * $radius * $dr *
($topmolenum + $botmolenum) / (2 * $cellarea));
}

```

A.2 – Utilization of the Program

This script was designed to be operated through a custom user menu within material studio. The details on how to set up such a menu can be found in the programs support files. To set up the menu, the input arguments required are:

- “Document_Name”
 - Data type -> string
 - Default Value -> leave blank
- “Start_Frame”
 - Data type -> floating point

- Default Value -> 100
- “Number_of_Frames”
 - Data type -> floating point
 - Default Value -> 50
- “End_Frame”
 - Data type -> floating point
 - Default Value -> 1000
- “R_max”
 - Data type -> floating point
 - Default Value -> 50
- “dr”
 - Data type -> floating point
 - Default Value -> 100

The version of the script listed will run automatically on the active trajectory document open in the visualizer. It requires no special set of the trajectory file to operate and produces three RDF profiles from the simulations, one for each surface, and a combined average of the two. Note the third option is useful for good statistics, however it is not wise to use on some systems if the two surfaces are in different structural arrangements. The restrictions places on how information can be manually called from the trajectory files means that the program unfortunately must store each frame analyzed as its own document, making this script rapidly run out of memory dependent on the size of the system. For a 100 molecule system, it was determined that 50 frames was sufficient for good statistic. For a 240 molecule system, the calculations would run out of memory after around 20 analyzed frames, however the statistics were generally still sufficient with this number. If better statistics are required than is achievable in the memory limit, the analysis should be run in smaller fragments and combined.

The program distinguishes the two surfaces from one another by assuming that the substrate lies at the mid-point of the simulation box. There are three known scenarios where this fully automated version will not work as intended. The first is if a separate analysis needs to be run on separate layers of a multilayer system. The second is if the “molecule” identifier used

by the software was never added to the adsorbate, as this identifier is needed for analysis. The third is if the substrate slab is not centered vertically in the cell. In these instances a second version of the script was created, with one difference, the molecules for each layer to be analyzed, two at a time, are added to “set” within the visualizer, these sets must be labeled “top” and “bottom” in order to function properly. The code variant simply requires the omission of lines 85 through 136 from the script (the “create sets” section).

A.3 – Future development

The largest issue that remains with the script in its current form is its slow rate of speed and high memory usage. These issues are the result of the limitations of the scripting commands allowed within Materials Studio. It is possible there is a work around for one or both these issues, and would be an objective for further potential improvements.

A second improvement may be to automate the multilayer system. It should be possible to add further arguments to script with can allow a user to the z coordinate for each layer as an input argument, and have select molecules within some tolerance of that value to belong to a certain layer.

Other small improvements may be made in the identification of molecule self-correlation as a result of periodic boundary conditions. Currently large spikes occur in specific bins corresponding to the distances to the same coordinates as the molecule centers in adjacent supercells due to the periodic boundary conditions. Lastly, the same process may be used to calculate the structure factors at the same time as the RDFs in the algorithm.

B - Automated Program for Two-Dimensional Diffraction Refinement

An important work of this dissertation was the analysis and refinement of a liquid-solid coexistence (or possible tetratic phase) for acetylene on graphite. The method that has been used quite successfully in the past by this group utilizes a Fortran program that generates diffraction lineshapes for a specified structure. This system required manual creation of input in a properly formatted text file, with a separate file required for each structure to test, and they can only be run one at a time. This method has been reliable, but it is most definitely not high throughput, has no form of user interface to interpret data, and requires a significant amount of

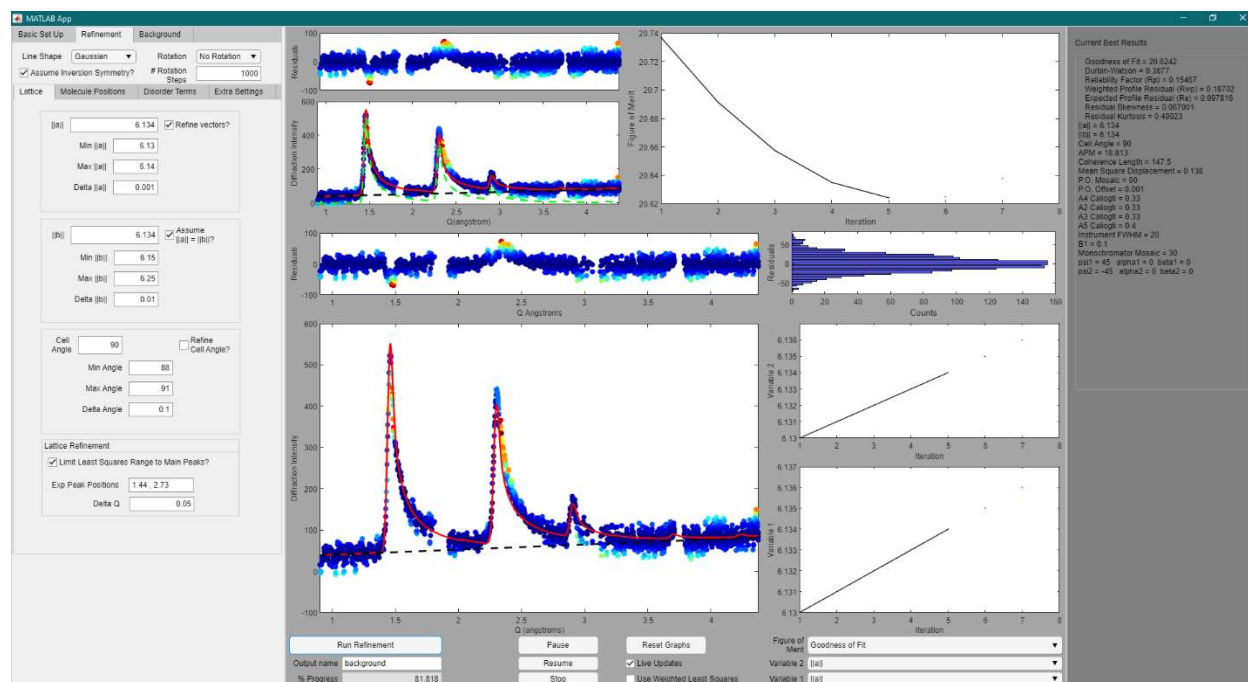


Figure B1: The Refinement GUI window

user involvement. High quality analysis of diffraction data from multiple temperatures of a two phase coexistence region was something that was not practical following a manual analysis method. A Matlab app was designed that acts as an automatic controller and GUI for the lineshape generation program. Through the use of an interactive process one or many of the possible input parameters (structural, instrumental, disorder, etc.) it is able to perform a crude but effective version of Rietveld refinement on two-dimensional diffraction data.

B.1-Program Outline

The program is not incomplete in terms of finer details that will be needed in the future, but in its current form its code is 330 pages of text in length, and for considerations of content it will not be possible to fully describe here. Instead the basic form of the program will be described. The first main improvement this system brings to the lineshape fitting process is the addition of a GUI to remove much of the need for manual data processing (figure B1)

On the left of the interface is where the inputs may be specified. The user may also select one or more variable for refinement here, for each variable to be refined, and minimum and maximum range as well as iteration increment must be specified. When executed, the program will initiate a process that uses a large series of nested loops to iterate over all the permutations of the variables selected for refinement. For each loop, the program will gather all the required parameters and use them to generate the input file for the Fortran program. When this program finishes its calculation, the interface program reads the output file for the lineshape. It then performs a least squares optimization of the calculated lineshape with a scaling factor and a user selected background function against the raw diffraction data. The results least squares value for the best first for this iteration is recorded, and the loop is repeated and the fit quality is tracked using the goodness of fit from each iteration.

B.2 – Goodness of Fit metric

An important detail that was realized during development is that the standard measure for goodness of fit in Rietveld analysis is not viable in two dimensions for two noted reasons. This value takes the simple sum of squares formula and normalizes it by multiplying the residuals by

the inverse of the experimental diffraction intensity at each point. This statistical consideration is valid in normal counting experiments (i.e. negative values are not permissible). As the two-dimensional diffraction data is a difference counting experiment, negative values are possible in the data. The second issues had to do with a problem in two-dimensional diffraction that couples the correlation length and the peak height. The Rietveld goodness of fit metric puts less weight on higher intensity values. When used as part of this refinement process, it developed an issue of run-away fitting in peak height where it would indefinitely make peaks narrow and taller to improve the fitting of the baseline, at the expense of the rest of the data. Alternative metrics used for three-dimensional refinement such as the Durbin-Watson statistic performed equally poorly. The best statistic examined turned out to be a simple least squares method. Such a statistic has a drawback in that it is not normalized to the data being fit, and will take different minimum values for systems of different noise for otherwise equally good fits. However, it provided the most stable and consistent metric for obtaining good agreement between calculated and experimental diffraction.

B.3 – Fitting Algorithm

The following section is an outline of the fitting process and algorithm used in the refinement process. The algorithm uses a series of nested loops to iterate over the all value combinations based on the refinement selection:

- 1) Lattice constants
- 2) Lattice angle
- 3) Euler angles
 - a) Psi
 - b) Alpha
 - c) Beta
- 4) Coherence length
- 5) Mean squared displacement
- 6) Preferred orientation fwhm
- 7) Preferred orientation mosaicity
- 8) Instrument parameters (Caglioti parameters)

When the program starts, the following is the operational sequence of the program:

- 1) Retrieve non-refined parameters
- 2) Check for refinement selections and retrieve refinement boundaries and intervals
- 3) Retrieve values for non-refined parameters
- 4) Refinement loops
 - a) Print lineshape input file
 - b) Execute lineshape generation
 - c) Retrieve output data
 - d) If dual phase refinement is selected
 - i) Second refinement loop
 - (1) Print lineshape input
 - (2) Execute lineshape generation
 - (3) Retrieve output data
 - (4) Go to (e)
 - e) Run baseline and scaling fit
 - f) Check goodness of fit
 - i) Check if best fit and save if best
 - g) Display current progress
 - h) Repeat loop
- 9) Save progress to spreadsheet

Vita

Andrew Pedersen was born and raised in Weddington, North Carolina, a small town just outside of Charlotte with a rich history of horse farms. While attending the University of North Carolina at Charlotte on a music scholarship for his performance as a bass trombonist, Andrew found his passion for physical chemistry with a special interest in research applicable to optimization of alternative energy sources, particularly solar energy. Andrew proceeded to complete a Master's Degree in Chemistry at this same institution, under the continued mentorship of Dr. Marcus Jones. It was at this time that he met the one who would become his wife, and they together received opportunities to pursue their doctorates at the University of Tennessee, Knoxville. The dissertation enclosed herein is the culminating work representative of Andrew's efforts towards a Doctorate in Chemistry, with a concentration in Physical Chemistry. While Andrew continues to seek his perfect career path, he maintains a strong interest in research and development for alternative energy sources, materials characterization, and education.