

ADSORPTION OF CYCLOALKANES ON SURFACES WITH DIFFERENT SYMMETRY AND COMPOSITION

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

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May 2019

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ACKNOWLEDGEMENTS

I am grateful to a number of people who believed in me and inspired me throughout my educational journey. The greatest inspiration was my father who had always encouraged me to think positive and stay dedicated to work. Thank you Abbu! I now know how much you had to sacrifice, so I can chase my own dream.

My mother has been the biggest advocate for my decision to pursue a PhD. She has constantly taught me to push my limit and bring the best out of me. Thank you Ammu for being my mother! Your passion for learning new things have always influenced me in all aspects of life.

I am utterly thankful to my husband, Fahad. Thank you for calming me down in my most stressful days. I wouldn't be where I am today if you weren't there for me. With you, I am happily evolving to be a better person every day.

My sisters have been the greatest protector of me. Thank you Bordi and Didimi for always shielding me from all the struggles that you had to face. You are more than just sisters and no less than a mother to me!

Maheer, Tuni, Jannati and Zarif--- thank you kids for your unconditional love and support. I had to study with a little more responsibility than usual just thinking about you!

I have been very lucky to have a number of great friends throughout my entire life. Thank you all for caring for me. A very special mention goes to Zahir Sohag---- thank you for being my brother from another mother.

A notable mention goes to my math teacher Nihar Ranjan Biswas sir. Thank you for helping me discover my potential and open up the door of knowledge—both science and literature---in front of me.

To Mimu, you were such a blessing in my life during the graduate years. Thank you for your unconditional companionship and love! I miss your presence every night I stay up studying late. There will always be a very special place saved in my heart for you.

And thank you Smoky for making our life more cheerful by your funny tail wagging and lighting up the tough days with your hilarious acts!

My in-laws, aunts, uncles and dearest cousins, thank you very much for all your support and encouragement. Special thanks to my grandma for being my childhood idol. You are greatly missed Nani!

I am very much fortunate to work with some awesome colleagues in Larese group--- Zachary Stroupe, Daniele Paradiso, Chris Crain, Nathaniel Bass, Nicholas Strange, Luther II Langston and Andrew Pedersen. Thank you for all your assistance and useful conversation.

A special thanks goes to Shull Wollan Center – the Joint Institute of Neutron Sciences for awarding me the prestigious Shull Wollan graduate research fellowship. This fellowship supported me through the last two years of my graduate study and was immensely helpful for the advancement of my research. I would also like to thank the Department of Chemistry of UTK, Joint Institute of Advanced Materials (JIAM) and Oak Ridge National Laboratory for giving me the opportunity to perform my research using their facilities.

Last but not the least the biggest contribution for all my academic learning comes from Professor J.Z. Larese. Thank you Dr. Larese for mentoring me! Your unique way of training has positively forced me to improve my problem-solving skills. Thanks for not spoon-feeding me with solutions rather encouraging me to learn how to solve research problems myself. This way I have earned so much more analytical and technical knowledge which wouldn't be possible otherwise! I will always cherish my experience of performing graduate research under your supervision. Thank you for being the “Scientific dad” to all the Larese group family.

ABSTRACT

Adsorption of gas molecules on solid surfaces plays a major role in many physical and chemical processes involved in catalysis, surface wetting, lubrication, gas storage and separation. The homologous series of cycloalkane is an important group of compounds in petrochemical and synthetic industries. These molecules offer conformational varieties that change dramatically with the change in ring size. In this study the effect of surface and molecular symmetry on the physical adsorption properties of thin films of cycloalkanes on three different substrates were investigated. The changes in molecular configuration and dynamics within these films were studied using thermodynamic and molecular modeling methods. High-resolution volumetric adsorption isotherms of cycloalkane (C5- to C8-) on magnesium oxide (MgO) (100), graphite and hexagonal boron nitride (hBN) basal planes were recorded over a broad range of temperature (195K-263K). These isotherms were analyzed to determine the thermodynamics of adsorption (i.e. heats of adsorption, isosteric heats, differential enthalpy and entropy) and to identify regions of possible phase transitions. Molecular dynamics simulations of mono- and multilayers of cycloalkanes (C5- to C8-) on these surfaces were used to obtain binding energies, molecular trajectories, pair-correlation functions and molecular distribution perpendicular to the surface plane of the adsorbent substrate. These experimental and modeling results can serve as the prelude to elastic and inelastic neutron scattering experiments.

TABLE OF CONTENTS

CHAPTER 1 INTRODUCTION AND BACKGROUND.....	1
1.1 OVERVIEW.....	2
1.2 ADSORBENT SURFACES	5
1.3 ADSORBATE MOLECULES.....	7
1.4 INTRODUCTION TO ADSORPTION ISOTHERMS	8
1.4.1 LANGMUIR ISOTHERM MODEL	10
1.4.2 BET MODEL.....	10
1.5 SURFACE WETTING.....	11
1.6 COMMENSURABILITY AND OVERLAYER STRUCTURES.....	11
1.7 THERMODYNAMICS OF ADSORPTION	15
1.7.1 SURFACE AREA.....	17
1.7.2 AREA PER MOLECULE (APM).....	17
1.7.3 CLAUSIUS-CLAPEYRON ANALYSIS.....	17
1.8 INTRODUCTION TO MOLECULAR DYNAMICS	20
1.8.1 FORCE FIELDS.....	21
1.9 TRAJECTORY ANALYSIS	22
1.9.1 RADIAL DISTRIBUTION FUNCTION (RDF) ANALYSIS.....	22
1.9.2 CONCENTRATION PROFILE ANALYSIS (C(z)).....	23
CHAPTER 2 MATERIALS AND METHODS	24
2.1 ADSORBENT SURFACE SYNTHESIS AND PREPARATION	25
2.1.1 SYNTHESIS OF MGO	25
2.1.2 EXPERIMENTAL SET-UP	25
2.1.3 HEAT TREATMENT AND PURIFICATION OF SUBSTRATE SURFACE.....	26
2.2 PURIFICATION OF THE ADSORBATES.....	29
2.2.1 DISTILLATION METHOD	29
2.2.2 FREEZE-PUMP-THAW	29
2.3 ADSORPTION ISOTHERM MEASUREMENT APPARATUS.....	29
2.3.1 ISOTHERM STATION	29
2.3.2 SAMPLE CELL.....	30

2.3.3	TEMPERATURE CONTROL	32
2.4	MOLECULAR DYNAMICS SIMULATION	32
2.4.1	PARAMETERS FOR TRAJECTORY SIMULATION.....	32
2.4.2	FORCEFIELD.....	33
2.4.3	ENSEMBLE	33
2.4.4	THERMOSTAT	33

CHAPTER 3 ADSORPTION OF CYCLOPENTANE ON MGO (100), HEXAGONAL BORON NITRIDE, AND GRAPHITE BASAL PLANES: A THERMODYNAMIC AND MODELING STUDY

3.1	ABSTRACT.....	35
3.2	INTRODUCTION.....	36
3.3	EXPERIMENTAL SECTION.....	37
3.3.1	THERMODYNAMICS	37
3.3.2	MD SIMULATION	38
3.4	RESULTS AND DISCUSSION.....	39
3.4.1	THERMODYNAMICS	39
3.4.2	MODELING	51
3.5	CONCLUSION	76

CHAPTER 4 ADSORPTION OF CYCLOHEXANE ON MGO, HBN, AND GRAPHITE BASAL PLANE.....

4.1	INTRODUCTION.....	78
4.2	EXPERIMENTAL METHODS	78
4.3	RESULTS AND DISCUSSION.....	79
4.3.1	THERMODYNAMICS OF ADSORPTION	79
4.3.2	MD SIMULATIONS	92
4.4	CONCLUSIONS	105

CHAPTER 5 ADSORPTION OF CYCLOHEPTANE AND CYCLOOCTANE ON MGO, HBN, AND GRAPHITE BASAL PLANE

		106
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5.1 THERMODYNAMICS OF ADSORPTION ON HBN AND GRAPHITE	107
5.2 MODELING.....	119
<u>CHAPTER 6 CONCLUSIONS AND FUTURE WORK.....</u>	<u>130</u>
<u>LIST OF REFERENCES</u>	<u>133</u>
<u>VITA.....</u>	<u>141</u>

LIST OF TABLES

TABLE 1.1 PHYSICAL PROPERTIES AND STRUCTURAL INFORMATION OF C3- TO C8 CYCLOALKANES	9
TABLE 2.1 SUPERCELL DIMENSIONS USED IN MD SIMULATIONS	33
TABLE 3.1 THERMODYNAMIC VALUES CALCULATED FROM THE ADSORPTION ISOTHERMS USING EQUATION AND CLAUSIUS-CLAPEYRON PLOT (FIGURE 3.4, FIGURE 3.5, FIGURE 3.6)	47
TABLE 3.2 TOTAL AND NON-BONDING ENERGY CALCULATED FROM THE GEOMETRY OPTIMIZATION AT HIGH SYMMETRY ADSORPTION SITES OF THE SURFACES	57
TABLE 4.1 THERMODYNAMIC VALUES CALCULATED FROM THE CYCLOHEXANE ADSORPTION ISOTHERMS USING EQUATION AND CLAUSIUS-CLAPEYRON PLOT (FIGURE 4.5, FIGURE 4.6 AND FIGURE 4.7).	88
TABLE 4.2 NON-BOND ENERGY OF ISOLATED CYCLOHEXANE MOLECULE ON THE SURFACES	94
TABLE 5.1 THERMODYNAMIC PROPERTIES OF CYCLOHEPTANE ON GRAPHITE AND HBN SURFACES.	117
TABLE 5.2 THERMODYNAMIC PROPERTIES OF CYCLOOCTANE ON GRAPHITE AND HBN SURFACES.	118
TABLE 5.3 MINIMUM NON-BOND ENERGY OF CYCLOHEPTANE AND CYCLOOCTANE ON THE SURFACES	121
TABLE 5.4 LATTICE CONSTANTS OF CYCLOALKANES OBTAINED ON ALL THE SURFACES	126

LIST OF FIGURES

FIGURE 1.1 CRYSTAL STRUCTURE OF MgO, GRAPHITE AND HBN	7
FIGURE 1.2 LOW ENERGY CONFORMATION OF CYCLOOCTANE RECREATED FROM THE WORK OF PAKES AND STRAUSS [37]	9
FIGURE 1.3 CONTACT ANGLE BETWEEN THE LIQUID DROPLET AND THE SOLID SURFACE	12
FIGURE 1.4 DIFFERENT DEGREES OF SURFACE WETTING BY LIQUID DROPLET	12
FIGURE 1.5 SOME EXAMPLES OF COMMENSURATE OVERLAYER STRUCTURE ON FCC(100) SURFACE LATTICE	13
FIGURE 1.6 EXAMPLE OVERLAYER STRUCTURES ON HEXAGONAL CLOSED PACK FCC(111) SURFACE LATTICE	14
FIGURE 1.7 ADSORPTION ISOTHERM OF METHANE ON GRAPHITE AT $T = 77.4$ K	16
FIGURE 1.8 EXAMPLE OF THE POINT B METHOD FOR TO OBTAIN MONOLAYER COVERAGE ON GRAPHITE AT $T = 77.4$ K.	18
FIGURE 2.1 SCHEMATIC OF MgO SYNTHESIS FROM Mg VAPOR VIA METAL CARBIDE ROUTE. THE DIAGRAM IS RECREATED FROM THE PATENT [51].	27
FIGURE 2.2 REACTION CHAMBER USED FOR MgO SYNTHESIS. THE LARGE QUARTZ COLUMN IS ILLUMINATED DURING THE PRODUCTION OF MgO VIA THE IGNITION OF Mg VAPOR. INSET SHOWS THE RF GENERATOR COIL USED FOR CONTROLLING TEMPERATURE.	28
FIGURE 3.1 VOLUMETRIC ISOTHERMS OF CYCLOPENTANE ON MgO(100) AT 262.2K (RED) AND 206.0K (BLUE) WITH ITS NUMERICAL DERIVATIVE (BLUE SOLID LINE). AT LOWER TEMPERATURE, THE LAYERING "STEPS" ARE WELL PRONOUNCED WITH SHARP WITH TALL DERIVATIVE PEAKS.	41
FIGURE 3.2 VOLUMETRIC ISOTHERMS OF CYCLOPENTANE ON HBN AT 263.7K (RED) AND 206.3K (BLUE) WITH ITS NUMERICAL DERIVATIVE (BLUE SOLID LINE).	42
FIGURE 3.3 VOLUMETRIC ISOTHERMS OF CYCLOPENTANE ON GRAPHITE AT 261.9K (RED) AND 205.6K (BLUE) WITH ITS NUMERICAL DERIVATIVE (BLUE SOLID LINE).	43
FIGURE 3.4 CLAUSIUS-CLAPEYRON FIT ON THE EQUILIBRIUM PRESSURE (p_{fi}) FROM THE TWO CYCLOPENTANE LAYERS ON MgO(100) AND THE SATURATED VAPOR PRESSURES. THE FIRST AND SECOND LAYERS AND THE SVP ARE REPRESENTED WITH RED, BLUE AND BLACK COLORS RESPECTIVELY.	44
FIGURE 3.5 CLAUSIUS-CLAPEYRON FIT ON THE EQUILIBRIUM PRESSURE (p_{fi}) FROM THE TWO CYCLOPENTANE LAYERS ON HBN AND THE SVP. THE FIRST AND SECOND LAYERS AND THE SVP ARE REPRESENTED WITH RED, BLUE AND BLACK COLORS RESPECTIVELY.	45
FIGURE 3.6 CLAUSIUS-CLAPEYRON FIT ON THE EQUILIBRIUM PRESSURE (p_{fi}) FROM THE THREE CYCLOPENTANE LAYERS ON GRAPHITE AND THE SVP. THE FIRST, SECOND AND THIRD LAYERS AND THE SVP ARE REPRESENTED WITH RED, BLUE, GREEN AND BLACK COLORS RESPECTIVELY.	46
FIGURE 3.7 REPRESENTATIVE PLOTS OF THE ISOTHERMAL TWO DIMENSIONAL COMPRESSIBILITY AS A FUNCTION OF THE NET CHEMICAL POTENTIAL OF THE CYCLOPENTANE FILMS ON MgO(100). THE $K'2D$	

PEAKS OF THE SECOND LAYERING TRANSITIONS SHOWN AT THE RIGHT SIDE OF THE BREAK ARE PRESENTED ON AN ENLARGED SCALE. 49

FIGURE 3.8 REPRESENTATIVE PLOTS OF THE ISOTHERMAL TWO-DIMENSIONAL COMPRESSIBILITY AS A FUNCTION OF THE NET CHEMICAL POTENTIAL OF THE CYCLOPENTANE FILMS ON HBN. THE K^2D PEAKS OF THE SECOND LAYERING TRANSITIONS SHOWN AT THE RIGHT SIDE OF THE BREAK ARE PRESENTED ON AN ENLARGED SCALE. 49

FIGURE 3.9 REPRESENTATIVE PLOTS OF THE ISOTHERMAL TWO-DIMENSIONAL COMPRESSIBILITY AS A FUNCTION OF THE NET CHEMICAL POTENTIAL OF THE CYCLOPENTANE FILMS ON GRAPHITE. DUE TO THE STEEPNESS OF THE 1ST LAYERING STEPS AT LOW PRESSURE REGION ($< 0.01P_f/P_0$), THE COMPRESSIBILITY OF THE FIRST LAYER WAS NOT RESOLVED. THE K^2D PEAKS OF THE THIRD LAYERING TRANSITIONS SHOWN AT THE RIGHT SIDE OF THE BREAK ARE PRESENTED ON AN ENLARGED SCALE. 50

FIGURE 3.10 THE FULL-WIDTH AT THE HALF MAXIMUM OF THE FITTED LORENTZIAN FUNCTION TO THE 2D COMPRESSIBILITY OF THE CYCLOPENTANE LAYERS ON MgO(100) AGAINST THE TEMPERATURES OF THE ISOTHERMS. SHARP CHANGES IN THE SLOPE SUGGEST PHASE TRANSITION FOR THE FIRST AND THE SECOND ADSORBED LAYERS AT 236.1K AND 237.5K RESPECTIVELY. 52

FIGURE 3.11 THE FULL-WIDTH AT THE HALF MAXIMUM OF THE FITTED LORENTZIAN FUNCTION TO THE 2D COMPRESSIBILITY OF THE CYCLOPENTANE LAYERS ON HBN AGAINST THE TEMPERATURES OF THE ISOTHERMS. SHARP CHANGES IN SLOPE SUGGEST PHASE TRANSITION FOR THE FIRST AND THE SECOND ADSORBED LAYERS AT 228.4K AND 229.6K RESPECTIVELY. 53

FIGURE 3.12 THE FULL-WIDTH AT THE HALF MAXIMUM OF THE FITTED LORENTZIAN FUNCTION TO THE 2D COMPRESSIBILITY OF THE SECOND AND THIRD LAYERS ON GRAPHITE BASAL PLANE AGAINST THE TEMPERATURES OF THE ISOTHERMS. SHARP CHANGES IN SLOPE SUGGEST PHASE TRANSITION FOR THE SECOND AND THE THIRD ADSORBED LAYERS AT 229.8K AND 248.9K RESPECTIVELY. 54

FIGURE 3.13 MINIMUM ENERGY CONFIGURATIONS OF ISOLATED CYCLOPENTANE MOLECULE OBTAINED ON MgO (100) SURFACE. THE GEOMETRY OPTIMIZATION CALCULATION WAS PERFORMED ON THE MOLECULES WITH INITIAL POSITION AT THE HIGH SYMMETRY SITES (Mg^{2+} , O_2^- , HOLLOW AND BOND). 56

FIGURE 3.14 MINIMUM ENERGY CONFIGURATIONS OF ISOLATED CYCLOPENTANE MOLECULE OBTAINED ON HBN SURFACE. THE GEOMETRY OPTIMIZATION CALCULATION WAS PERFORMED ON THE MOLECULES WITH INITIAL POSITION AT THE HIGH SYMMETRY SITES (B, N, HOLLOW AND BOND). 56

FIGURE 3.15 MINIMUM ENERGY CONFIGURATIONS OF ISOLATED CYCLOPENTANE MOLECULE OBTAINED ON GRAPHITE SURFACE. THE GEOMETRY OPTIMIZATION CALCULATION WAS PERFORMED ON THE MOLECULES WITH INITIAL POSITION AT THE HIGH SYMMETRY SITES (C, HOLLOW AND BOND). 57

FIGURE 3.16 MONOLAYER STRUCTURE ON MgO FROM THE ANALYSIS OF THE TRAJECTORY FILES. (A) SNAPSHOT FROM THE DYNAMICS SIMULATION AT 5K, (B) INTERMOLECULAR COMPONENTS OF THE RDF, (C) MOLECULES WERE REPRESENTED AS ELLIPSOID FOR A BETTER DEMONSTRATION OF THE

LATTICE. THE LATTICE VECTOR, b_1 OF CYCLOPENTANE LATTICE IS AT AN ANGLE OF $\approx 22.5^\circ$ WITH $\text{MgO} \langle 10 \rangle$, (D) RDF OF THE CENTROIDS OF THE CYCLOPENTANE MOLECULES. 59

FIGURE 3.17 MONOLAYER STRUCTURE ON HBN FROM THE ANALYSIS OF THE TRAJECTORY FILES. (A) SNAPSHOT FROM THE DYNAMICS SIMULATION AT 5K, (B) INTERMOLECULAR COMPONENTS OF THE RDF, (C) MOLECULES WERE REPRESENTED AS ELLIPSOID FOR A BETTER DEMONSTRATION OF THE LATTICE. THE LATTICE VECTOR, b_1 OF CYCLOPENTANE LATTICE IS AT AN ANGLE OF $\approx 9.5^\circ$ WITH HBN BASAL PLANES BASIS VECTOR, a_1 , (D) RDF OF THE CENTROIDS OF THE CYCLOPENTANE. 60

FIGURE 3.18 MONOLAYER STRUCTURE ON GRAPHITE BASAL PLANE FROM THE ANALYSIS OF THE TRAJECTORY FILES. (A) SNAPSHOT FROM THE DYNAMICS SIMULATION AT 5K, (B) INTERMOLECULAR COMPONENTS OF THE RDF, (C) MOLECULES WERE REPRESENTED AS ELLIPSOID FOR A BETTER DEMONSTRATION OF THE LATTICE. THE LATTICE VECTOR, b_1 OF CYCLOPENTANE LATTICE IS AT AN ANGLE OF $\approx 23^\circ$ WITH GRAPHITE BASIS VECTOR c_1 , (D) RDF OF THE CENTROIDS OF THE CYCLOPENTANE MOLECULES. 61

FIGURE 3.19 CONCENTRATION PROFILES OF THE CARBON AND HYDROGEN ATOMS OF CYCLOPENTANE AS A FUNCTION OF THE DISTANCE FROM THE SURFACE OF $\text{MgO}(100)$. THE $C(z)$ OF THE MOLECULES ADSORBED (A) PARALLEL TO THE SURFACE AND (B) PERPENDICULAR TO THE SURFACE ARE PARTICULARLY DISTINGUISHED BY THE SINGLE HYDROGEN PEAK AT $\sim 6.3\text{\AA}$. 63

FIGURE 3.20 ADJUSTMENT IN MOLECULAR ORIENTATION WITH INCREASING SURFACE COVERAGE. SNAPSHOT AT 5K AT NOMINAL COVERAGES OF (A) 83% OF A MONOLAYER, (B) ONE MONOLAYER, AND (C) 13% HIGHER THAN A MONOLAYER. THE CORRESPONDING CONCENTRATION PROFILES OF THE LAYERS AS A FUNCTION OF TEMPERATURE ARE SHOWN IN THE PLOTS D, E, AND F RESPECTIVELY. OBVIOUS CHANGE IN PEAK SHAPE OCCURS IN THE REGION BEYOND $\sim 4.5\text{\AA}$ DUE TO AN ACCOMMODATION OF MOLECULES IN PERPENDICULAR ORIENTATION 65

FIGURE 3.21 CONCENTRATION PROFILES OF THE CARBON AND HYDROGEN ATOMS OF A CYCLOPENTANE MOLECULE ADSORBED IN PARALLEL AS A FUNCTION OF THE DISTANCE FROM HBN SURFACE. 66

FIGURE 3.22 A REPRESENTATIVE SELECTION OF THE CONCENTRATION PROFILES, $C(z)$ AT NOMINAL MONOLAYER COVERAGE IN THE Z-DIRECTION FOR CYCLOPENTANE MOLECULES ON HBN. THE APPEARANCES OF THE PEAKS AT SIMILAR DISTANCES FROM THE SURFACE AS IN THE $C(z)$ OF AN ISOLATED MOLECULE ADSORBED IN PARALLEL VERIFIES THE PREFERENCE IN PARALLEL ORIENTATION OF THE MOLECULES TO THE SURFACE AT HIGHER COVERAGE. 67

FIGURE 3.23 CONCENTRATION PROFILES OF THE CARBON AND HYDROGEN ATOMS OF CYCLOPENTANE MOLECULE ADSORBED IN PARALLEL AS A FUNCTION OF THE DISTANCE FROM GRAPHITE BASAL PLANE. 68

FIGURE 3.24 A REPRESENTATIVE SELECTION OF THE CONCENTRATION PROFILES, $C(z)$ AT NOMINAL MONOLAYER COVERAGE IN THE Z-DIRECTION FOR CYCLOPENTANE MOLECULES ON GRAPHITE BASAL PLANE. THE APPEARANCES OF THE PEAKS AT SIMILAR DISTANCES FROM THE SURFACE AS IN THE $C(z)$

OF AN ISOLATED MOLECULE ADSORBED IN PARALLEL VERIFIES THE PREFERENCE IN PARALLEL ORIENTATION TO THE SURFACE AT HIGHER COVERAGE. 69

FIGURE 3.25 A REPRESENTATIVE SELECTION OF THE CONCENTRATION PROFILES, $C(z)$ AT NOMINAL BILAYER COVERAGE IN THE Z-DIRECTION FOR CYCLOPENTANE MOLECULES ON MgO. THE MOLECULES IN THE FIRST AND SECOND LAYERS ARE HIGHLIGHTED IN TEAL AND ROYAL BLUE COLORS TO SHOW THE INTERLAYER MOLECULAR MOBILITY WITH THE CHANGE IN TEMPERATURE. THE SUBFIGURES IN B AND C ARE THE SNAPSHOT FROM MOLECULAR TRAJECTORIES AT 270K AND 40K RESPECTIVELY. 70

FIGURE 3.26 A REPRESENTATIVE SELECTION OF THE CONCENTRATION PROFILES, $C(z)$ AT NOMINAL BILAYER COVERAGE IN THE Z-DIRECTION FOR CYCLOPENTANE MOLECULES ON hBN. THE MOLECULES IN THE FIRST AND SECOND LAYERS ARE HIGHLIGHTED IN TEAL AND ROYAL BLUE COLORS TO SHOW THE INTERLAYER MOLECULAR MOBILITY WITH THE CHANGE IN TEMPERATURE. THE SUBFIGURES IN B AND C ARE THE SNAPSHOT FROM MOLECULAR TRAJECTORIES AT 270K AND 40K RESPECTIVELY. 71

FIGURE 3.27 A REPRESENTATIVE SELECTION OF THE CONCENTRATION PROFILES, $C(z)$ AT NOMINAL BILAYER COVERAGE IN THE Z-DIRECTION FOR CYCLOPENTANE MOLECULES ON GRAPHITE SURFACE. THE MOLECULES IN THE FIRST AND SECOND LAYERS ARE HIGHLIGHTED IN TEAL AND ROYAL BLUE COLORS TO SHOW THE INTERLAYER MOLECULAR MOBILITY WITH THE CHANGE IN TEMPERATURE. THE SUBFIGURES IN B AND C ARE THE SNAPSHOT FROM MOLECULAR TRAJECTORIES AT 270K AND 40K. 72

FIGURE 3.28 A REPRESENTATIVE SELECTION OF THE CONCENTRATION PROFILES, $C(z)$ AT NOMINAL TRI-LAYER COVERAGE IN THE Z-DIRECTION FOR CYCLOPENTANE MOLECULES ON MgO(100). THE MOLECULES IN THE FIRST, SECOND AND THIRD LAYERS ARE HIGHLIGHTED IN TEAL, ROYAL BLUE AND CYAN COLORS TO SHOW THE INTERLAYER MOLECULAR MOBILITY WITH THE CHANGE IN TEMPERATURE. THE SUBFIGURES IN B AND C ARE THE SNAPSHOT FROM MOLECULAR TRAJECTORIES AT 270K AND 40K RESPECTIVELY. 73

FIGURE 3.29 A REPRESENTATIVE SELECTION OF THE CONCENTRATION PROFILES, $C(z)$ AT NOMINAL TRI-LAYER COVERAGE IN THE Z-DIRECTION FOR CYCLOPENTANE MOLECULES ON hBN. THE MOLECULES IN THE FIRST, SECOND AND THIRD LAYERS ARE HIGHLIGHTED IN TEAL, ROYAL BLUE AND CYAN COLORS TO SHOW THE INTERLAYER MOLECULAR MOBILITY WITH THE CHANGE IN TEMPERATURE. THE SUBFIGURES IN B AND C ARE THE SNAPSHOT FROM MOLECULAR TRAJECTORIES AT 270K AND 40K RESPECTIVELY. 74

FIGURE 3.30 A REPRESENTATIVE SELECTION OF THE CONCENTRATION PROFILES, $C(z)$ AT NOMINAL TRI-LAYER COVERAGE IN THE Z-DIRECTION FOR CYCLOPENTANE MOLECULES ON GRAPHITE. THE MOLECULES IN THE FIRST, SECOND AND THIRD LAYERS ARE HIGHLIGHTED IN TEAL, ROYAL BLUE AND CYAN COLORS TO SHOW THE INTERLAYER MOLECULAR MOBILITY WITH THE CHANGE IN TEMPERATURE. THE SUBFIGURES IN B AND C ARE THE SNAPSHOT FROM MOLECULAR TRAJECTORIES AT 270K AND 40K RESPECTIVELY. 75

FIGURE 4.1 SELECT ADSORPTION ISOTHERMS OF CYCLOHEXANE ON MgO WITHIN 204-288K. 80

- FIGURE 4.2 ADSORPTION ISOTHERM OF CYCLOHEXANE ON MGO AT 257.2K (RED) WITH CORRESPONDING NUMERICAL DERIVATIVE (BLUE). 81
- FIGURE 4.3 ADSORPTION ISOTHERM OF CYCLOHEXANE ON GRAPHITE AT 254.8K (RED) WITH CORRESPONDING NUMERICAL DERIVATIVE (BLUE). 82
- FIGURE 4.4 ADSORPTION ISOTHERM OF CYCLOHEXANE ON HBN AT 254.1K (RED) WITH CORRESPONDING NUMERICAL DERIVATIVE (BLUE). 83
- FIGURE 4.5 CLAUSIUS-CLAPEYRON PLOT FOR CYCLOHEXANE ADSORBED ON THE SURFACE OF MGO. THE INDIVIDUAL LAYERS ARE REPRESENTED BY RED CIRCLES (1ST LAYER) AND BLUE SQUARES (2ND LAYER), AND SATURATED VAPOR PRESSURE IS REPRESENTED BY BLACK DIAMONDS. 85
- FIGURE 4.6 CLAUSIUS-CLAPEYRON PLOT FOR CYCLOHEXANE ADSORBED ON THE SURFACE OF GRAPHITE. THE INDIVIDUAL LAYERS ARE REPRESENTED BY RED CIRCLES (1ST LAYER) AND BLUE SQUARES (2ND LAYER), GREEN TRIANGLES (3RD LAYER) AND BLACK SQUARES (SVP). 86
- FIGURE 4.7 CLAUSIUS-CLAPEYRON PLOT FOR CYCLOHEXANE ADSORBED ON THE SURFACE OF HBN. THE INDIVIDUAL LAYERS ARE REPRESENTED BY RED CIRCLES (1ST LAYER) AND BLUE CIRCLES (2ND LAYER), GREEN TRIANGLES (3RD LAYER) AND BLACK SQUARES (SVP). 87
- FIGURE 4.8 THE FULL-WIDTH AT THE HALF MAXIMUM OF THE FITTED LORENTZIAN FUNCTION TO THE 2D COMPRESSIBILITY OF THE CYCLOHEXANE LAYERS ON MGO (100) AGAINST THE TEMPERATURES OF THE ISOTHERMS. SHARP CHANGES IN THE SLOPE SUGGEST PHASE TRANSITION FOR THE FIRST AND THE SECOND AT 264K AND 277K RESPECTIVELY. 89
- FIGURE 4.9 THE FULL-WIDTH AT THE HALF MAXIMUM OF THE FITTED LORENTZIAN FUNCTION TO THE 2D COMPRESSIBILITY OF THE CYCLOHEXANE LAYERS ON GRAPHITE AGAINST THE TEMPERATURES OF THE ISOTHERMS. SHARP CHANGES IN THE SLOPE SUGGEST PHASE TRANSITION FOR THE SECOND AND THE THIRD ADSORBED LAYERS AT 269K AND 272K RESPECTIVELY. 90
- FIGURE 4.10 THE FULL-WIDTH AT THE HALF MAXIMUM OF THE FITTED LORENTZIAN FUNCTION TO THE 2D COMPRESSIBILITY OF THE CYCLOHEXANE LAYERS ON HBN AGAINST THE TEMPERATURES OF THE ISOTHERMS. SHARP CHANGES IN THE SLOPE SUGGEST PHASE TRANSITION FOR THE SECOND AND THE THIRD ADSORBED LAYERS AT 266.8K AND 268.4K RESPECTIVELY. 91
- FIGURE 4.11 MINIMUM ENERGY STRUCTURE OF ISOLATED CYCLOHEXANE MOLECULE A. ON MGO, B. ON GRAPHITE, C. ON HBN 93
- FIGURE 4.12 A PERSPECTIVE SIDE VIEW OF CYCLOHEXANE MOLECULE ON GRAPHITE SHOWS THE POSITION OF AXIAL HYDROGENS (YELLOW) WITH RESPECT TO THE SURFACE HOLLOW SITES (GREEN). 94
- FIGURE 4.13 MONOLAYER STRUCTURE OF CYCLOHEXANE ON MGO. A. MOLECULES ARE DEPICTED AS CENTROIDS FOR A CLEAR DEMONSTRATION OF THE HEXAGONAL STRUCTURE B. IN-PLANE RDF CALCULATED USING THE CENTER OF THE MASS OF THE MOLECULES. 96
- FIGURE 4.14 MONOLAYER STRUCTURE OF CYCLOHEXANE ON GRAPHITE. A. MOLECULES AND THE SUBSTRATES ARE DEPICTED USING BALLS-AND-STICK MODEL TO SHOW THE COMMENSURABILITY OF

THE STRUCTURE OF CYCLOHEXANE ON GRAPHITE. B. IN-PLANE RDF CALCULATED USING THE CENTER OF THE MASS OF THE MOLECULES.	96
FIGURE 4.15 MONOLAYER STRUCTURE OF CYCLOHEXANE ON HBN. A. MOLECULES AND THE SUBSTRATES ARE DEPICTED USING BALLS-AND-STICK MODEL TO SHOW THE COMMENSURABILITY OF THE STRUCTURE OF CYCLOHEXANE ON GRAPHITE. B. IN-PLANE RDF CALCULATED USING THE CENTER OF THE MASS OF THE MOLECULES.	97
FIGURE 4.16 CONCENTRATION PROFILE OF H (RED) AND C (BLUE) ATOMS OF A SINGLE CYCLOHEXANE MOLECULE ON MgO (100) SURFACE.	98
FIGURE 4.17 CONCENTRATION PROFILE OF H (RED) AND C (BLUE) ATOMS OF A SINGLE CYCLOHEXANE MOLECULE ON GRAPHITE SURFACE	98
FIGURE 4.18 CONCENTRATION PROFILE OF H (RED) AND C (BLUE) ATOMS OF A SINGLE CYCLOHEXANE MOLECULE ON HBN SURFACE	99
FIGURE 4.19 MOLECULAR C(z) CALCULATED FOR NOMINAL MONOLAYER COVERAGE OF CYCLOHEXANE ON MgO AS A FUNCTION OF TEMPERATURE (300K-5K). BULK TRIPLE POINT OF CYCLOHEXANE IS 279.48K. SIDE VIEW OF A MONOLAYER COVERAGE ON SURFACE ARE SHOWN INSET.	100
FIGURE 4.20 MOLECULAR C(z) CALCULATED FOR NOMINAL MONOLAYER COVERAGE OF CYCLOHEXANE ON GRAPHITE AS A FUNCTION OF TEMPERATURE (300K-5K). SIDE VIEW OF A MONOLAYER COVERAGE ON SURFACE ARE SHOWN INSET.	101
FIGURE 4.21 MOLECULAR C(z) CALCULATED FOR NOMINAL MONOLAYER COVERAGE OF CYCLOHEXANE ON HBN AS A FUNCTION OF TEMPERATURE (300K-5K). SIDE VIEW OF A MONOLAYER COVERAGE ON SURFACE ARE SHOWN INSET.	102
FIGURE 4.22 MOLECULAR C(z) CALCULATED FOR NOMINAL A. BILAYER AND B. TRILAYER COVERAGE OF CYCLOHEXANE ON MgO AS A FUNCTION OF TEMPERATURE (300K-5K).	103
FIGURE 4.23 MOLECULAR C(z) CALCULATED FOR NOMINAL A. BILAYER AND B. TRILAYER COVERAGE OF CYCLOHEXANE ON GRAPHITE AS A FUNCTION OF TEMPERATURE (300K-5K).	103
FIGURE 4.24 MOLECULAR C(z) CALCULATED FOR NOMINAL A. BILAYER AND B. TRILAYER COVERAGE OF CYCLOHEXANE ON HBN AS A FUNCTION OF TEMPERATURE (300K-5K).	104
FIGURE 5.1 REPRESENTATIVE ADSORPTION ISOTHERM OF CYCLOHEPTANE ON GRAPHITE AT 254.1K WITH CORRESPONDING DERIVATIVE PLOT.	108
FIGURE 5.2 REPRESENTATIVE ADSORPTION ISOTHERM OF CYCLOHEPTANE ON HBN AT 266.3K WITH CORRESPONDING DERIVATIVE PLOT.	109
FIGURE 5.3 EXAMPLE OF AN AREA PER MOLECULE (APM) CALCULATED FOR CYCLOHEPTANE ON GRAPHITE.	110
FIGURE 5.4 CLAUSIUS-CLAPEYRON ANALYSIS OF CYCLOHEPTANE ON GRAPHITE	111
FIGURE 5.5 CLAUSIUS-CLAPEYRON ANALYSIS OF CYCLOHEPTANE ON HBN.	112
FIGURE 5.6 REPRESENTATIVE PLOT OF CYCLOOCTANE ON GRAPHITE AT 260.0K	113
FIGURE 5.7 REPRESENTATIVE PLOT OF CYCLOOCTANE ON HBN AT 260.0K.	114

FIGURE 5.9 CLAUSIUS-CLAPEYRON ANALYSIS OF CYCLOOCTANE ON HBN	116
FIGURE 5.10 MINIMUM ENERGY STRUCTURES OF CYCLOHEPTANE ON A. GRAPHITE, B. HBN AND C. MGO (100) SURFACES.	120
FIGURE 5.11 MINIMUM ENERGY STRUCTURES OF CYCLOOCTANE ON A. GRAPHITE, B. HBN AND C. MGO (100) SURFACES.	120_Toc6032719
FIGURE 5.12 IN-PLANE RADIAL DISTRIBUTION FUNCTION OF THE COM OF CYCLOHEPTANE MOLECULES IN A MONOLAYER ON GRAPHITE SURFACE	121
FIGURE 5.13 IN PLANE RDF OF THE COM OF CYCLOHEPTANE MOLECULES IN A MONOLAYER ON HBN SURFACE	122
FIGURE 5.14 IN PLANE RDF OF THE COM OF CYCLOHEPTANE MOLECULES IN A MONOLAYER ON MGO SURFACE	123
FIGURE 5.15 IN PLANE RDF OF THE COM OF CYCLOOCTANE MOLECULES IN A MONOLAYER ON GRAPHITE SURFACE.	124
FIGURE 5.16 IN PLANE RDF OF THE COM OF CYCLOOCTANE MOLECULES IN A MONOLAYER ON HBN SURFACE.	125
FIGURE 5.17 IN PLANE RDF OF THE COM OF CYCLOOCTANE MOLECULES IN A MONOLAYER ON MGO SURFACE	126
FIGURE 5.18 CONCENTRATION PROFILE OF CYCLOHEPTANE ON GRAPHITE. MOLECULAR DISTRIBUTION IN A. MONOLAYER VS B. AT NOMINAL TRILAYER COVERAGE.	127
FIGURE 5.19 CONCENTRATION PROFILE OF CYCLOHEPTANE ON HBN. MOLECULAR DISTRIBUTION IN A. MONOLAYER VS B. AT A NOMINAL TRILAYER COVERAGE.	127
FIGURE 5.20 CONCENTRATION PROFILE OF CYCLOHEPTANE ON MGO. MOLECULAR DISTRIBUTION IN A. MONOLAYER VS B. SLIGHTLY ABOVE A TRILAYER COVERAGE.	128
FIGURE 5.21 CONCENTRATION PROFILE OF CYCLOOCTANE ON GRAPHITE. MOLECULAR DISTRIBUTION IN A. MONOLAYER VS B. AT NOMINAL TRILAYER COVERAGE.	128
FIGURE 5.22 CONCENTRATION PROFILE OF CYCLOOCTANE ON HBN. MOLECULAR DISTRIBUTION IN A. MONOLAYER VS B. AT NOMINAL TRILAYER COVERAGE.	129
FIGURE 5.23 CONCENTRATION PROFILE OF CYCLOOCTANE ON HBN. MOLECULAR DISTRIBUTION IN A. MONOLAYER VS B. AT NOMINAL TRILAYER COVERAGE.	129
FIGURE 6.1 PRELIMINARY INVESTIGATION OF THE MINIMUM ENERGY STRUCTURE OF CYCLOPROPANE AND CYCLOBUTANE	132

Chapter 1 **INTRODUCTION AND BACKGROUND**

1.1 Overview

Molecular adsorption on surfaces such as metal oxides, carbonaceous materials (carbon nanotubes, nanohorns etc.), inorganic porous structures e.g. porous silica, layered materials e.g. chalcogenides, clay minerals e.g. zeolites and metal organic framework materials (MOFs) have numerous applications in petroleum industries, electronics and optoelectronics, sensors and in separation science[1-5]. In this study, an investigation of the effects of molecular and adsorbate symmetry on the adsorption properties have been carried out. In particular, the investigation is focused to establish a detailed understanding of the thermodynamics and structure of cycloalkane adsorbates on the surfaces of MgO (100), hexagonal boron nitride and graphite basal plane. This dissertation discusses detailed thermodynamics of adsorption using volumetric adsorption isotherms and molecular modeling investigations on the structures and dynamics of cycloalkanes. The research findings from this study will enrich the field of surface science by adding values to the database of adsorption thermodynamics as well as improving fundamental understanding of the adsorbate-adsorbent interactions. It will also help developing and understanding the reactions (e.g. dehydrogenation) of new energy storage materials such as liquid organic hydrogen carriers. Furthermore, the results of the adsorption experiments and modeling can be used in for further investigation of microscopic structure and dynamics using neutron spectroscopy.

MgO was selected as a surface as a prototypical metal oxide with fourfold symmetry, ionic structure; interpenetrating cubic lattices of magnesium and oxygen atoms. It can be produced with minimum edge effect, single 100 facet exposure and very narrow size distribution[6]. These properties make MgO a perfect candidate for fundamental surface studies. Graphite was used in this study because of its comparable symmetry and the availability of a broad range of thermodynamic information obtained from previous fundamental surface studies. The graphite basal plane has large crystal sizes, low surface potential corrugation, structural simplicity, chemical inertness and its compatibility with various experimental techniques [7]. Furthermore, microscopic properties of molecular adsorbates on graphite such as two-dimensional melting, liquid vapor co-existence, orientational ordering, and commensurate-incommensurate transitions have been investigated by many other research groups [8, 9]. The availability of these data complements the characterization of molecule-surface interaction for particular adsorbates via adsorption, modeling and neutron studies. Although MgO and graphite has

their obvious difference in surface symmetry (sixfold vs fourfold) and in chemical and physical properties, the dynamical film adsorbed on these two surfaces are strikingly similar. Hexagonal boron nitride is isostructural with graphite with a slight increase in lattice dimensions. It is widely used as a high and low temperature lubricant. A comparative adsorption study on hBN with the other two surfaces can open avenue for many novel applications in catalysis, electronics and high vacuum technologies.

Cycloalkane molecules have been chosen primarily to investigate the effect that molecular symmetry has on adsorption properties. Additionally, some properties of the molecules are of fundamental interest, such as their rotational and vibrational behavior, and practical applications in synthetic chemistry. Cyclopentane and cycloheptane exhibit pseudorotational motion around the fivefold and sevenfold symmetry axis [10]. Cyclohexane adopts the chair conformation to minimize energy and lower angle and torsional strain. It is also an industrially important compound due its use in the synthesis of Nylon 66 precursors, adipic acid and caprolactam. Cyclooctane adopts a boat-chair conformation and have been widely used for its many other low energy conformations [11, 12]. The surface science provides insight on the fundamental physical and/or chemical interactions at the interface of two-dimensional systems. Beyond the scope of fundamental perspective, this information has applications in many industries including, gas separation and storage, catalysis, lubrication and surface wetting.

The goal of this research was to probe the role of surface and molecular symmetry on the physicochemical properties of 2D layers of cyclic molecules adsorbed on metal oxide and semiconductor substrates. Initially our characterization was focused on the thermodynamic and microscopic structure and dynamics of cyclopentane and cyclohexane on the MgO (100) surface and graphite basal plane. Later the research was expanded to larger ring systems e.g. c7- and c8- cycloalkanes and on hexagonal boron nitride. In order to realize this goal adsorption isotherms and molecular dynamics (MD) simulation studies were performed to investigate the mechanism responsible for the similarities and differences in the structure, dynamics and wetting properties on different surfaces.

Volumetric adsorption isotherms recorded over a wide range of temperatures were used to determine the thermodynamics of adsorption and location of possible phase transitions. These thermodynamic studies were used to develop realistic potential energy surfaces, which can describe how the molecules of adsorbates interact with the adsorbent surfaces. Adsorption studies of methane on MgO [3] showed that if the adsorbed film

structural properties are compatible with the surface symmetry and structural properties of the bulk adsorbent, the microscopic conditions favor the formation of one or more adlayers.

The wetting of a solid surface by a molecular film can exhibit one of several forms. Complete wetting of the substrate occurs when the surface film grows uniformly to macroscopic dimensions covering the entire surface. In addition to the incompatibility of molecule-surface (M-S) interaction the molecule-molecule (M-M) interaction and the presence of surface defects are also responsible for incomplete wetting or non-wetting. Thus, the adsorption on surfaces involves an interplay between M-M and M-S interactions to establish the optimum energy state. To establish an equilibrium structure and dynamics the molecule can change its symmetry, conformations, orientation, packing behavior and at the same time the surface can also change its electronic and chemical properties.

The tessellation of a flat surface is the tiling of a plane using two dimensional shapes so that no gaps or overlaps remain between any two shapes. The hexagonal projection of cyclohexane ring is one of the geometric shapes that can act as a tile to cover the whole surface while the pentagonal projection of cyclopentane is a geometric shape that neither serves as a periodic nor a non-periodic tile. Penrose tiling is a non-periodic tiling that arranges pentagons and uses other secondary shapes generated from the pentagon (e.g. rhombi and kites) to fill up the gaps for the tessellation. Hence, from strictly from a geometric viewpoint, plane filling behavior predicts that the formation of compact commensurate films on hBN and graphite (0001) surfaces is more probable for cyclohexane molecules than for cyclopentane. The non-periodic pentagonal structure of cyclopentane molecules prevent them from settling on a favorable location on the MgO lattice with four-fold symmetry and the graphite lattice with threefold and six-fold symmetry. On the other hand, the possibility of growing commensurate cyclohexane films and adlayers is much likely on graphite and hBN surface than on MgO (100) surface due to the hexagonal symmetry of graphite. As we will see in the next chapters the high-resolution volumetric adsorption isotherms taken on the above-mentioned systems reflects this prediction (in terms of the number of layer formation on MgO, graphite and hBN). To examine the symmetry driven M-S interactions and subsequent adsorbed film growth the incorporation of microscopic measurements and analysis is necessary to complement the thermodynamic investigation.

In order to gain a microscopic insight into the M-S and M-M interaction of the adsorbed films more quantitatively, molecular dynamics (MD) simulations were employed using

Accelrys' Materials studio package. A series of geometry optimization and dynamics calculations of adsorbate molecules were performed on a larger supercell to extract the energy contributions from different interactions. The output trajectory files from dynamics simulations were inspected to follow the molecular motions on the surfaces and identify the changes in the MD.

When a molecule in the adsorbed films move further from the substrate surface, it feels less attractive forces from the substrate due to both by the decrease in Lennard – Jones (6-12) potential and by the shielding of the interaction with the surface by other adlayers between the molecule and the surface. The intermolecular interactions play a vital role in the formation and stability of the adlayers formed after the monolayer formation. While a number of studies using electron diffractions and MD simulations have been carried out to characterize the vibrational and rotational motions in cyclopentane and cyclohexane molecules [10, 13] and the crystal packing of crystalline bulk phases, sufficient studies have not been performed to characterize the dynamics and the 2D lattice structures adsorbed on surfaces. The result of these thermodynamic and modeling studies performed in this study will provide an avenue for generating a quantitative description of potential energy surface that govern the microscopic behavior of the adsorption system.

1.2 Adsorbent Surfaces

Adsorption of gases on metal oxides and layered materials has wide applications in many industries including energy storage, pharmaceuticals, opto-electronics, catalysis, ceramics, and sensors [14-23]. Therefore, it is crucial to gain fundamental knowledge on the surface properties (i.e. surface wetting, physical adsorption) of these materials. In this dissertation, three surface substrates were chosen to study the adsorption of cycloalkanes: magnesium oxide (MgO), hexagonal boron nitride (hBN) and graphite basal planes.

MgO has many industrial applications including catalysis, fire retardants, microelectronics, fuel additives and environmental remediation [15, 18, 24-26]. MgO has a cubic crystalline structure (lattice constant 4.212 Å). The crystal structures of MgO surface offers four-fold symmetry with largely exposed (100) facets [27]. Due to the surface homogeneity and pure form, the surface of MgO has been widely studied for understanding gas adsorption. The nature of the adsorption sites depends on the atomic composition and nature of crystal facet(s) exposed. On MgO surface, there are three major adsorption sites- corresponding to the potential energy minima of the surface [4]. The bond

site which is a saddle point on the potential energy surface lies in between two atoms e.g. the bridge between magnesium and oxygen atom. This site is a local minimum of the system. The hollow site is located at the center of four atoms on the surface is a global minimum of the system. The third type is the atom site, for example in MgO these are located atop the Mg^{2+} and O^{2-} . These types of sites are not located at the energy minimum, but they are considered as the adsorption site because of their symmetry resulting from the closeness to four hollow sites. Figure 1.1 shows the comparative structures of these surfaces.

The crystalline structure of graphite consists of parallel honeycomb shaped carbon layers [28]. The in-plane lattice constant of graphite is 2.461 Å [29] and has a six fold symmetry. Each layered network is sp^2 hybridized which offers a strong binding. However, the π -orbitals between the layers results in a weak van der Waals force. The lattice constant in the c-direction of layer stacking is 6.708 Å. Graphite is also an excellent candidate as substrate for understanding physicochemical adsorption. Microscopic properties of molecular adsorbates on graphite such as two-dimensional melting, vapor-liquid co-existence, orientational ordering, and commensurate-incommensurate transitions have been widely investigated [8, 9]. Beside the surface symmetry, the chemical properties of MgO and graphite surfaces vary from each other. MgO is an electrical insulator and characterized by ionic bonds. In contrast, graphite is a well-known conductor and has covalent bonds. However, earlier studies indicate that, adsorption behavior on these two substrates can be very similar [30]. Therefore, understanding the adsorption of cycloalkane molecules on these fundamentally different yet often similar substrates can provide valuable information on adsorption.

The (0001) surface of graphite (i.e. the Basal plane) exhibits a six-fold symmetry resulting in a PES that is different from MgO. In the AB stacking of graphite layers, the threefold hollow site is located at the center of three atoms. The center hollow site of a layer lies above a carbon atom from the next layer. The bridge site is located in between two carbon atoms and is a saddle point on PES similar to MgO. The atom site lies above the surface atom and has access to both the three fold symmetry of the hollow sites and the six fold symmetry of the bond sites [5]

Hexagonal boron nitride has a similar crystal structure to that of graphite [31, 32] with a 2% increase in the lattice constant due to varying chemical composition of the materials resulting in two different atom sites. The weak van der Waals interactions stack the layers of BN and thus, impart their lubricating property [32]. However, due to the considerable

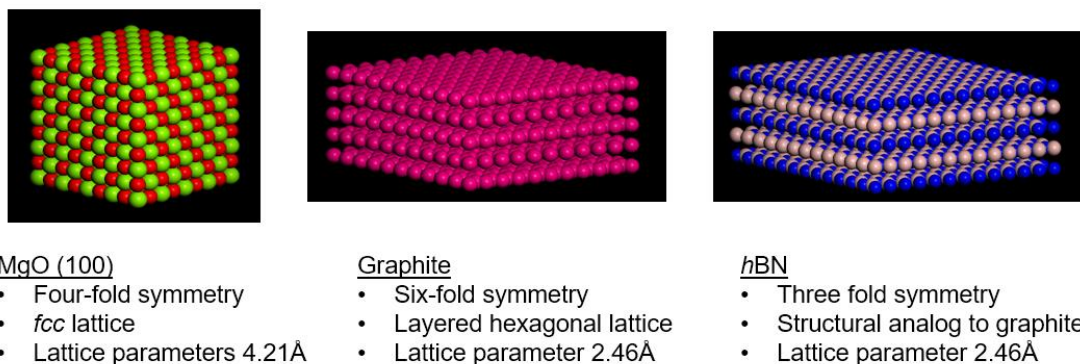


Figure 1.1 Crystal structure of MgO, graphite and hBN

difference in electronegativity between boron and nitrogen atoms, they possess a partial ionic characteristic. The surface of hBN offers three-fold symmetry with defect free large surface area.

1.3 Adsorbate Molecules

The adsorbates selected initially were cyclopentane and cyclohexane. The study was later extended to cycloheptane and cyclooctane with larger ring sizes. The planar structures of cycloalkanes are not the energy minima but the saddle points on the potential energy surfaces. The saturated carbon rings on cycloalkanes curl up to form a puckered structure to release ring strains (only exception is cyclopropane).

Cyclopentane molecules adopt two isoenergetic forms, a C_s and a C_2 structure in its minimum energy state [8]. Each of these structures are doubly degenerate and exhibit ten equivalent, puckered ring conformers which correspond to a total of twenty local minima separated by twenty saddle points [9] on potential energy surface. The interconversion between the two structures generate a nuclear motion which is comparable to nearly a free rotation of a particle on a ring known as pseudorotation [10]. The crystalline bulk cyclopentane has three different phases. Phase-I (138-178K) and phase-II (118-136K) are the plastic phases and phase-III (<118K) is a solid phase [33]. The cyclopentane[34] molecules undergo pseudorotation in phase I and phase II. However, the molecule is frozen below 118K. So, the pseudorotation reverts to an out-of-plane ring vibration.

Cyclohexane also exhibits a number of lower energy conformations the distribution among them depends on the temperature. The lowest energy chair conformation results as a consequence of the reduction in both the ring strain and the steric hindrance between the equatorial and axial hydrogen atoms. The second lowest energy configuration is the twist conformation which is also free from the angle strain similar to the chair structure but suffers from the steric hindrance introduced by the two axial hydrogens. The highest energy conformation is the boat conformation which exists only as a translational states due to high steric and torsional strains [6]. In bulk phase, solid cyclohexane has two different types of crystal structures [7]. Above 186K, the 'Phase I' forms a cubic unit cell with $Fm3m$ symmetry and below 186K cyclohexane 'Phase I' forms a monoclinic unit cell with C_{2c} symmetry.

Cycloheptane exhibits two sets of pseudorotational conformations with equal populations. One is chair-twist chair and another is boat-twist boat [35]. Cycloheptane forms several solid phases from 120K to 265K. However, structural symmetry assignment in bulk phase is difficult due to its complicated pseudorotational transitions[12]. Both cyclopentane and cycloheptane have lower bulk triple points than expected due to the pseudorotational vibrational modes (Table 1.1).

Cyclooctane adopts a boat chair conformation as the lowest energy structure. Another slightly less stable structure is the crown structure [11, 35, 36]. Cyclooctane is the most complex cycloalkane since it exhibits a number of conformers of comparable energy (Figure 1.2).

While the pseudorotation and conformations of odd-even cycloalkane may play vital roles in the microscopic behavior of the adsorbed layers, the symmetry of the planar structures of these molecules should also influence the stability and commensurability of the films growth on these surfaces.

1.4 Introduction to Adsorption Isotherms

Two of the most famous adsorption models are Langmuir and BET models. The adsorption isotherms under investigation vary significantly from these two models. However, for historic importance and as the fundamentals of adsorption study these two models are briefly described below:

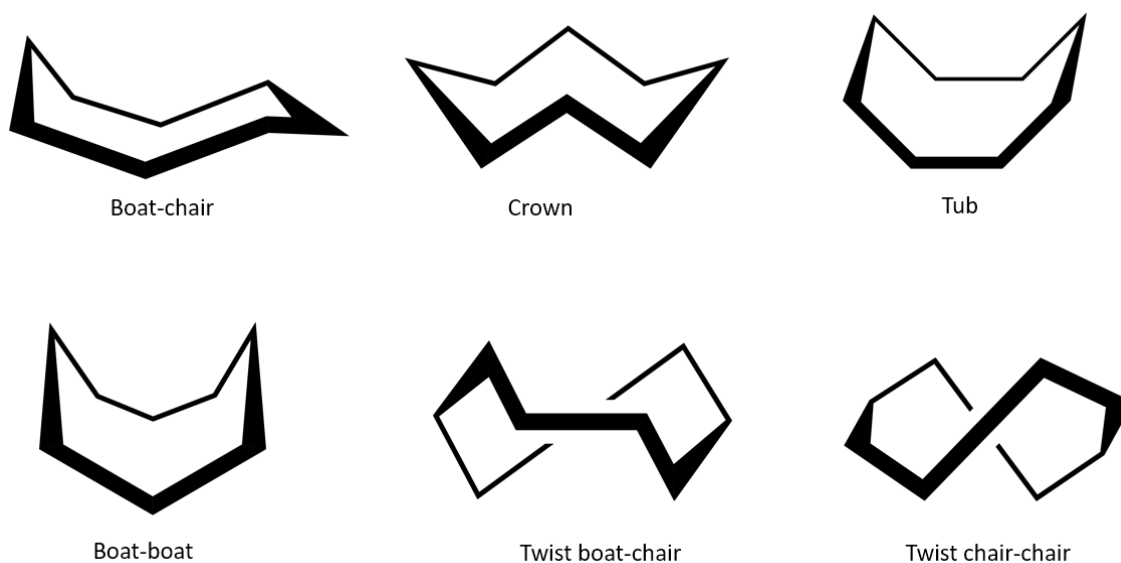


Figure 1.2 Low energy conformation of cyclooctane recreated from the work of Pakes and Strauss [37]

Table 1.1 Physical properties and structural information of C3- to C8 cycloalkanes

Cycloalkane	Mol. Wt. (amu)	Triple point (K)	$\angle$ C-C-C angle ($^{\circ}$)	C-C bond length ($\text{\AA}$)
Cyclopropane	42.08	145.80	60.0	1.505
Cyclobutane	56.11	182.40	88.3	1.543
Cyclopentane	70.13	179.71	102.9 105.0 105.9	1.531 1.541 1.553
Cyclohexane	84.16	279.62	109.5	1.520 1.560
Cycloheptane	98.19	265.12	113.5 116.5	1.535 1.536 1.543
Cyclooctane	112.21	287.97	118.1	1.533

1.4.1 Langmuir Isotherm Model

Langmuir model describes the adsorption of a fluid adsorbate onto the surface of an adsorbent (typically a solid) based on a few assumptions: i) the adsorbent surface is in contact with adsorbate, ii) the surface has a definite number of adsorption sites, iii) only monolayer of adsorbate molecules can attach to the surface and iv) there is no mutual interaction between the adsorbate molecules on the sites of adsorption. Mathematically, Langmuir isotherm can be expressed as,

$$\theta = \frac{v}{v_m} = \frac{bP}{(1 + bP)}$$

Here, θ represents the fractional coverage of the adsorption sites, v is the volume adsorbed on the surface, v_m represents the volume of the monolayer, P indicates the partial pressure of the adsorbate molecule and b is the rate constant. Although, this model neglects the molecular interaction between adsorbed molecules, however, it is evident that intermolecular interactions play a crucial role in the adsorption behavior of the adsorbates. Furthermore, Langmuir isotherm is only restricted to monolayer surface adsorption. Therefore, later models eventually had bidirectional aim to consider both molecular interactions and multilayer adsorption to describe the surface adsorption phenomena.

1.4.2 BET Model

An alternative model for describing the surface adsorption was proposed by Brunauer, Emmet and Teller (BET) [38]. The BET isotherm is an extension of the Langmuir model that includes multilayer adsorption by considering following assumptions: i) the adsorbate molecules can only interact with two adjacent layers, ii) Langmuir isotherm can be individually applied to each adsorbate layer. The BET isotherm equation can be generalized as:

$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m c} + \frac{c - 1}{v_m c} \times \frac{p}{p_0}$$

Here, p indicates the equilibrium vapor pressure, p_0 represents the saturated vapor pressure, and c represents the BET constant which depends on the heats of adsorption. From this equation, a linear fit of $\frac{p}{v(p_0 - p)}$ against $\frac{p}{p_0}$ can determine the volume of the monolayer as well as the heat of adsorption. Although BET isotherm does not consider

the molecular adsorption within each layer, it still has application in predicting the thermodynamics of adsorption.

1.5 Surface Wetting

Surface wetting is an important phenomenon dictated by both the intermolecular interactions of the adsorbate molecules and the interactions between the molecules and the substrate surface. This phenomenon is particularly associated with the adsorption of a liquid on solid surface. Primarily, there are three categories of wetting: incomplete, complete and non-wetting. Incomplete wetting is the most common form of wetting occurring on real solid surfaces. The contact angle between the liquid droplet and the solid surface determines the degree of wetting (Figure 1.3). When the angle is close to 0° the surface is completely wetted by the adsorbate molecule. When the angle is 180° the intermolecular attraction between molecules in the droplet is very high compared to M-S attraction and the surface is not wetted by the molecules. All other contact angles between 0° to 180° falls into the category of incomplete wetting. Sometimes the angle above or below 90° are used to distinguish between high wettability and low wettability of a solid-liquid interface. Figure 1.4 illustrates different types of wetting on solid surface. The nature of the adsorbed layers is dependent on the type of wetting that occurs on the surface.

1.6 Commensurability and Overlayer Structures

When the lattice of the adsorbed layer on a crystalline surface is in registry with the surface lattice the adlayers, there will be a single vector for all the identical positions of the surface layer that connects to the identical position of the overlayer. Such overlayers are considered to be commensurate with the surface. The adlayers can be commensurate with the substrate as well as with one another. Figure 1.5 and Figure 1.6 illustrates a few examples of commensurate overlayer structures formed on fcc(100) and fcc(111) surface planes. A general way to express the overlayer lattice is using Wood's notation. In this method the ratio of the lattice vectors of the adlayers to those of the substrate surface are expressed along with the angle of rotation of the surface lattice with respect to the surface lattice. For example, if the lattice vectors of substrate surface are $\vec{a}_1$ and $\vec{a}_2$ and those of the adlayers are $\vec{b}_1$ and $\vec{b}_2$ and the angle between $\vec{a}_1$ and $\vec{b}_1$ is 45° , then the overlayer structure in Wood's notation is expressed as $(\frac{\vec{b}_1}{\vec{a}_1} \times \frac{\vec{b}_2}{\vec{a}_2})R45^\circ$.

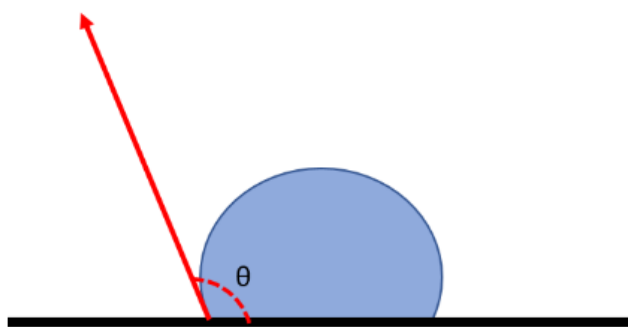


Figure 1.3 Contact angle between the liquid droplet and the solid surface

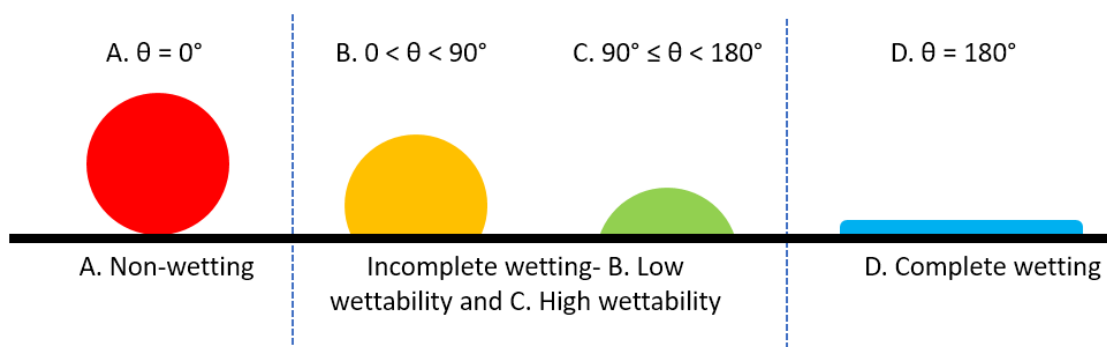


Figure 1.4 Different degrees of surface wetting by liquid droplet

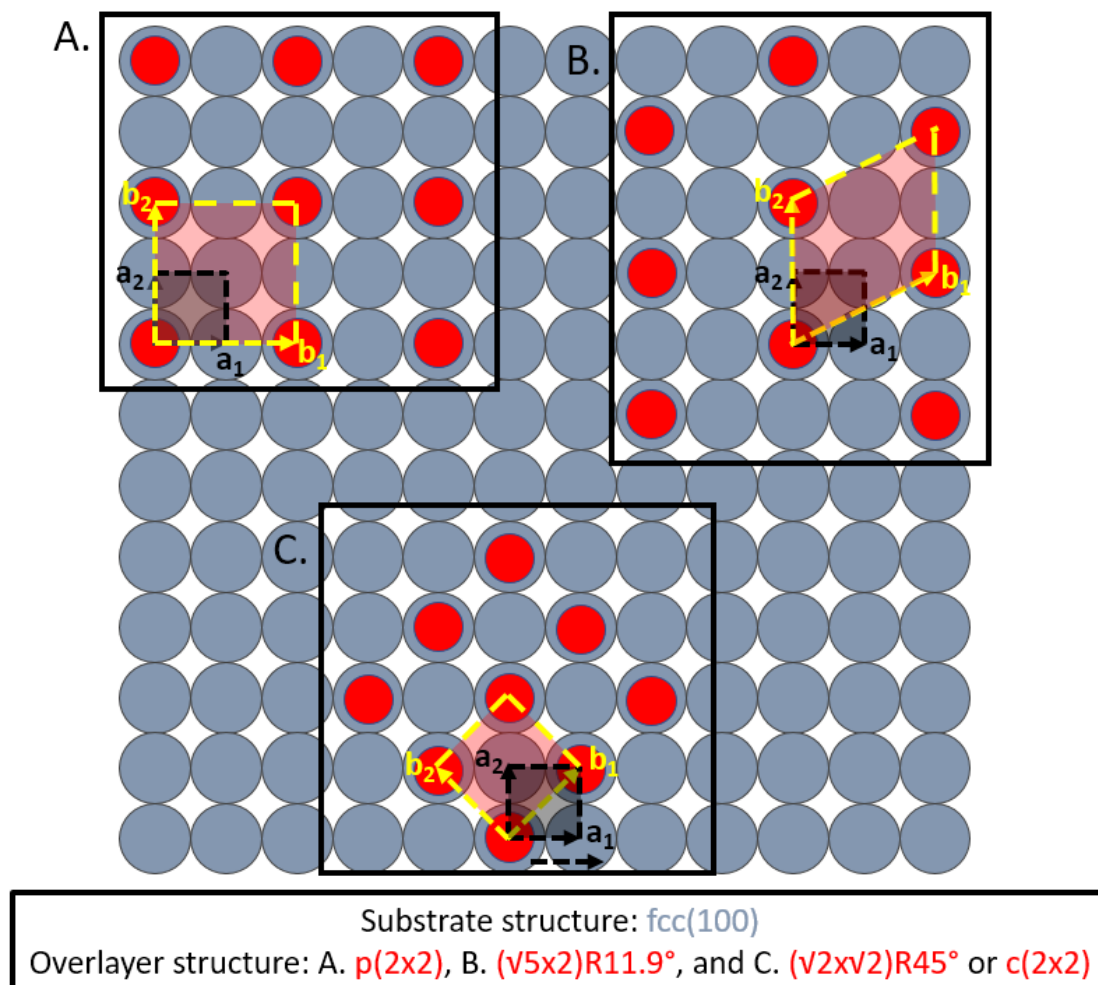


Figure 1.5 Some examples of commensurate overlayer structure on $\text{fcc}(100)$ surface lattice

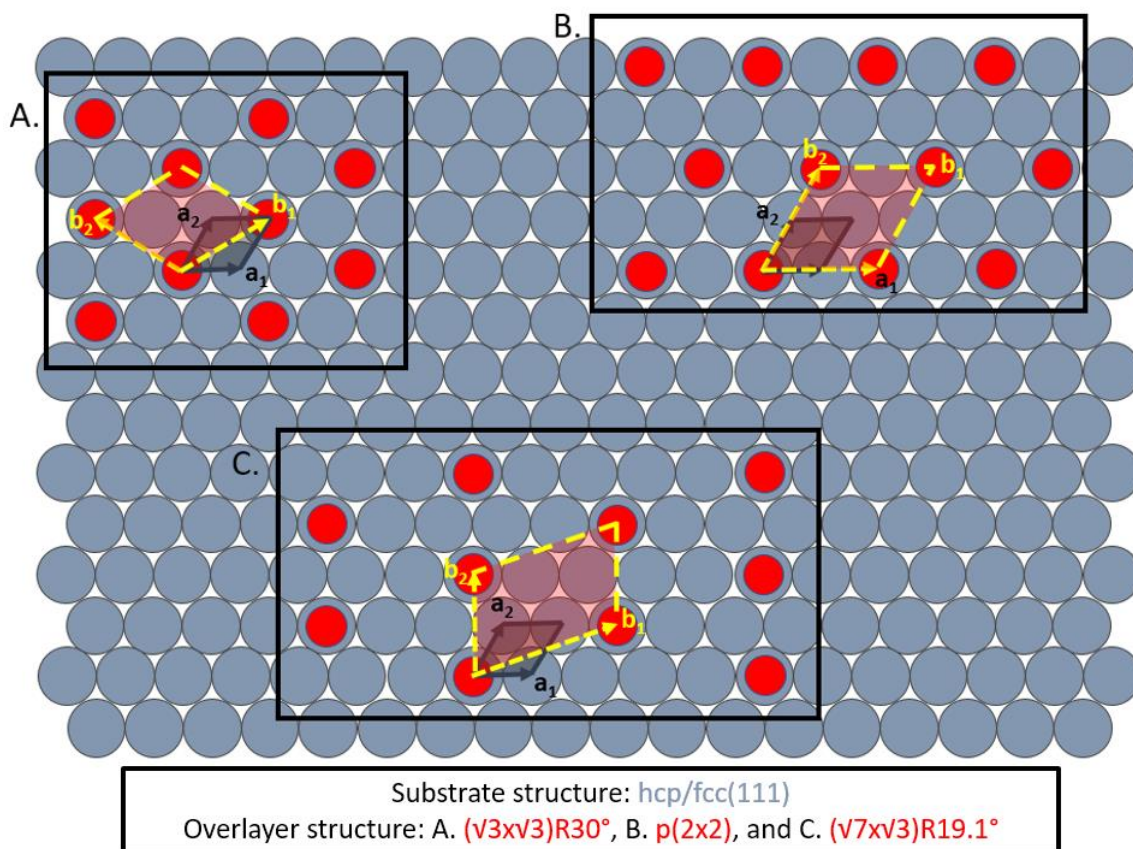


Figure 1.6 Example overlayer structures on hexagonal closed pack fcc(111) surface lattice

1.7 Thermodynamics of Adsorption

During an isotherm experiment, precise aliquots of adsorbate gas are admitted to a sample cell that contains the substrate of interest which is maintained at the desired isotherm temperature. The gas is first dosed into a volume which is pre-calibrated, and the pressure is recorded. The gas is then let expand on the sample cell maintained at constant temperature. The pressure is then dropped because of both volume expansion and adsorption onto the surface. Each shot of gas is allowed to reach thermodynamic equilibrium with the surface and the equilibrium pressures are recorded by a computer-controlled program.

$$n_{adsorbed} = n_{entering\ cell} - n_{deadspace}$$

By accounting for the volume inside sample cell unoccupied by the substrate sample (often regarded as “deadspace” volume) and the difference in pressure before and after opening the sample volume, the moles adsorbed for each dosing is found using the following equation:

$$n_{adsorbed} = \frac{\Delta P_{dose} V_{dose}}{RT_{room}} - \frac{P_{vapor} V_{deadspace}}{RT_{isotherm}}$$

This sequence is repeated until the equilibrium pressure of the system reaches the saturated vapor pressure (SVP) of bulk phase and the total moles adsorbed on a particular point of the isotherm is calculated using the following equation:

$$\sum_{i=1}^m n_{adsorbed_i} = \frac{\sum_{i=1}^m \Delta P_{dose_i} V_{dose}}{RT_{room}} - \frac{P_{vapor_i} V_{deadspace}}{RT_{isotherm}}$$

A sample adsorption isotherm representing moles of gas adsorbed against equilibrium pressure is shown in Figure 1.7. Another useful way to express the abscissa is in terms of reduced pressure (P/P_0) where the equilibrium vapor pressure is normalized by the SVP at the sample temperature. This reduced pressure is a measure of the change in chemical potential via the following equation:

$$\mu - \mu_0 = -RT \ln(P/P_0)$$

The temperature of the adsorption cell during isotherm measurement was monitored and controlled using either platinum resistance thermometers or silicon diode sensors. To check the thermometry of the measurement temperature was also calculated and checked from SVP using Antoine equation:

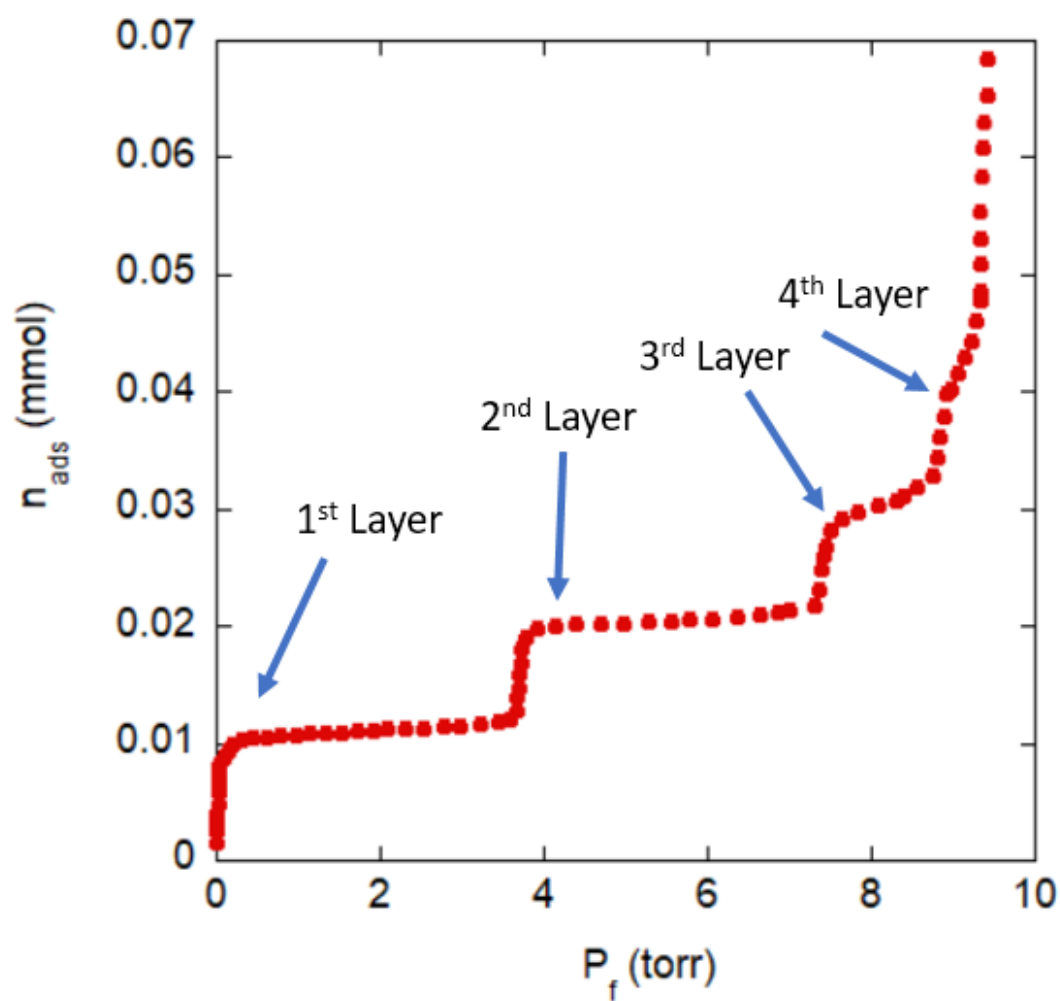


Figure 1.7 Adsorption isotherm of methane on graphite at $T = 77.4 \text{ K}$

$$\log_{10} P = A - \frac{B}{T + C}$$

A, B and C parameters are obtained from fits to the experimental data over a certain temperature range.

1.7.1 Surface Area

The monolayer adsorption capacity of a surface is determined from the number of moles obtained from the isotherm that are associated with the monolayer completion. Subsequently, the surface area of the substrate sample is calculated from its monolayer capacity. Adsorption isotherm on each substrate sample collected with methane gas at 77K using a cryostat or liquid nitrogen bath is used to calculate surface area. Brunauer and Emmett's "Point B Method" [39] is used to obtain the number of moles of gas equivalent to the monolayer coverage from the first step of the isotherm. A typical example of monolayer capacity calculation using this method is shown in Figure 1.8. The number of molecules of methane is then multiplied by methane's molecular footprint on the surfaces determined in previous studies by neutron scattering techniques[40, 41]. Multiplying the number of methane molecules adsorbed at the completion of monolayer with the molecular area of methane molecule the total surface area of the sample is determined.

1.7.2 Area per molecule (APM)

From the total surface area and the monolayer capacity of the substrate associated with the relevant adsorbate gas, the average area occupied by each adsorbate molecule is determined. The area per molecule (APM) of the adsorbate is then calculated using following equation:

$$APM = \frac{\text{Total Surface area of the sample}}{\# \text{ of molecules adsorbed}}$$

1.7.3 Clausius-Clapeyron Analysis

One of the most useful thermodynamic analysis procedures uses a variation of the Clausius-Clapeyron equation,

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

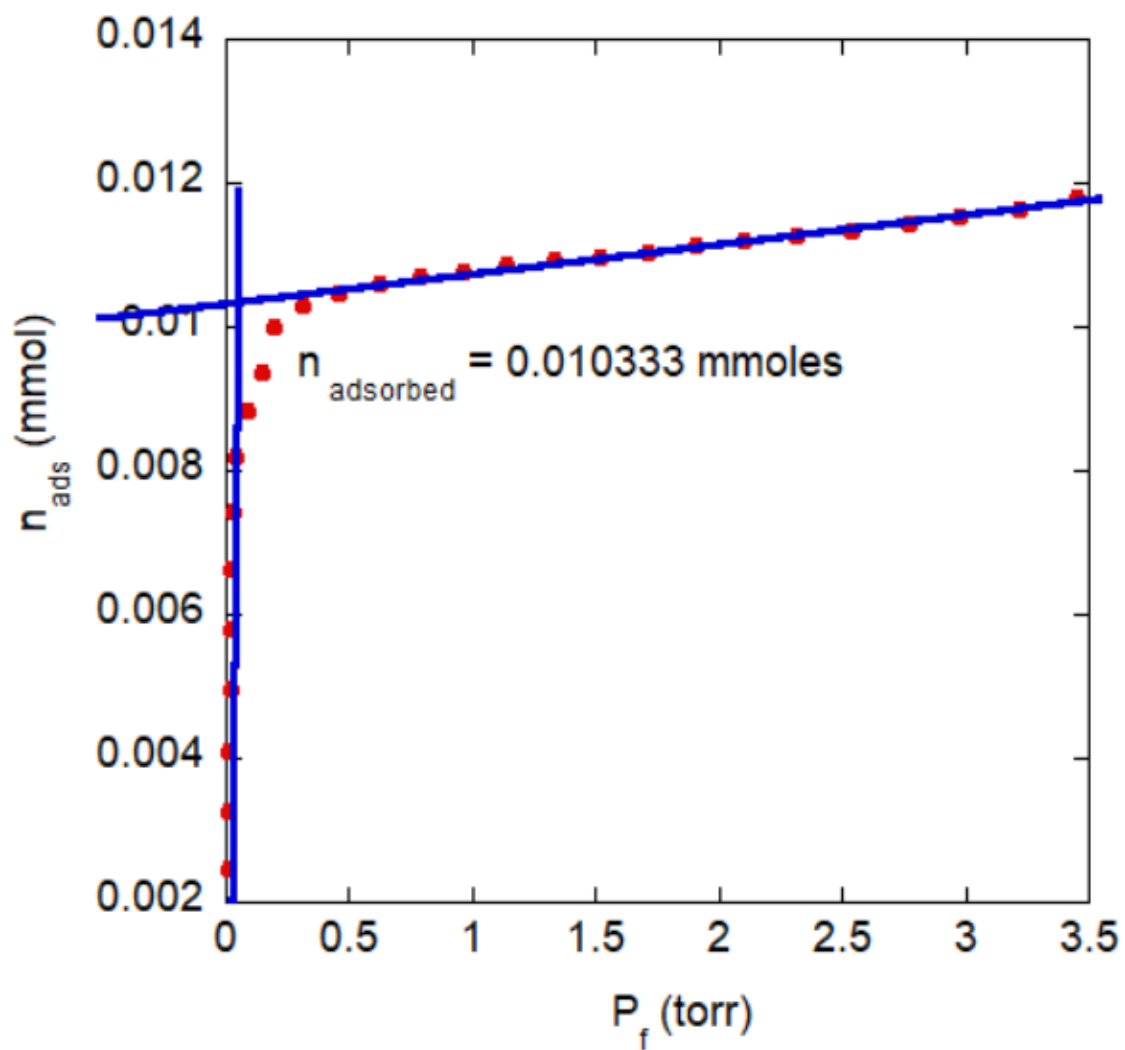


Figure 1.8 Example of the Point B method for to obtain monolayer coverage on graphite at $T = 77.4$ K.

$A^{(n)}$ and $B^{(n)}$ parameters of this equation is obtained by plotting the logarithmic pressure associated with the formation of the n th layer step against the inverse of the corresponding isotherm temperature. The parameters A and B is used to calculate thermodynamic properties such as differential enthalpy, ΔH , and differential entropy, ΔS ,

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

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

where R is the universal gas constant ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$). The $\Delta H^{(n)}$ and $\Delta S^{(n)}$ denote the difference between the enthalpy and entropy of the bulk value ($n=\infty$) and those of the n th layer. With the pressure of the gas in the sample cell approaching the saturated vapor pressure, $\Delta H^{(n)}$ and $\Delta S^{(n)}$ both approach zero. The average heat of adsorption for n th layer $Q_{ads}^{(n)}$ is determined using,

$$Q_{ads}^{(n)} = RA^{(n)}$$

Two-dimensional Compressibility and Phase Change

Isothermal compressibility is the measure of change in the volume of a fluid in response to the change in pressure at a constant temperature.

$$K_{3D} = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

In two-dimensional layer, compressibility measures the change in surface area of the adsorbate with the change in spreading pressure. The 2D compressibility, K_{2D} , is expressed by the following equation [42],

$$K_{2D} = -\frac{1}{\sigma} \left(\frac{\partial \sigma}{\partial \varphi} \right)_T$$

K_{2D} can be obtained by analyzing the data collected from adsorption isotherm experiment and the above expression for K_{2D} becomes,

$$K_{2D} = -\frac{AP}{N_A k_B T N_{ads}^2} \left(\frac{dN_{ads}}{dP} \right)_T$$

Where, A is the surface area of the adsorbent; P is equilibrium adsorbate pressure; N_A is Avogadro's Number; k_B is the Boltzmann's constant; T is the temperature of the isotherm; and N is the number of moles adsorbed; $\left(\frac{dN}{dP} \right)_T$ is the first derivative of the moles adsorbed with respect to equilibrium pressure. K_{2D} when plotted against chemical potential provides indication of the possibility of a phase change in the adsorbed layer.

The abrupt change in K_{2D} peak at a certain temperature indicates a potential phase transition temperature.

1.8 Introduction to Molecular Dynamics

Molecular Dynamics (MD) can gain understanding on the microscopic interaction between the molecules and predicting their molecular trajectories. There are two common approaches for probing this dynamic interaction; *ab-initio* and classical molecular dynamics. In both cases, the molecular interactions are represented by intermolecular force field equation. The molecular trajectories are then determined by applying Newton's equation of motion to the atomic co-ordinates. The *ab-initio* molecular dynamics is calculated using Born-Oppenheimer approximation where density functional theory (DFT) investigates the potential energy of the system. In classical molecular dynamics, the molecular trajectories are calculated using intermolecular force fields [43].

While *ab-initio* molecular dynamics approach can probe many factors, it is often mathematically complex and computationally expensive. In contrast, the intermolecular potential within the force field of classical molecular dynamics are well-defined and parameterized with experiments. Therefore, *ab-initio* simulations are practically limited to small molecular systems for a relatively shorter timeframe. For this reason, the classical molecular dynamics simulation was utilized in this dissertation. With the aim to understand the microscopic molecular interactions of cycloalkane adsorbed on surfaces, COMPASS and Universal force field packages were employed [44, 45].

In this study, MD simulations were performed using the MD option within the Accelrys' Material Studio Package. During the molecular dynamics simulations, the program uses the NVT ensemble by keeping the number of moles, N, volume, V and temperature, T constant. The MD calculations involved following the trajectories of molecules by solving Newtonian equation of motion:

$$\mathbf{F}_i = m_i \mathbf{a}_i(t)$$

The force on an atom, i, is calculated from the derivative of the potential with respect to its coordinate, r,

$$-\frac{\partial V}{\partial r_i} = m_i \frac{\partial^2 r_i}{\partial t^2}$$

The output file generated upon the completion of a MD calculation describes the trajectory of every particle within the system. In our calculations the positions of all the adsorbent atoms are kept fixed while allowing the adsorbed molecules to move in

response to the $k_B T$ and the M-M and M-S interaction potential. The temperature is initially increased up to 2.5 times of the bulk triple point of the adsorbate to provide the molecule with a great deal of energy in order to randomly position them on the surface. For a typical MD calculation, the dynamics are run for 50ps length with 1fs time step. Upon completion of each step calculation, the temperature of the system is decreased by 10K. The process keeps repeating until sufficient number of frames are collected for a trajectory file. The Nosé-Hoover-Langevin (NHL) thermostat[46] is chosen to control the temperature because this method is reliable for systems at or near equilibrium and accounts for non-ergodic behavior of the system by adding a Langevin friction and noise term. The electronic interactions for van der Waals force are calculated using Ewald sums. Two-dimensional boundary conditions and a closed volume is employed so that molecules cannot escape in the vapor phase (i.e. leave the simulation box) when the temperature is sufficiently high.

1.8.1 Force fields

A force field is comprised of several functional forms and parameters to describe the intermolecular and intramolecular interactions and the energy of a particular configuration in a collection of atoms. In this study two Class II force fields --- COMPASS and Universal --- have been used. COMPASS[44] ((Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) is the first ab-initio semiempirical forcefield that was applicable for predicting properties of both gaseous and condensed matter phase at the same time. In this study COMPASS was employed for the MD simulation of cycloalkane on MgO and graphite. This forcefield was selected because it is well parameterized and thoroughly validated for organic, polymer and small gas molecules [44, 47-49]. The parameters for COMPASS was derived using ab-initio calculations and optimized using experimental data. The functional form for valence energy includes both diagonal terms i.e. bond, angle, torsion, inversion (out of plane) and cross terms e.g. stretch-stretch, bend-stretch, bend-bend, stretch-torsion, bend-bend-torsion etc. The functional forms for non-bond energy are electrostatic and non-bonded terms.

For the simulation of cycloalkanes on hBN were performed using Universal force field (UFF) [45]. UFF is purely diagonal forcefield and include the interactions of all atoms in the periodic table. Currently very few forcefields are available that include interactions with boron and it is one of them which is available for using with Forcite module. The primary interaction between the molecules and adsorbent surface MgO, graphite and hBN is

governed by van der Waals (vdW) force which is commonly calculated using the Lennard-Jones (LJ) potential model. The non-bond functional of UFF is a 12-6 L-J whereas for COMPASS it is 9-6 variant of the LJ model. The general expression of these two LJ models are as follows:

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

$$V_{LJ} = \varepsilon \left[2 \left(\frac{\sigma}{r} \right)^9 - 3 \left(\frac{\sigma}{r} \right)^6 \right]$$

Where ε is the potential well depth, σ is a measure of van der Waals radius and r is the separation distance of the particles. The r^{-12} or r^{-6} term represent the repulsive interaction while the r^{-6} term represents the attraction between two atoms.

1.9 Trajectory Analysis

Molecular trajectories generated from an MD simulation run can be subsequently analyzed for extracting a number of time correlation functions and structural distribution functions such as pair correlation function, concentration profile, mean square displacement, velocity autocorrelation function, rotational auto-correlation function. Two the major analysis performed on the molecular trajectory generated by the simulation are described below:

1.9.1 Radial Distribution Function (RDF) Analysis

RDF analysis is particularly important for investigating packing behavior in both solid and liquid. The crystallinity of the adsorbed layer can be qualitatively measured by this function. RDF is a radial form of pair correlation function, $g(r)$ which gives the probability of finding two atoms a distance r from each other. In general, for a monoatomic fluid pair correlation function can be expressed by the following equation,

$$g(r) = \frac{V}{N^2} \langle \sum_i \sum_{i \neq j} \delta(\mathbf{r} - \mathbf{r}_{ij}) \rangle, \text{ where } r_{ij} = r_i - r_j$$

For a system consisting of atoms with different chemical types RDF has been defined by Hansen and McDonald[50],

$$\text{RDF} = \chi_\alpha \chi_\beta \rho g_{\alpha\beta}(\mathbf{r}) = \frac{1}{N^2} \left\langle \sum_i^{N_\alpha} \sum_{i \neq j}^{N_\beta} \delta(\mathbf{r} - \mathbf{r}_{ij}) \right\rangle$$

Where χ_α , χ_β and N_α , N_β are the mole fractions and number of atom type α and β respectively, ρ is the overall number density and N is the total number of atoms. RDF calculated from a simulation can help in both predicting and interpreting X-ray/ neutron diffraction results of adsorbed molecular layers. Mathematically, RDF is directly linked to the experimental scattering function via Fourier transformation.

In our analysis, RDFs have been computed by selecting a set of atoms or centroids within the defined cutoff values. In addition to the total radial distribution function, its component of intra- and intermolecular interactions can also be obtained separately. In this study, the structural order and lattice constants have been estimated using both the intermolecular component of RDF and the RDF analysis of the center of mass of the molecules.

1.9.2 Concentration Profile Analysis (C(z))

In a concentration profile analysis, the profile of atom density can be computed in any direction by defining the miller indices of that particular plane. In this study, C(z) has been calculated in evenly space slices perpendicular to the surface normal vector. The direction chosen is first divided into a specified number of bins. The relative contribution of from atoms in each cell in the direction of binning vector is calculated as follows,

$$\text{relative concentration, } C(z) = \frac{\frac{\text{number of atoms in slab}}{\text{volume of slab}}}{\frac{\text{Total number atoms in system}}{\text{volume of system}}}$$

C(z) is dimensionless and can be calculated for any subset of atoms selected from the input structure. In this study concentration profile analysis have been performed on the trajectory files of mono- and multilayer coverages as a function of temperature. The results of the analysis have been used to obtain insight about the effect of coverage and temperature on the dynamics and ordering in the adlayers as well as the interlayer transition of molecules.

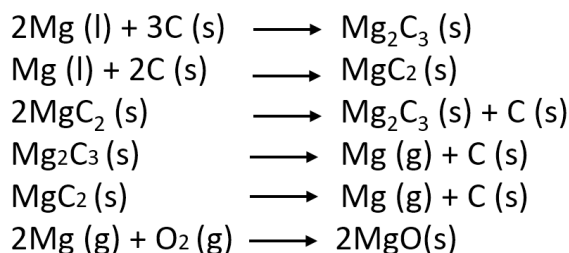
CHAPTER 2 MATERIALS AND METHODS

2.1 Adsorbent Surface Synthesis and Preparation

The formation of adlayers on a surface is dependent upon the surface topography and purity. To study the properties of adlayers adsorbent with large and uniform contaminant-free surface is a prerequisite. The synthesis method dictates the quality of the surface largely especially those surfaces that are sensitive to the exposure to ambient. In this study every surface is purified before loading into the sample cell for adsorption isotherm measurement. The synthesis method of magnesium oxide and purification of all surfaces are discussed below.

2.1.1 Synthesis of MgO

The MgO powder used for adsorption studies were synthesized using a vapor entrainment method patented by Kunman and Larese [51]. In this method, first the magnesium vapor is produced via a metal carbide route bypassing the liquid molten metal phase. Mg vapor is then allowed to react with a controlled flow of oxygen gas in an argon atmosphere to produce MgO nanoparticles. The reaction routes are as follows:



The white crystalline MgO is collected from the reaction chamber wall and preserved in a desiccator under argon. MgO particle synthesized in this method have cubic rock salt structure with almost exclusive 100 facet exposure and almost free from edge effect. Details of the experimental set up of MgO synthesis is provided below:

2.1.2 Experimental Set-up

At first, cubic magnesium metal pieces of dimension about 1cm × 1cm × 1cm are washed in 6M HCl acid to clean off the oxidized surface layer and any contaminant that may be present at the surface. Graphite chunks are crushed into approximately 1mm pieces and loaded into a graphite crucible with the magnesium metal pieces. The ratio between the graphite and MgO are approximately 2:1. The crucible is then positioned on

a quartz spacer inside the RF generator coil of the reaction chamber. The spacer allows heat convection through Argon gas flow. The graphite crucible is shielded from the RF generator coil using a refractory alumina tube. The reaction column is a large quartz cylinder that is covered using a stainless-steel baffled lid at the top which is connected to the exhaust line. A Lepel™ radiofrequency generator is used for heating the metal and a set of heating parameters are followed throughout the synthesis steps. Figure 2.1 shows a schematic of the MgO synthesis reaction. Figure 2.2 shows images of the reaction column used for the preparation of MgO powder.

2.1.3 Heat Treatment and purification of substrate surface

Before measuring an isotherm, the MgO sample is heat treated under vacuum ($\sim 10^{-7}$ torr) at 950°C for at least 48hrs in a quartz-borosilicate graded tube using a Lindberg/Blue M™ tube furnace. The heat treatment step makes the surface structure uniform and ensures the (100) equilibrium surface exposure on all facets [52].

The graphite used for the adsorption study was obtained from Union Carbide in the form of compressed graphite 'worms' with surface area of $\sim 20 \text{ m}^2/\text{g}$. Prior to adsorption isotherm measurement, graphite samples were heat treated at 750°C for ~ 4 hrs to evaporate the moisture and organics. The physically bound contaminant in the samples are evaporated off of the graphite surface at about $\sim 200^\circ\text{C}$ [53].

Hexagonal boron nitride of grade AC6004 was obtained from Momentive Performance Materials. The surface area specified for this grade is $\sim 2 \text{ m}^2/\text{g}$ with mean particle diameter of $\sim 12\mu\text{m}$. Previous adsorption studies on hBN surfaces shows that material with larger particle size provide more surface uniformity and fewer high energy binding sites which facilitates the isotherm studies with more distinct features[54]. To remove the contaminants such as borates and organics hBN is thoroughly washed in methanol for at least 2hrs and oven dried at 109°C for at least 1hr[55]. It is then heat treated at 900°C for ~ 12 hrs in the furnace. The heat treated samples are handled inside argon glove box transferring into the sample cells and characterized using methane adsorption isotherms to confirm their monolayer and multilayer adsorption capacity before using for adsorption studies.

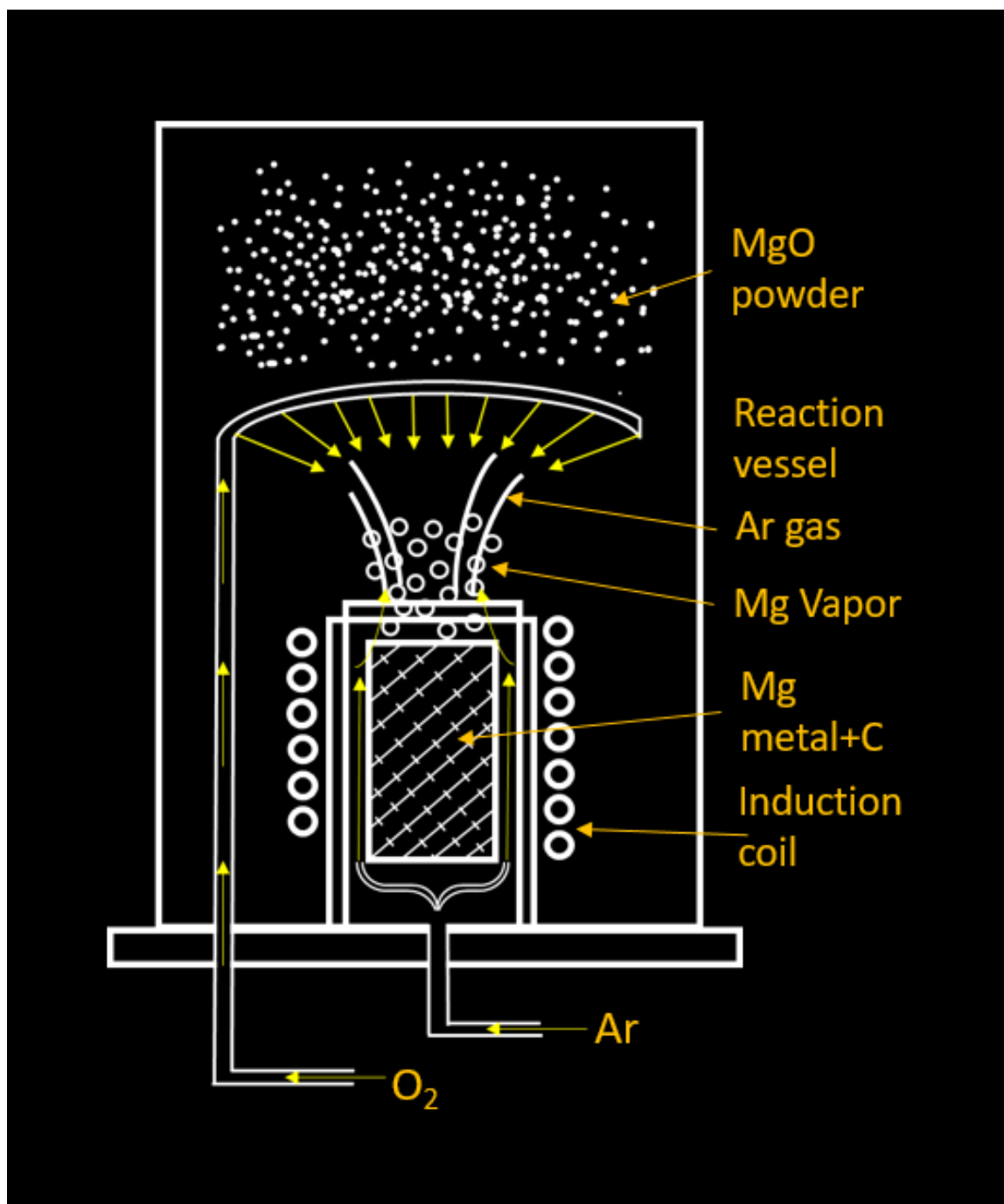


Figure 2.1 Schematic of MgO synthesis from Mg vapor via metal carbide route. The diagram is recreated from the patent [51].

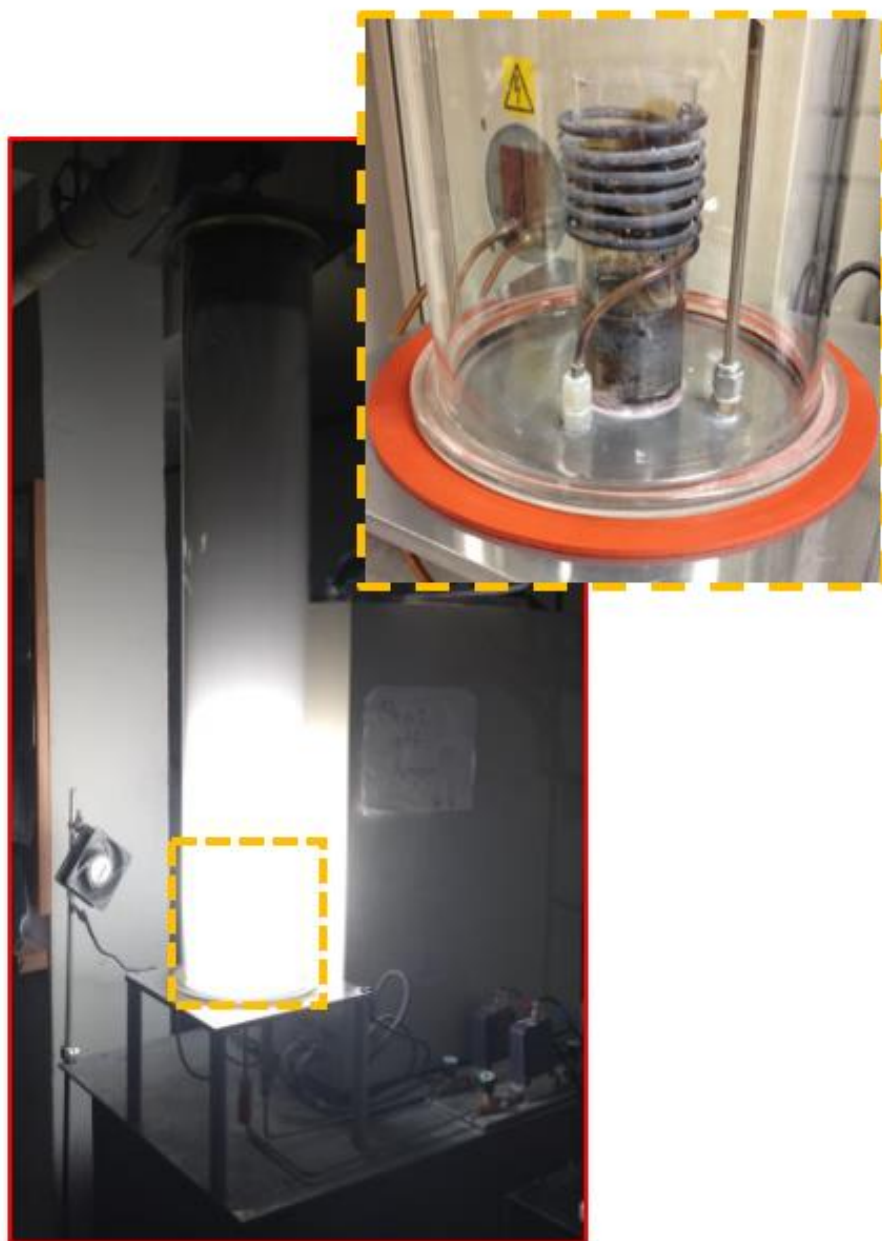


Figure 2.2 Reaction chamber used for MgO synthesis. The large quartz column is illuminated during the production of MgO via the ignition of Mg vapor. Inset shows the RF generator coil used for controlling temperature.

2.2 Purification of the adsorbates

The cycloalkanes used for this study have been obtained from commercial vendors with a grade of at least >99% purity. To remove the dissolved moisture and gases a two-step purification has been followed. The details of the dehydration and purification are as follows:

2.2.1 Distillation method

The adsorbate cycloalkanes were first dehydrated using freshly cut metallic sodium. The solvent was then distilled under argon atmosphere through a drierite column and refluxed onto activated molecular sieves. The solvent was sealed into a glass container and handled inside a glove bag filled with ultra-high purity argon. The adsorbates were then transferred into stainless steel 50 mL/10mL volumes for further purification and adsorption study.

2.2.2 Freeze-pump-thaw

The dried solvents were then purified via a freeze-pump-thaw distillation technique for removing soluble gases such as Ar, N₂, O₂ etc. In this method the adsorbates were first crystallized in liquid nitrogen at 77K and subsequently evacuated using a turbomolecular pump. The solvents were then allowed to warm up slowly below its melting point to release the gases. This gas pressure was monitored by a ionization gauge which indicated the release of dissolved gases by a sharp spike in the pressure reading. The method was dependent on the adsorbate melting point and vapor pressure difference with the impurity gas. The Freeze-pump-thaw cycle was repeated until the sharp increase on the ionization gauge during the pumping step was absent.

2.3 Adsorption Isotherm Measurement Apparatus

2.3.1 Isotherm Station

Volumetric adsorption isotherms were performed using automated high resolution custom build adsorption apparatus typically referred as “isotherm station” first constructed by Mursic and Larese[56]. The main gas handling manifold is equipped with several

manual and automated actuator-controlled valves and voltage driven proportional valves.

The calibrated volume is connected to the following parts:

- 1) Adsorbate liquid/gas reservoir: The adsorbate cycloalkanes are liquid at room temperature and kept inside stainless-steel volume connected to manifold through a valve. The gas enters into the calibrated volume at a predetermined dosing size through a metering valve. The amount of gas is also controlled using the turbo molecular pump.
- 2) Capacitance manometers connected with signal conditioner and pressure readouts: High resolution MKS baratron 1, 10, 100 and 1000 torr manometers have been used depending on the vapor pressure of the adsorbate. The resolution is $\sim 10^{-6}$ times the full-scale range.
- 3) Sample cell assembly inside temperature-controlled solvent bath or cryostat: the sample cells maintained at a constant temperature inside the temperature controller (discussed in detail below) are connected to the system through $\frac{1}{4}$ inch SS tubing and $\frac{1}{16}$ inch capillary tubing.
- 4) Turbo molecular pump: Turbomolecular pumps i.e. Agilent TPS compact pump or Leybold-Heraeus high vacuum pumps were used to maintain vacuum and to control dosing during the isotherm measurement. After recording each isotherm, the gas manifold and sample cell are evacuated to a base pressure $\sim 10^{-8}$ torr before recording another isotherm.

Approximately 150 datapoints are recorded to construct an isotherm. The measurement is controlled automatically using a Labview based isoimac program. A schematic of the isotherm measurement is shown in Figure 2.3.

2.3.2 Sample Cell

Mainly two types of sample cells were used in this study: 1) a quartz/Pyrex tube, 2) oxygen free high occupancy (OFHC) copper cell. The quartz tube is connected with a kovar opening through quartz-borosilicate graded seal. The OFHC cell is connected with a stainless-steel capillary tube. The cell has two parts: a sample holder and a lid. After loading the sample into the holder, the lid is vacuum tight with an indium seal.

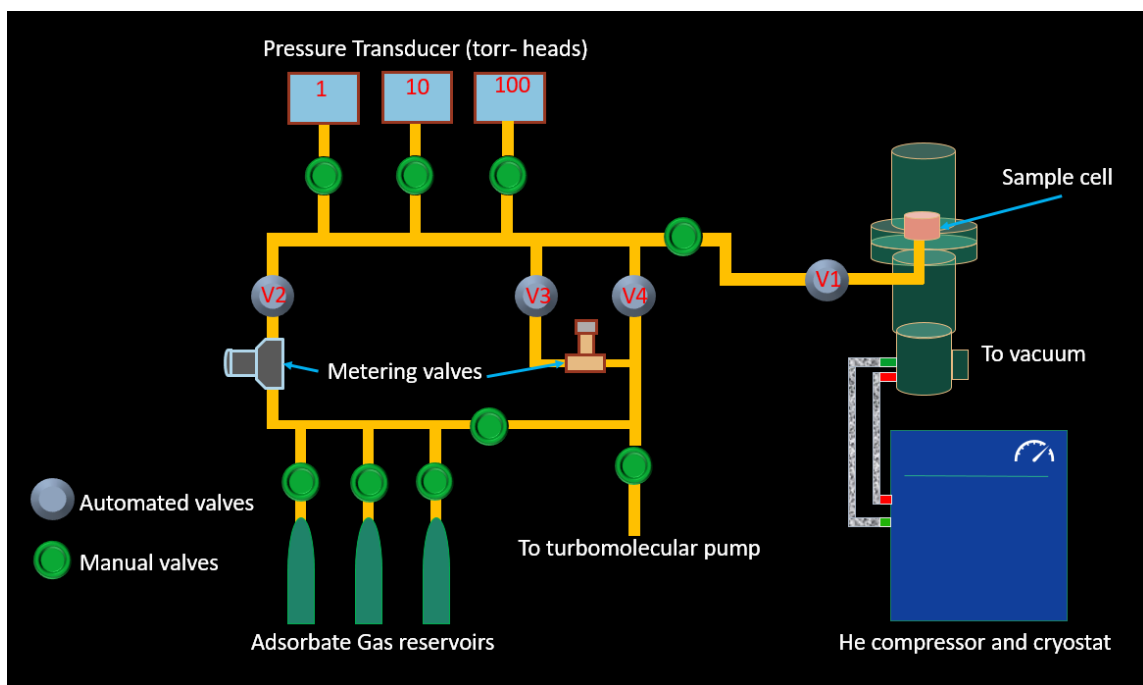


Figure 2.3 Schematic of a custom-built volumetric adsorption isotherm apparatus used to measure the adsorption isotherms in this study.

2.3.3 Temperature control

In this study, the sample temperature of the isotherm measurements was controlled using three methods:

- 1) Cryogen filled Dewar: In this method most frequently used cryogen was liquid nitrogen to maintain the temperature of the isotherm at 77.4K. The sample cell used with the Dewar was typically a quartz tube.
- 2) Recirculating solvent bath: Throughout the study a Thermo Neslab RTE 10 and a modified Haake-Brinkmann recirculating baths were employed for measurements above 250K. The temperature was monitor using both the internal built in sensor as well as an external platinum resistance thermometer (PRT) Pt1000 in conjunction with a CryoCon 32B temperature controller. Some of the common bath solvents used were DI water, water-methanol mixture and water-ethylene glycol mixtures. The sample cell used were both quartz and Pyrex tubes as well as vacuum jacketed OFHC copper cell. The temperature fluctuation in the water bath was ensured to be within $\pm 8.0\text{mK}$.
- 3) Closed System cryostats: Closed cycle helium cryostats manufactured by APD Cryogenics (model HC-2) or Advanced Research System (model ARS 4HW) were used to control temperature below 250K. the temperature was regulated using PRT pt100 and/or silicon diode sensors connected with CryoCon temperature controller. The temperature fluctuation in a helium cryostat is typically within $\pm 2.5\text{mK}$.

2.4 Molecular Dynamics Simulation

2.4.1 Parameters for trajectory simulation

In order to initiate the MD simulations of the cycloalkane and substrate interactions, few parameters were required. The previously reported literature values for the coordinates of the substrates' (MgO, graphite and hBN) unit cell were utilized in this calculation [29, 31, 57]. For each cycloalkane and substrate pair, the unit cells were replicated along the x , y and z axes to construct the dimension of the supercells. The supercell dimensions for each system simulated for this study is provided below in Table 2.1. The desired thickness of each substrate was regulated by cleaving the crystal along the z -axis. The cycloalkane and substrate interactions were probed on both sides of the

Table 2.1 Supercell dimensions used in MD simulations

Cycloalkanes	MgO ($\text{\AA} \times \text{\AA} \times \text{\AA}$)	Graphite ($\text{\AA} \times \text{\AA} \times \text{\AA}$)	hBN ($\text{\AA} \times \text{\AA} \times \text{\AA}$)
Cyclopentane	42.1×42.1×10.5	39.4×39.4×13.6	50.0×50.0×13.4
Cyclohexane	50.5×50.5×8.4	51.7×51.7×13.6	50.2×50.2×13.4
Cycloheptane	50.5×50.5 ×8.4	39.4×39.4×16.7	50.2×50.2×13.4
Cyclooctane	50.5×50.5×8.4	39.4×39.4×16.7	50.2×50.2×13.4

substrate. A vacuum slab was constructed on each side to conserve the total number of molecules during the simulation period.

The calculations were performed for a total of 50 – 200ps with 1 fs time steps (500-2000 steps) where fluctuations were minimized in energy and temperature after approximately 5-7 ps. The output of trajectory frames was modified between every 5 – 100 steps depending on the relaxation time of the dynamics of interest. Non-bonding energies were truncated at a cutoff distance of 20 $\text{\AA}$. The inter- and intramolecular contributions to the total energy were determined using the COMPASS and Universal force fields.

2.4.2 Forcefield

The inter- and intramolecular contributions to the total energy were calculated using the class II COMPASS for graphite and MgO and Universal force fields (UFF) for hBN.

2.4.3 Ensemble

The simulations utilized canonical NVT or canonical ensemble where the mole number (N), volume (V) and temperature (T) are kept constant. This ensemble was chosen to mimick experimental conditions of an equilibrium layer formed during adsorption study.

2.4.4 Thermostat

The temperatures of all cycloalkane–substrate simulation were controlled by the Nosé-Hoover-Langevin thermostat with 2.5 fs decaying constant [58, 59].

**CHAPTER 3 ADSORPTION OF CYCLOPENTANE ON MGO
(100), HEXAGONAL BORON NITRIDE, AND GRAPHITE
BASAL PLANES: A THERMODYNAMIC AND MODELING
STUDY**

This chapter is based on the following publication by Fatema Wahida and J. Z. Larese:

F. Wahida*, J. Z. Larese, 2018, **Adsorption of Cyclopentane on MgO(100), Hexagonal Boron Nitride, and Graphite Basal Planes: A Thermodynamic and Modeling Study**, J. Phys. Chem. C, 2018, 122 (44), pp 25301–25313, DOI: 10.1021/acs.jpcc.8b06487.

This author's primary contribution to the above publication includes: i) all of the volumetric adsorption isotherm measurements and analysis for cyclopentane on all three surfaces, ii) All of the Modeling and analysis.

3.1 Abstract

The adsorption of cyclopentane on the surface of magnesium oxide(100), hexagonal boron nitride (hBN) and the graphite (basal plane) crystalline nanoparticles were studied to investigate how surface symmetry influences the physico-chemical properties. The effects of symmetry mismatch between the molecular adsorbate and the surface is clearly reflected in the layering behavior as established by a series of high-resolution volumetric adsorption isotherms recorded over the temperature range of 195-264K on each of the substrates. Two distinct layering transitions were observed on MgO(100) and hBN whereas three were recorded on graphite basal plane. The heat of adsorption, differential enthalpy, and differential entropy were calculated from the adsorption isotherms. The locations of potential phase transitions were identified using the two-dimensional (2D) isothermal compressibility as a function of temperature and coverage. Additional insight into the microscopic structure and dynamics of the adsorbed layers was revealed using classical molecular dynamics (MD) simulations. Molecular trajectories generated in the temperature range 5K-500K were used to obtain the concentration profiles ($C(z)$) of the adsorbed layers perpendicular to the surface. The simulations were also used to determine the radial distribution function (RDF) to examine the effects of surface symmetry on the spatial order within the solid molecular films. The results reported here form the foundation for future investigations using neutron and x-ray scattering techniques.

3.2 Introduction

The study of adsorbed molecular films on the surface of metal oxide nanoparticles and layered materials has significant scientific and industrial importance. These materials are widely used in pharmaceuticals, optoelectronics, catalysis [60], sensors and in separation science. Developing a fundamental understanding of surface wetting and physical adsorption is a key element in the design or improvement of the novel or existing functional materials. In previous years, adsorption studies on archetypal surfaces have been used to illuminate the nature of the adsorbate-surface and adsorbate-adsorbate interactions and the resulting thermodynamic properties. In this study, we describe the results of our investigation of the adsorption thermodynamics and molecular dynamics (MD) of cyclopentane films on MgO(100) and the basal planes of graphite and hBN as part of our ongoing research interest in the adsorption of linear and cyclic alkanes on the surfaces. MgO has been widely used for the adsorption studies because of its simple crystal structures with largely exposed (100) facets and four-fold symmetry. The basal planes of graphite and hBN offer six-fold and three-fold symmetries respectively with relatively defect-free large surface area. Although MgO and graphite have their obvious differences in both surface symmetry (four-fold vs six-fold) and in chemical and physical properties (ionic vs covalent; electrical insulator vs conductor), the dynamical film adsorbed on these two surfaces are strikingly similar [61]. In the past few decades, the wetting behavior of small molecules (e.g. rare gases [42, 62, 63], NH_3 [64] and linear alkanes [65-69]) on MgO(100) and graphite have been thoroughly investigated. Earlier adsorption studies of rare gases [70, 71] and diatomic molecules [72] have focused on the melting of mono- and multilayer on hBN, concentrating on the effects of the corrugation of adsorbate-adsorbent interaction potential on the adsorption thermodynamics on hBN and graphite. However, while structural information on the adsorbed molecular layers on hBN exists much less is known about the microscopic dynamics of these layers because of the high neutron absorption cross section of boron.

Cyclopentane is an excellent candidate to investigate the effects of molecular symmetry on adsorption properties. The rotational and vibrational behavior of this molecule in the bulk phase have been intensely investigated [73] primarily because of its “pseudo-rotational” behavior. Furthermore, cyclopentane has important applications in the synthesis of resins and rubber adhesives and is being considered as an alternative of hydrochlorofluorocarbons (HCFCs) as polyurethane blowing agent for insulation materials

[74] and a promising refrigerant with a very low global warming potential [75]. Recently the role of cyclopentane as a promoter in gas hydrate formation is being investigated for potential natural gas storage applications [76]. We believe the fundamental findings of our experimental and modeling studies will advance the synthesis and applications of cyclopentane in future by improving the understanding of its interaction with solid surfaces.

In this study, high-resolution adsorption isotherms were performed over the temperature range of 195K-264K to elucidate the thermodynamic properties of the adsorbed films on the surface. The wetting properties of cyclopentane within this temperature range have been thoroughly investigated using the calculated thermodynamic quantities. In addition, to achieve knowledge on the microscopic dynamics and structure of the film we used classical molecular dynamics simulations within a broad range of temperatures (5K-500K). The trajectories of the molecules were analyzed to evaluate the change in molecular distribution normal to the surface with temperature and coverage. The structures of the monolayer films were examined using both the intermolecular radial distribution function (RDF) and the center of masses (COM) RDF of the molecules. In addition to providing microscopic insight into the wetting of cyclopentane, these modeling studies will be used to aid the interpretation of future neutron scattering experiments aimed at exploring the rotational and translational diffusion as well as the vibrational motion of single and multilayer molecular films.

3.3 Experimental Section

3.3.1 Thermodynamics

The MgO used in this study was synthesized using the technique patented by Kunman and Larese [51]. This method produces MgO nanocubes with essentially single (100) facet exposures and a narrow size distribution of ~250 nm edge length and an average surface area of ~10 m²/g. The graphite used in this study was obtained from Union Carbide in the form of compressed graphite 'worms' with measured surface area of ~20 m²/g. hBN powders (AC6004 grade) were obtained from Momentive™ Performance Materials with a surface area of ~2 m²/g. Prior to the studies the MgO and graphite were heat treated in vacuo (< 10⁻⁷ torr) at 950°C for >48h and at 750 °C for >3h respectively to remove any residual physisorbed water or molecular impurities. The hBN was first processed by thoroughly washing with methanol [55] and then heat-treated in vacuo at 900 °C for >12hrs. After heat treatment the substrate materials were loaded into oxygen

free high conductivity (OFHC) copper sample cells sealed with an indium gasket in an argon-filled glovebox to prevent hydration and surface contamination from the atmosphere. The loaded cell was then mounted inside a closed-cycle helium refrigerator (APD Cryogenics) connected to a specially designed, automated gas handling apparatus equipped with a turbo-molecular pump and MKS baratron capacitance manometers with signal conditioner units. The temperature of each measurement was regulated within ± 4 mK using a CryoCon 32B temperature controller equipped with a platinum resistance thermometer as the primary control and a secondary silicon diode sensor for additional monitoring. The substrate samples were initially characterized using high-resolution methane isotherms at 77K as a fiducial because the structure of monolayer methane and adsorption behavior on these adsorbents is known [40, 41, 61, 77-81]. A methane isotherm was subsequently repeated to ensure the surface quality regularly after several cyclopentane measurements. The cyclopentane (purity $\geq 98\%$) obtained from Alfa Aesar was initially dried over metallic sodium and then further purified via distillation through drierite and a series of freeze-pump-thaw cycles to remove any residual soluble gases. For each substrate, more than 20 isotherms were collected over the temperature range of 195-264K; the isotherms were measured at temperatures above the bulk triple point of 179.71K. The lowest temperature range was limited by the pressure resolution of the available capacitive manometers. The sample cell temperature was determined from the saturated vapor pressure (SVP) of cyclopentane using the semiempirical Antoine equation and parameters published in the NIST database [82].

3.3.2 MD Simulation

Classical MD simulations and analysis were performed using the Forcite module of BIOVIA Materials Studio package [83]. Geometry optimization and molecular interaction on the surface of MgO and graphite were carried out using the semiempirical forcefield COMPASS (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation studies) [44]. For the MD simulations on hBN surface, a more general universal forcefield (UFF) was employed [45]. The MD simulations used canonical NVT ensemble wherein the number of moles (N), volume (V) and Temperature (T) are held constant and have been shown to accurately represent the experimental isothermal measurements. During simulations, Newtonian equations of motion were iteratively solved for each atom per user defined time step for the total simulation time. Supercells of MgO, graphite and hBN with

dimensions of $42.1\text{\AA}\times42.1\text{\AA}\times10.5\text{\AA}$, $39.4\text{\AA}\times39.4\text{\AA}\times13.6\text{\AA}$, $50.0\text{\AA}\times50.0\text{\AA}\times13.3\text{\AA}$ respectively were constructed with periodic boundary conditions to eliminate edge effect. The top and bottom surface were cleaved prior to the simulations to ensure the exposure of equivalent facets. A vacuum slab on each side of the surface were constructed to conserve the total number of molecules throughout the entire simulation period. The simulation temperatures were regulated using Nosé-Hoover-Langevin (NHL) thermostat [58, 59] with a decay constant of 2.5fs. The surfaces were energetically optimized using the Smart algorithm, which is a combination of the steepest descent method, adjusted basis set Newton-Raphson (ABNR), and quasi-Newton methods to improve the efficiency of the calculations. The atom positions in the substrate lattice were kept constrained throughout the simulations. Molecules were introduced onto the surface up to the desired effective coverage (0.7ML, 1ML, 2ML, 3ML) and geometrically optimized prior to the dynamics calculation. The temperature of the surface-molecule system was initially set to $\sim 2.5\times$ of the bulk triple point of the adsorbate (cyclopentane) to eliminate the effect of any initial orientation or structural configuration. The equilibrated system obtained after a simulation at a certain temperature was used for the next run at a temperature 10K lower than the previous one. For a typical MD calculation, the dynamics were run for 50ps length with 1fs time step. The simulations of all three systems were performed for several coverages in the temperature range of 5K-500K. Molecular trajectories generated over this broad range of temperatures were analyzed to obtain microscopic properties such as radial distribution function (RDF) and concentration profile ($C(z)$). Both the intermolecular components of the RDF and the RDF of COM of the molecules over the temperature range were used to achieve insight into the structural order in the molecular layer. Single molecules were geometrically optimized on the high symmetry sites starting from all possible orientations to obtain the minimum binding energy. The internal modes were kept frozen to investigate the results of energy minimization and the concentration profile analysis.

3.4 Results and Discussion

3.4.1 Thermodynamics

As noted above, the adsorption measurements of cyclopentane over the 195K to 264K temperature range were collected and used to determine the layering behavior on all three surfaces. Within the temperature range of these experiments, two distinct

adsorption steps were observed on MgO(100) and hBN (Figure 3.1 and Figure 3.2). On graphite, however, an additional, less-pronounced, third step was recorded (Figure 3.3). The adsorption steps (especially those at the lower temperatures) clearly show these layering transitions on all three materials. To illustrate this behavior clearly Figure 3.1, Figure 3.2 and Figure 3.3 show representative high and low temperature isotherms of cyclopentane on the MgO, hBN and graphite surfaces and corresponding numerical derivatives. The isotherms were used to determine the area occupied by a single molecule (area per molecule, APM) on MgO, hBN and graphite basal planes.

The cyclopentane monolayer adsorption capacity of the surfaces at the lowest temperature of isotherm measurements were calculated using point B method [39] and compared with the methane monolayer capacity and molecular area on the surfaces (MgO, graphite) at 77K as previously established by neutron scattering experiments [41] to obtain the APM of single molecule. The APMs thus determined were found to be $\sim 34.78 \text{ \AA}^2$ at 198.6K, and $\sim 40.77 \text{ \AA}^2$ at 198.3K for MgO and graphite respectively. Due to the lack of neutron scattering data on molecular footprint of common gas adsorbents on hBN, the APM of cyclopentane on hBN was determined using the nominal surface area provided by the supplier ($\sim 2 \text{ m}^2/\text{g}$) and found to be $\sim 28.9 \text{ \AA}^2$ at 198.7K. Note that the APM were determined at a higher temperature where the molecular behavior is liquid like and largely dependent on the interaction with and the structure of the surface.

The numerical derivative of the moles of cyclopentane adsorbed vs the equilibrium pressure is used to precisely locate center of the layer formation. At lower temperatures, the numerical derivative plots exhibit sharp and narrow peaks at the layering steps. The width of these peaks broadens with increasing temperature and is related to the thermodynamic behavior of the adsorbed molecular layers e.g. the interlayer mobility and 2D compressibility which are discussed later. The third layer features on the graphite surface although less prominent in the isotherms, are readily distinguishable in the derivative plot (Figure 3.3). As in earlier studies [67-69, 84] using the method of Lahrer [85], the peak positions (p_f^i) were determined using Gaussian fits to the numerical derivative peaks and were plotted vs inverse temperature (see Figure 3.4, Figure 3.5, Figure 3.6) and used to determine several thermodynamic quantities using a modification of Clausius-Clapeyron equation,

$$\text{Ln}(p_f^i) = B^{(n)} - \frac{A^{(n)}}{T}$$

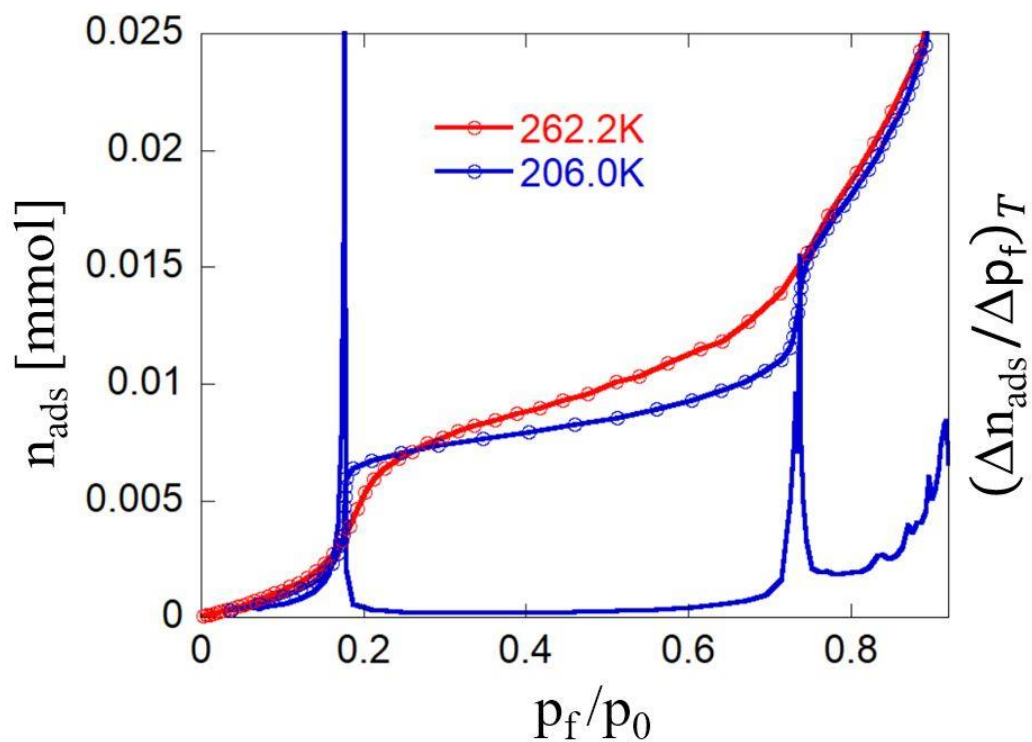


Figure 3.1 Volumetric isotherms of cyclopentane on MgO(100) at 262.2K (red) and 206.0K (blue) with its numerical derivative (blue solid line). At lower temperature, the layering “steps” are well pronounced with sharp with tall derivative peaks.

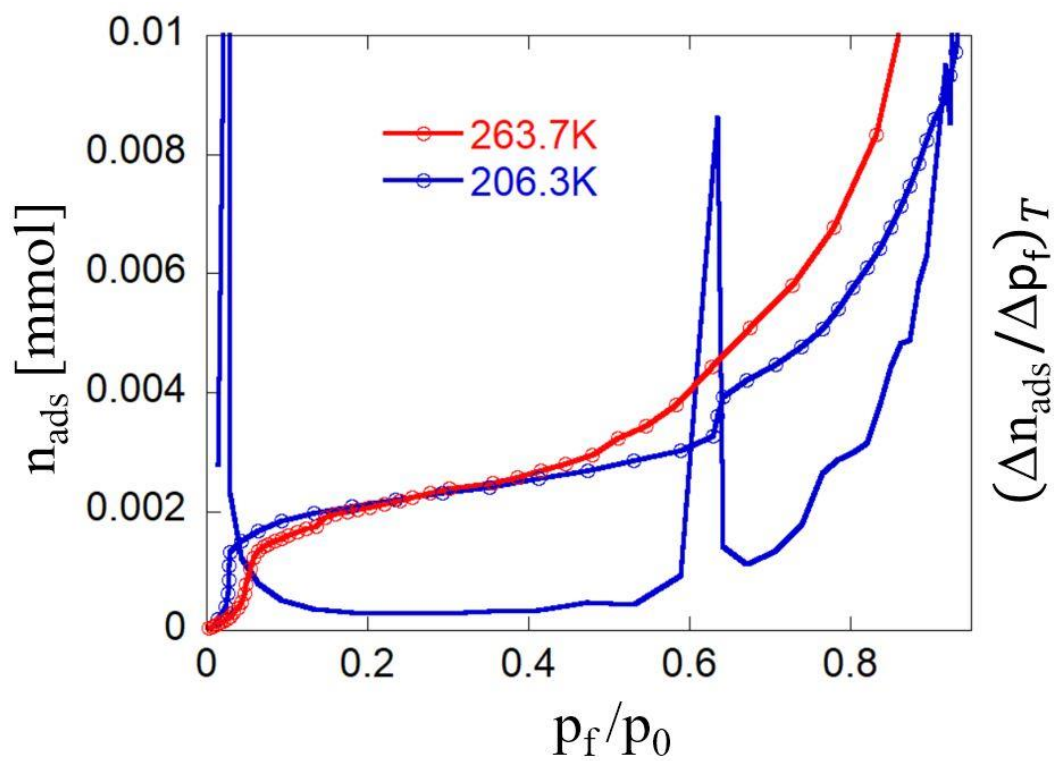


Figure 3.2 Volumetric isotherms of cyclopentane on hBN at 263.7K (red) and 206.3K (blue) with its numerical derivative (blue solid line).

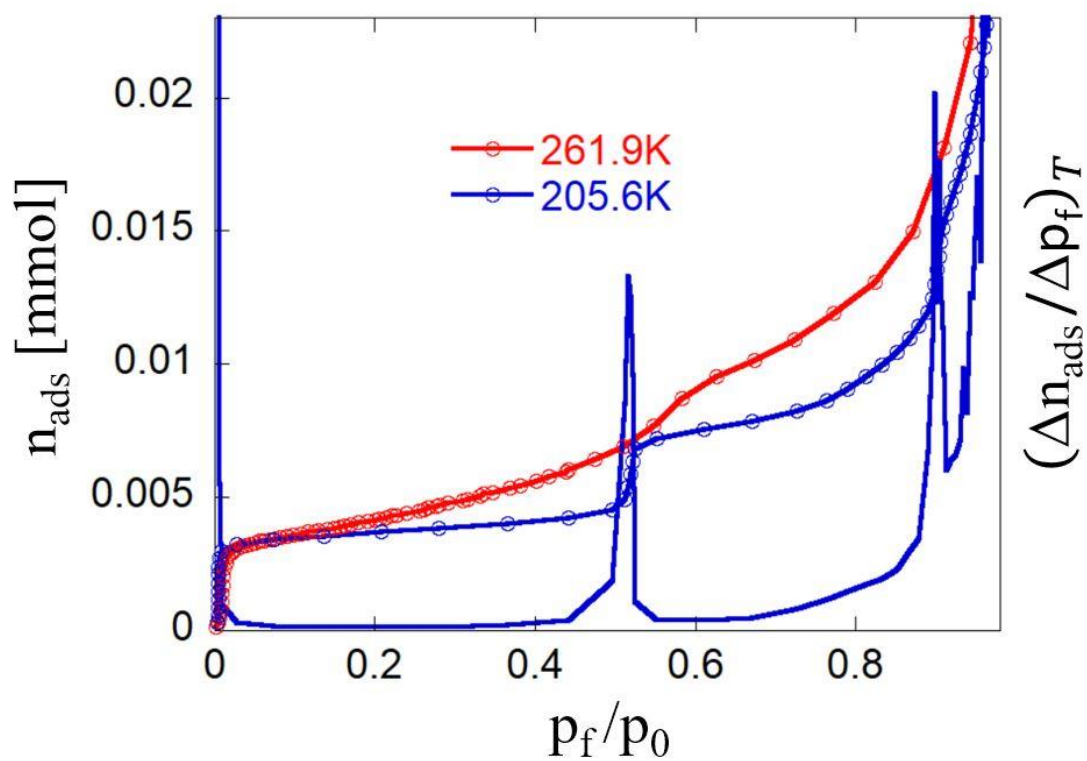


Figure 3.3 Volumetric isotherms of cyclopentane on graphite at 261.9K (red) and 205.6K (blue) with its numerical derivative (blue solid line).

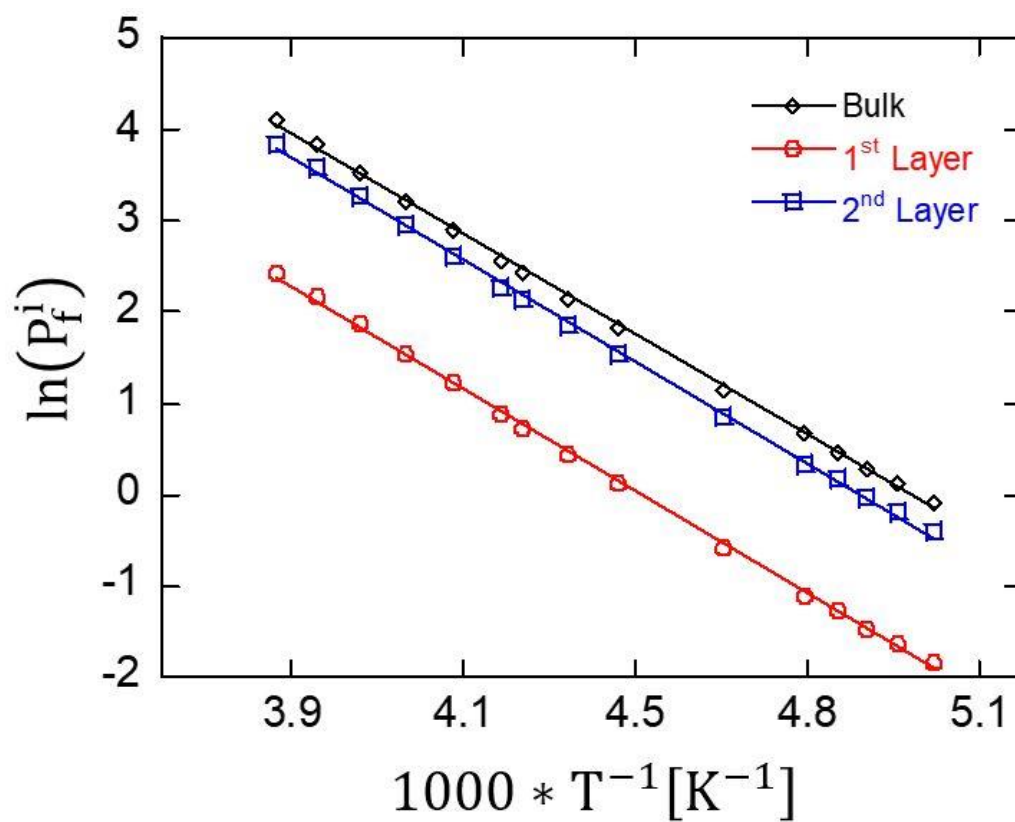


Figure 3.4 Clausius-Clapeyron fit on the equilibrium pressure (p_f^i) from the two cyclopentane layers on MgO(100) and the saturated vapor pressures. The first and second layers and the SVP are represented with red, blue and black colors respectively.

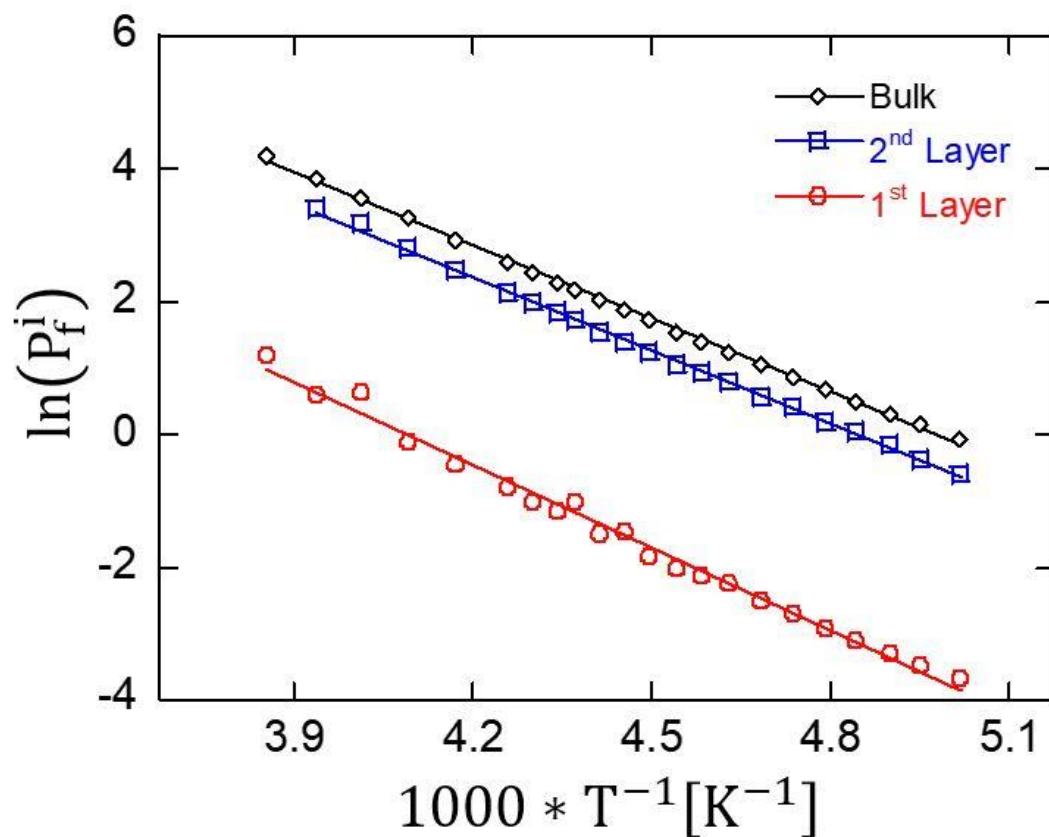


Figure 3.5 Clausius-Clapeyron fit on the equilibrium pressure (p_f^i) from the two cyclopentane layers on hBN and the SVP. The first and second layers and the SVP are represented with red, blue and black colors respectively.

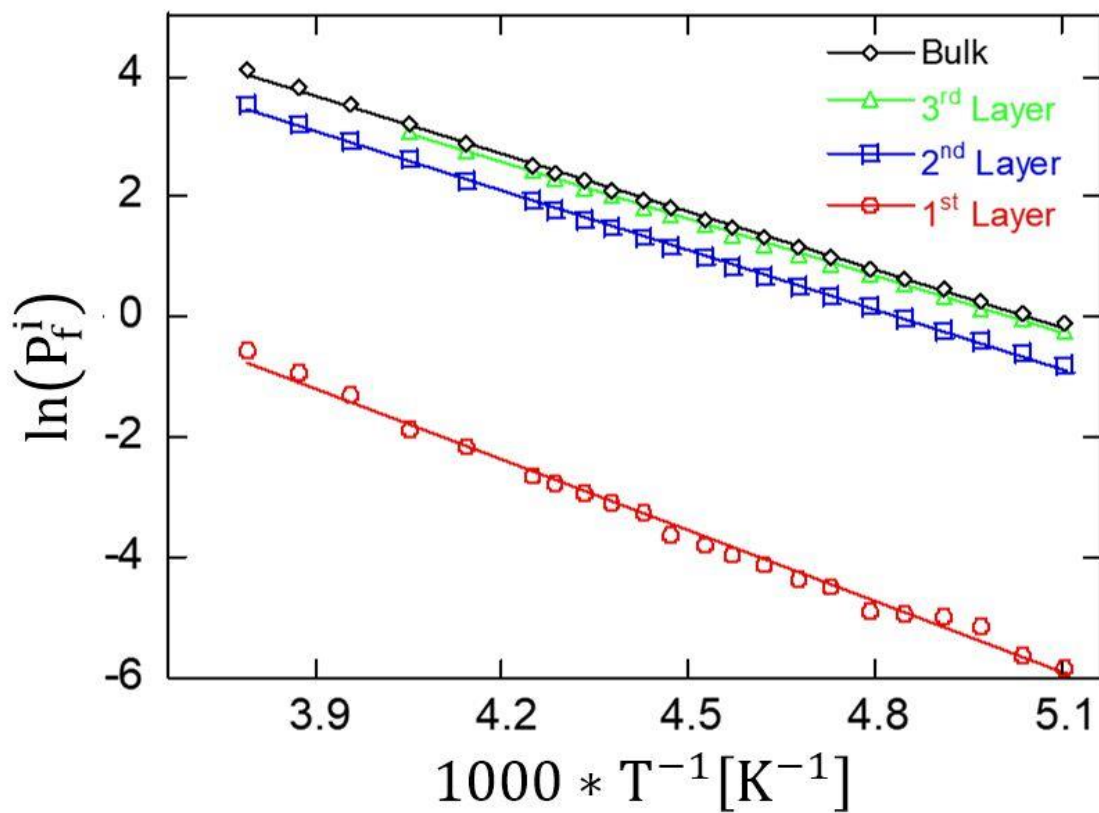


Figure 3.6 Clausius-Clapeyron fit on the equilibrium pressure (p_f^i) from the three cyclopentane layers on graphite and the SVP. The first, second and third layers and the SVP are represented with red, blue, green and black colors respectively.

The slope ($A^{(n)}$) and intercept ($B^{(n)}$) of these resulting linear plots, were used to deduce the thermodynamic properties such as heats of adsorption, differential enthalpies and differential entropies of the adsorbed molecular layers (see Table 3.1).

In this study, it is found that the heat of adsorption ($Q_{ads}^{(n)}$) of cyclopentane is the greatest on graphite, at 35.07 kJmol^{-1} while on hBN and MgO(100) these are 32.47 kJmol^{-1} and 29.25 kJmol^{-1} respectively. For all three systems, the bulk heat of adsorption $Q_{ads}^{(\infty)}$ was determined to be $\sim 28.6 \text{ kJmol}^{-1}$ which agrees with the values reported in the literature [86, 87]. We note that these thermodynamic results establish that the molecule-surface interaction decreases with increasing film thickness as indicated by a corresponding reduction in the heats of adsorption. The values of differential enthalpy and entropy follow a similar trend and thus indicate that it is energetically and entropically more favorable to the formation of the first and the second layer (second and third layer for graphite) before forming the bulk phase. Naturally, this decrease in molecule-substrate interaction (vs the molecule-molecule interaction) with film thickness suggests that the films behave more bulk-like further from the solid interface. The locations of possible phase transition can be identified using the behavior of the two-dimensional compressibility of the adsorbed films (K_{2D}) as a function of temperature [88]. As noted in earlier studies, by tracking the temperature dependence of the peak widths of K_{2D} the location of potential phase transitions can be established. We note that the isotherms recorded in this study were all well above the nominal monolayer melting point of cyclopentane (using the criteria that the T_{2D} melting $\sim 126\text{K}$ i.e. $\sim 70\%$ of the bulk triple point [89]). The critical temperature of bulk cyclopentane is $\sim 511.6\text{K}$. According to previous studies, the two-dimensional critical temperature typically falls within 30% to 50% of the bulk T_c . Hence the phase transition occurring in this temperature range is expected to be a liquid-liquid or a liquid-super critical fluid transition.

The representative traces of the 2D compressibility as a function the chemical potential are shown in Figure 3.7, Figure 3.8 and Figure 3.9. The K_{2D} was calculated using the following equation,

$$K_{2D} = \frac{Ap_f}{N_A k_B T n_{ads}^2} \frac{dn_{ads}}{dp_f} \quad (2)$$

where A is the total area of the surface, p_f is the equilibrium pressure, N_A is Avogadro's number, k_B is Boltzmann constant, T is temperature, and n_{ads} is the moles of cyclopentane adsorbed. Figure 3.7 and Figure 3.8 show the K_{2D} the first and 2nd layer on

Table 3.1 Thermodynamic values calculated from the adsorption isotherms using equation and Clausius-Clapeyron plot (Figure 3.4, Figure 3.5, Figure 3.6)

Surface	n	$A^{(n)}$ (K)	$B^{(n)}$	$Q_{ads}^{(n)*}$ (kJmol ⁻¹)	$\Delta H^{(n)**}$ (kJmol ⁻¹)	$\Delta S^{(n)***}$ (kJmol ⁻¹)
MgO	1	3517.7 ± 27.7	15.81 ± 0.12	29.25 ± 0.23	-0.67 ± 0.33	11.12 ± 1.46
	2	3459.9 ± 26.8	16.96 ± 0.12	28.77 ± 0.22	-0.19 ± 0.32	1.55 ± 1.44
	∞	3437.2 ± 28.1	17.16 ± 0.12	28.58 ± 0.23	—	—
hBN	1	3904.9 ± 82.4	15.80 ± 0.37	32.47 ± 0.69	-3.89 ± 0.72	11.21 ± 3.22
	2	3464.3 ± 29.2	16.80 ± 0.13	28.80 ± 0.24	-0.23 ± 0.33	2.86 ± 1.48
	∞	3437.1 ± 27.0	17.14 ± 0.12	28.58 ± 0.22	—	—
Graphite	1	4217.9 ± 81.2	15.34 ± 0.36	35.07 ± 0.68	-6.49 ± 0.71	14.98 ± 3.17
	2	3515.6 ± 24.5	16.87 ± 0.11	29.23 ± 0.20	-0.65 ± 0.29	2.34 ± 1.32
	3	3444.5 ± 25.9	17.04 ± 0.11	28.64 ± 0.22	-0.06 ± 0.30	0.85 ± 1.35
	∞	3437.3 ± 25.5	17.15 ± 0.11	28.58 ± 0.21	—	—

$$*Q_{ads}^{(n)} = RA^{(n)}$$

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

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

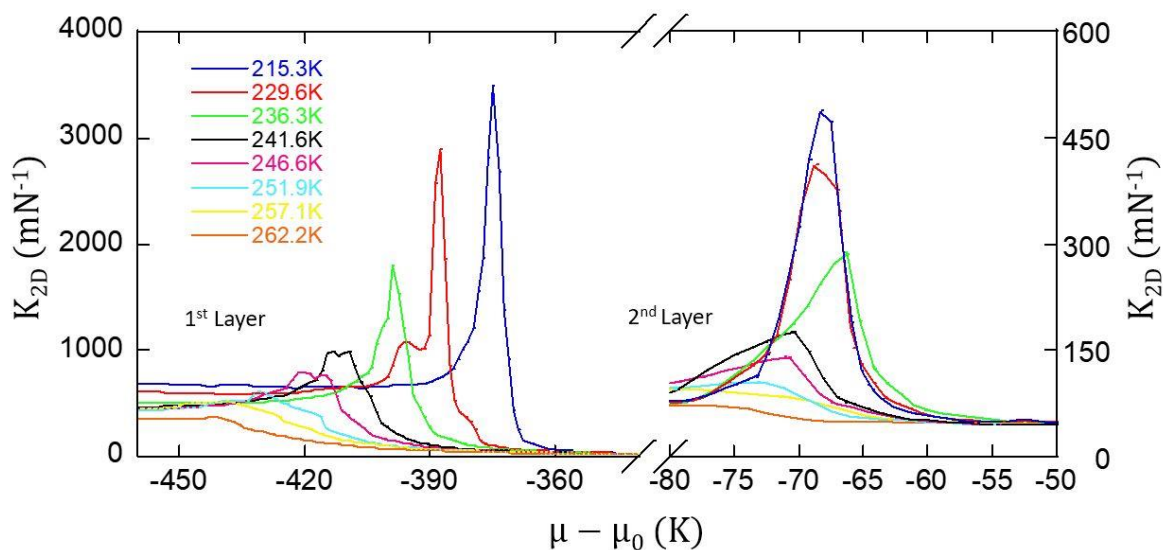


Figure 3.7 Representative plots of the isothermal two dimensional compressibility as a function of the net chemical potential of the cyclopentane films on MgO(100). The K_{2D} peaks of the second layering transitions shown at the right side of the break are presented on an enlarged scale.

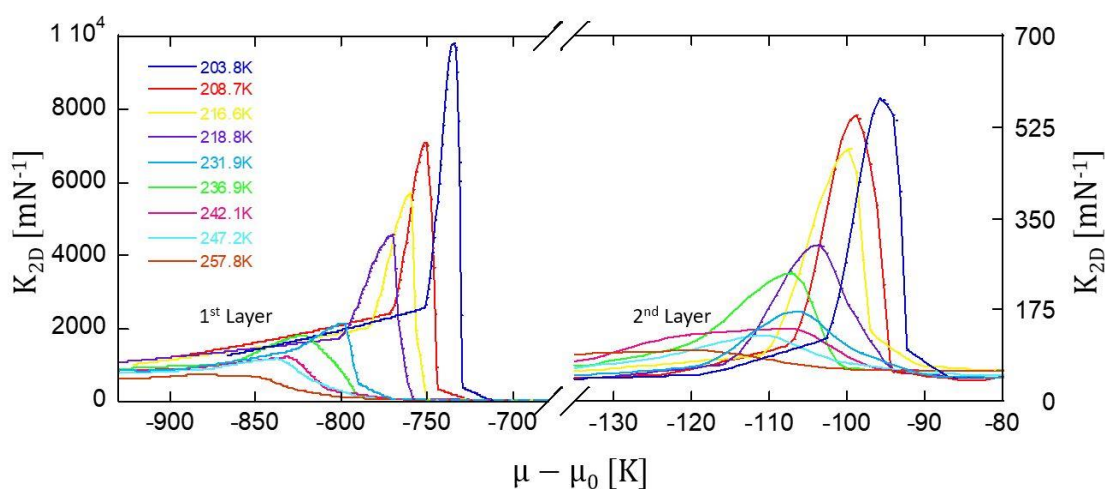


Figure 3.8 Representative plots of the isothermal two-dimensional compressibility as a function of the net chemical potential of the cyclopentane films on hBN. The K_{2D} peaks of the second layering transitions shown at the right side of the break are presented on an enlarged scale.

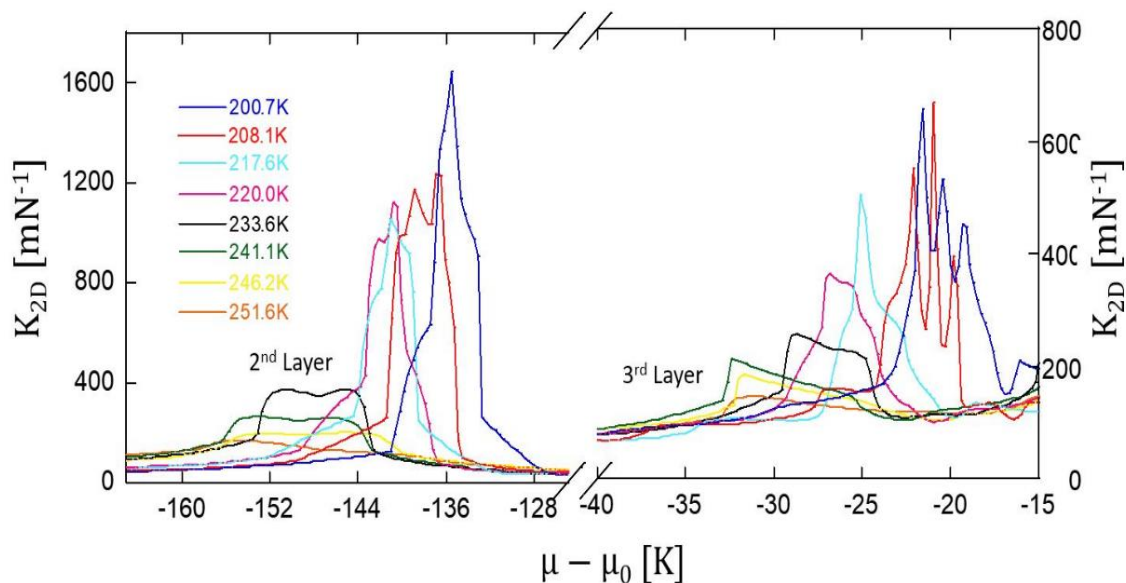


Figure 3.9 Representative plots of the isothermal two-dimensional compressibility as a function of the net chemical potential of the cyclopentane films on graphite. Due to the steepness of the 1st layering steps at low pressure region ($< 0.01P_f/P_0$), the compressibility of the first layer was not resolved. The K_{2D} peaks of the third layering transitions shown at the right side of the break are presented on an enlarged scale.

MgO (100) and hBN respectively, while Figure 3.9 shows the second and the third layer for graphite.

Due to the nearly vertical behavior of the adsorption isotherms in the monolayer region on graphite the compressibility of the first layer is extremely difficult to determine. As illustrated above, with decreasing temperature, the peaks associated with the numerical derivatives (and hence K_{2D}) of the isotherms become narrower and taller. Analogous to the three-dimensional isothermal compressibility this behavior of K_{2D} is directly related to a change in thermodynamic properties of the adsorbed molecules. In Figure 3.10, Figure 3.11 and Figure 3.12 the half-width half-maximum of the peaks obtained from the Lorentzian function fits to K_{2D} are plotted as a function of the temperature. The phase transition temperatures for the first and second layers on MgO were determined to be 236.1K and 237.5K respectively. The transition temperatures on hBN were found to be 228.4K and 229.6K respectively and for the second layer on graphite it is 229.8K. Although the FWHM of the third layer on graphite is relatively constant over a large range of temperature, the width starts to change toward the high temperature which suggests a transition temperature around 248.9K. The reduction in the critical temperature from the bulk is naturally related to the relative strength of the M-S interaction versus the M-M interaction and is more prominent for the layer nearest to the surface than those further away (which exhibit higher transition temperatures).

3.4.2 Modeling

Nonbonding energies

The MD simulations using the material studio software package has been used to provide insight into the microscopic structure and dynamics of the adsorbed layers. As in previous alkane adsorption studies, the geometry of an isolated molecule adsorbed near a high symmetry site on the three surfaces were optimized to gain insight into the possibility of preferential adsorption sites. We note that the COMPASS forcefield has been proven reliable in these previous studies of the linear alkanes on MgO and graphite [7, 4, 36]. As noted above the simulations on hBN used the Universal Force field (UFF). We

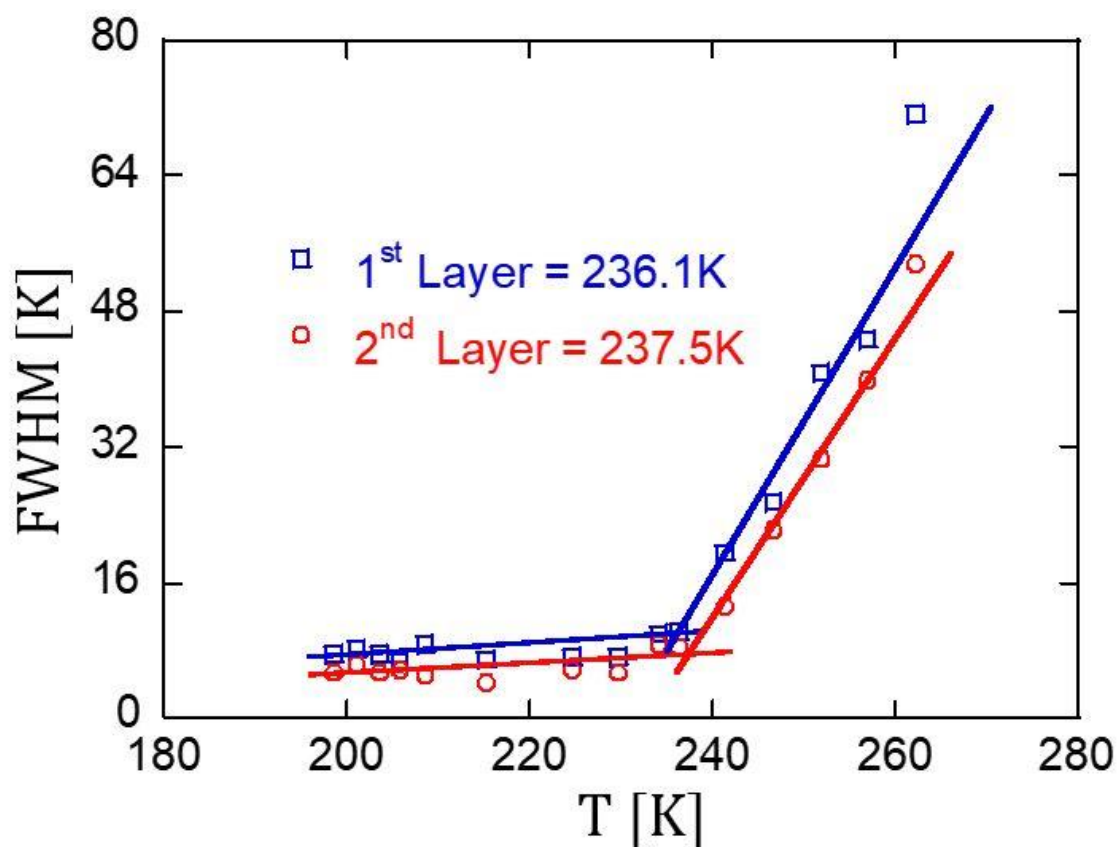


Figure 3.10 The full-width at the half maximum of the fitted Lorentzian function to the 2D compressibility of the cyclopentane layers on MgO(100) against the temperatures of the isotherms. Sharp changes in the slope suggest phase transition for the first and the second adsorbed layers at 236.1K and 237.5K respectively.

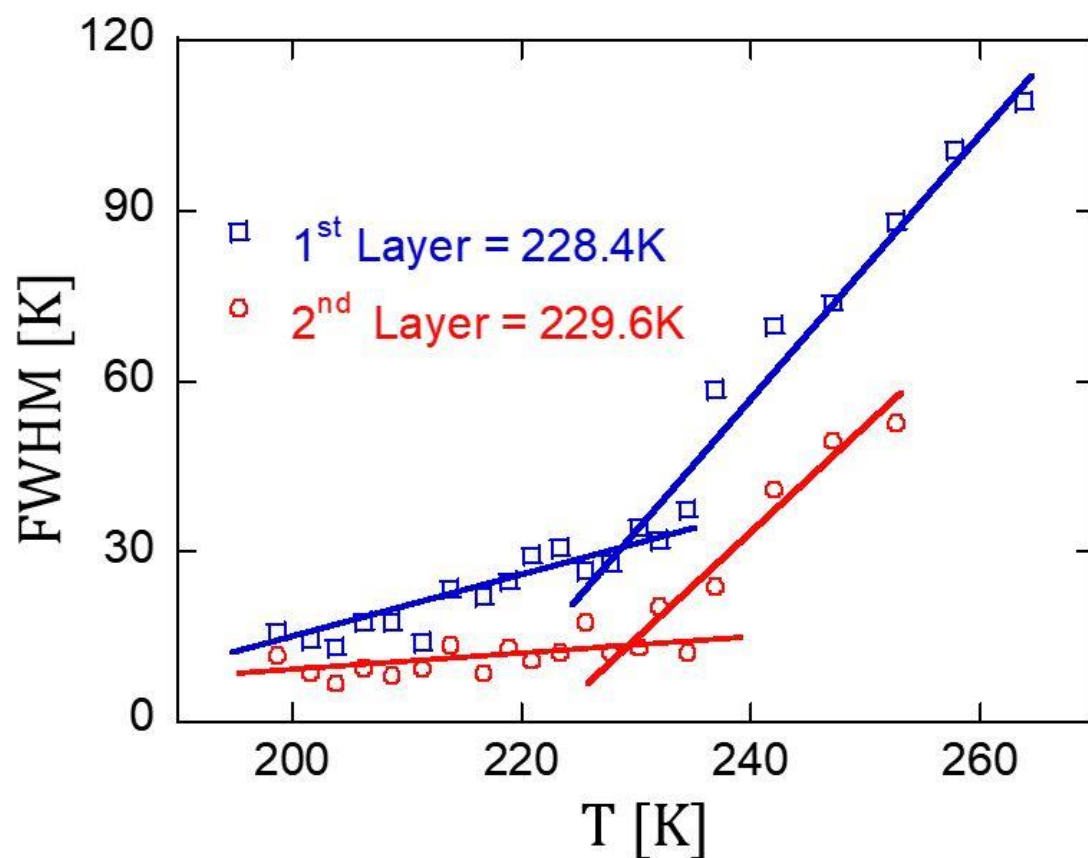


Figure 3.11 The full-width at the half maximum of the fitted Lorentzian function to the 2D compressibility of the cyclopentane layers on hBN against the temperatures of the isotherms. Sharp changes in slope suggest phase transition for the first and the second adsorbed layers at 228.4K and 229.6K respectively.

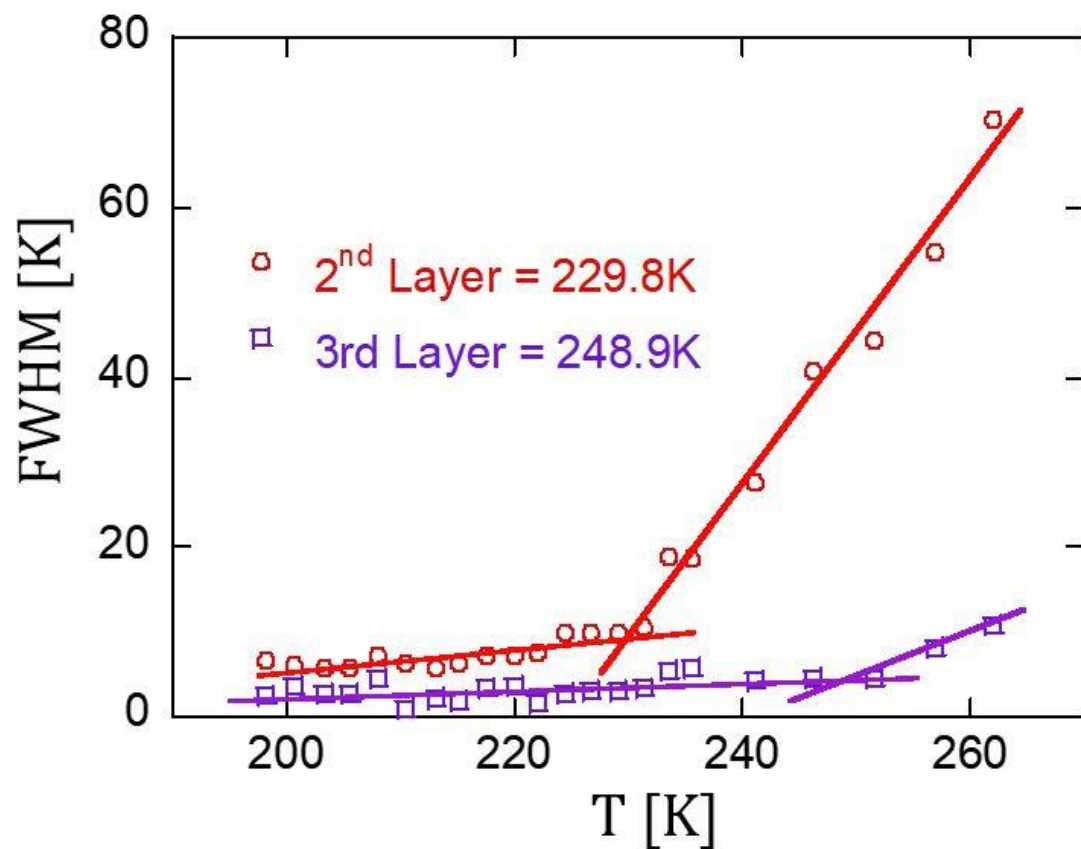


Figure 3.12 The full-width at the half maximum of the fitted Lorentzian function to the 2D compressibility of the second and third layers on graphite basal plane against the temperatures of the isotherms. Sharp changes in slope suggest phase transition for the second and the third adsorbed layers at 229.8K and 248.9K respectively.

point this out because making comparisons of geometrically minimized energy calculated using UFF versus those using COMPASS may not be as reliable for absolute comparison, the generated results are good enough to be used as a comparison of nonbonding energies at different adsorption sites on each surface individually. In our simulations, the center of mass (COM) of the molecule was initially located at one of the high symmetry sites (atom, hollow or bridge site) and then geometrically optimized. The initial orientation of the molecule was rotated about 3° and then re-optimized; this process was repeated until all the initial orientation of the molecule sampled the entire surface symmetry. In Figure 3.13, Figure 3.14, and Figure 3.15 the resulting minimum energy configurations of cyclopentane on the three surfaces are shown. The cyclopentane molecules are shown in ball-and-stick model while the surface is represented in space filling model for a clearer illustration of the molecular orientations.

One can observe that the most probable molecular orientation of an isolated molecule on all three surfaces occurs such that the hydrogen atoms nearest to the surfaces are pointed toward the surface hollow sites. The symmetry frustration between the molecule and surface is greatest on MgO which made it difficult to identify a preferred single orientation on MgO (100). In all three cases the minimum energy configuration of an isolated molecule is one where the molecular plane is lying parallel to the surface plane, hence, this configuration is referred to as “parallel” in the following portion of this discussion (Figure 3.13, Figure 3.14, and Figure 3.15).

Table 3.2 shows a summary of the minimum total energies and non-bond energies calculated on different adsorption sites. We remind the reader that as a result of using the two different forcefields, an absolute comparison of the single molecule binding energies on hBN to those on MgO and graphite is not reliable. Here the emphasis is placed on using the MD simulations as a guide to find the preferred surface orientation.

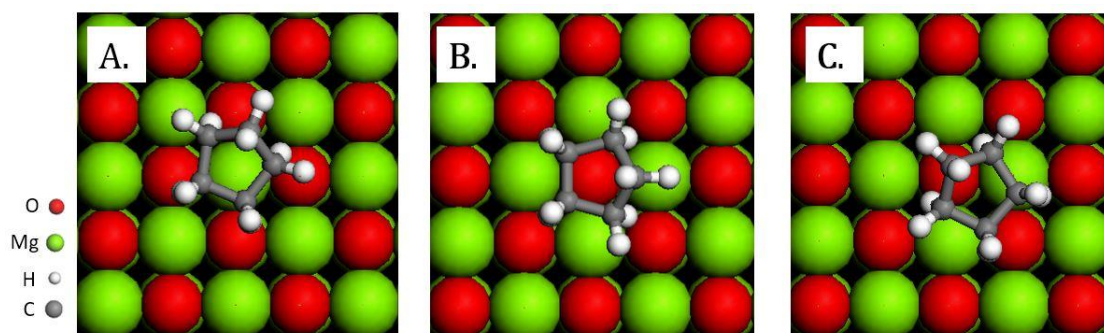


Figure 3.13 Minimum energy configurations of isolated cyclopentane molecule obtained on MgO (100) surface. The geometry optimization calculation was performed on the molecules with initial position at the high symmetry sites (Mg^{2+} , O^{2-} , hollow and bond).

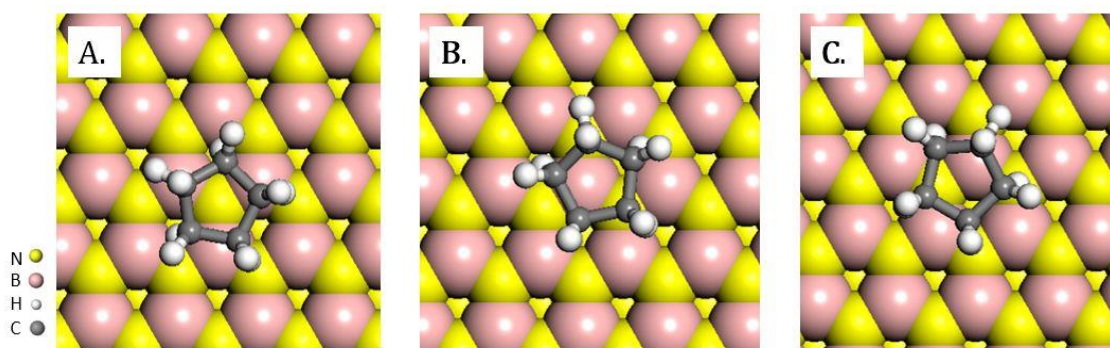


Figure 3.14 Minimum energy configurations of isolated cyclopentane molecule obtained on hBN surface. The geometry optimization calculation was performed on the molecules with initial position at the high symmetry sites (B, N, hollow and bond).

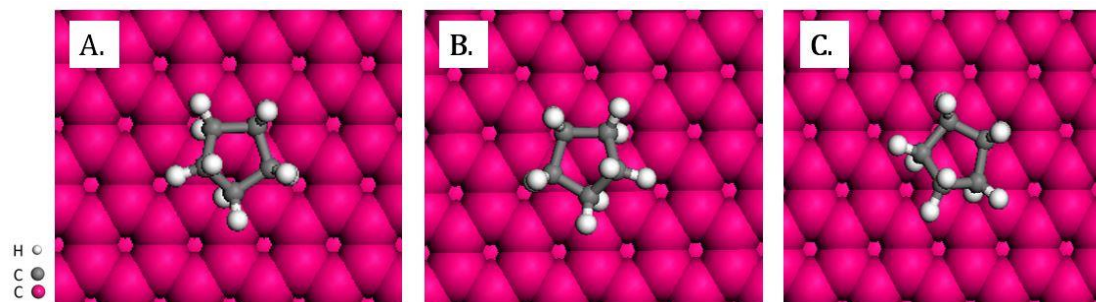


Figure 3.15 Minimum energy configurations of isolated cyclopentane molecule obtained on graphite surface. The geometry optimization calculation was performed on the molecules with initial position at the high symmetry sites (C, hollow and bond).

Table 3.2 Total and Non-bonding energy calculated from the geometry optimization at high symmetry adsorption sites of the surfaces

Surface	Forcefield	Adsorption Sites	Minimum total energy (kJmol^{-1})	Minimum non-bond energy (kJmol^{-1})
MgO	COMPASS	Mg^{2+}	-71.89	-43.45
		O^{2-}	-71.90	-43.49
hBN	Universal	B	-15.80	-57.17
		N	-15.65	-56.99
Graphite	COMPASS	C	-66.00	-37.68
		Bridge	-65.71	-37.31

Monolayer Structure from RDF

To explore the microscopic film behavior the MD simulations were extended to higher surface coverages and over a wide range of temperature including the temperature range of the adsorption isotherm experiments. The nominal mono-, bi- and tri-layer coverages are estimated using the APM calculated from the thermodynamic analysis. The details of the MD simulation strategy we employed has been described elsewhere [69]. After every MD run the trajectory files were closely examined and the monolayer structure of the cyclopentane was determined using a radial distribution function (RDF) analysis (Figure 3.16, Figure 3.17 and Figure 3.18). Snapshots of the molecular configurations recovered from a low temperature simulation show that the molecules are arranged in a hexagonal packing. This RDF was generated using all the frames of a trajectory files which consist of 500 frames at 1fs timestep over 50ps and is thus time averaged. The intermolecular components of the RDF can be used as a gauge of the intermolecular interaction (Figure 3.16B, Figure 3.17B and Figure 3.18B).

In order to simplify the initial RDF analysis, the molecules were replaced with ellipsoids at the COM. This was then used to calculate the RDF. This analysis of the RDF from the MD simulations finds that the first peak in the RDF for the cyclopentane monolayer at 5K on appears at 5.76Å, 5.91Å and 6.04Å and that the rotation of the hexagonal solid layer is rotated away from the surface lattice direction by 9.5°, 23° and 22°(Novaco-McTague rotation [90]) for hBN, graphite and MgO(100), respectively (see e.g. Figure 3.16D, Figure 3.17D and Figure 3.18D). Looking more closely at the COM RDF one also notices that the COM of the molecules appears to be in registry with the underlying surface in the MgO and graphite cases but not on the hBN surface. The distinction between the behavior is noticeable in the (time averaged) RDF for the molecules made up of the discrete atoms too. Here one observes that the overall shape of the intermolecular RDF peaks of cyclopentane monolayer on MgO and graphite (Figure 3.16D, Figure 3.17D and Figure 3.18D) are quite similar, however the peak shapes in RDF on hBN (Figure 3.17 B,D) is different (more structured) than those determined for the other two surfaces. The peaks in the hBN RDF plot at 2.6Å-3.7Å result presumably from the stronger intermolecular interaction between H and C atoms on neighboring molecules as reflected in the shorter intermolecular distance from the COM RDFs (Figure 3.17B) and the incommensurability of the structures with the underlying lattice which results in

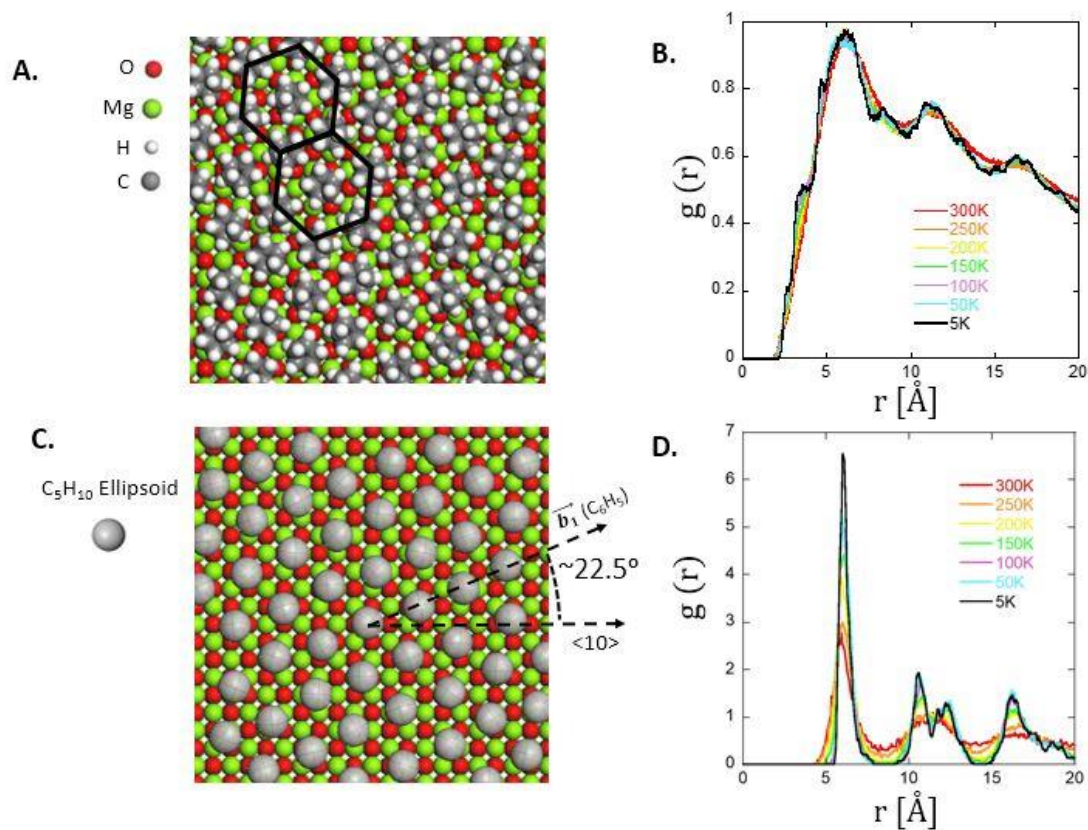


Figure 3.16 Monolayer structure on MgO from the analysis of the trajectory files. (A) Snapshot from the dynamics simulation at 5K, (B) intermolecular components of the RDF, (C) molecules were represented as ellipsoid for a better demonstration of the lattice. The lattice vector, $\vec{b}_1$ of cyclopentane lattice is at an angle of $\approx 22.5^\circ$ with MgO $\langle 10 \rangle$, (D) RDF of the centroids of the cyclopentane molecules.

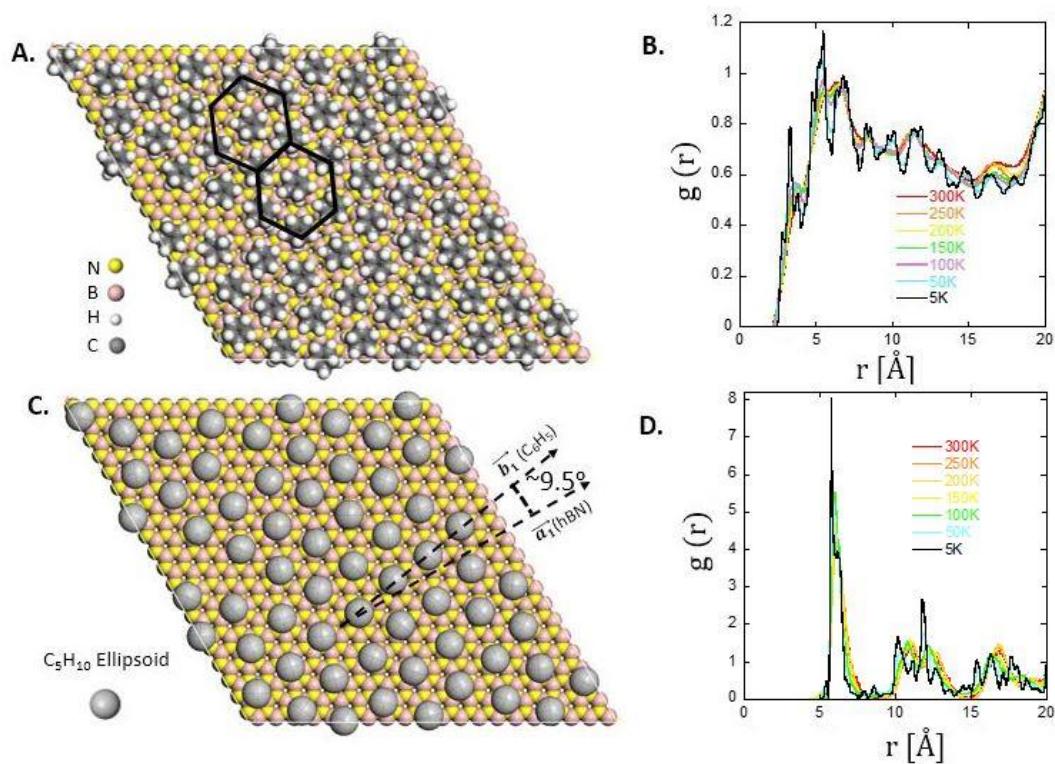


Figure 3.17 Monolayer structure on hBN from the analysis of the trajectory files. (A) Snapshot from the dynamics simulation at 5K, (B) intermolecular components of the RDF, (C) molecules were represented as ellipsoid for a better demonstration of the lattice. The lattice vector, $\vec{b}_1$ of cyclopentane lattice is at an angle of $\approx 9.5^\circ$ with hBN basal planes basis vector, $\vec{a}_1$, (D) RDF of the centroids of the cyclopentane.

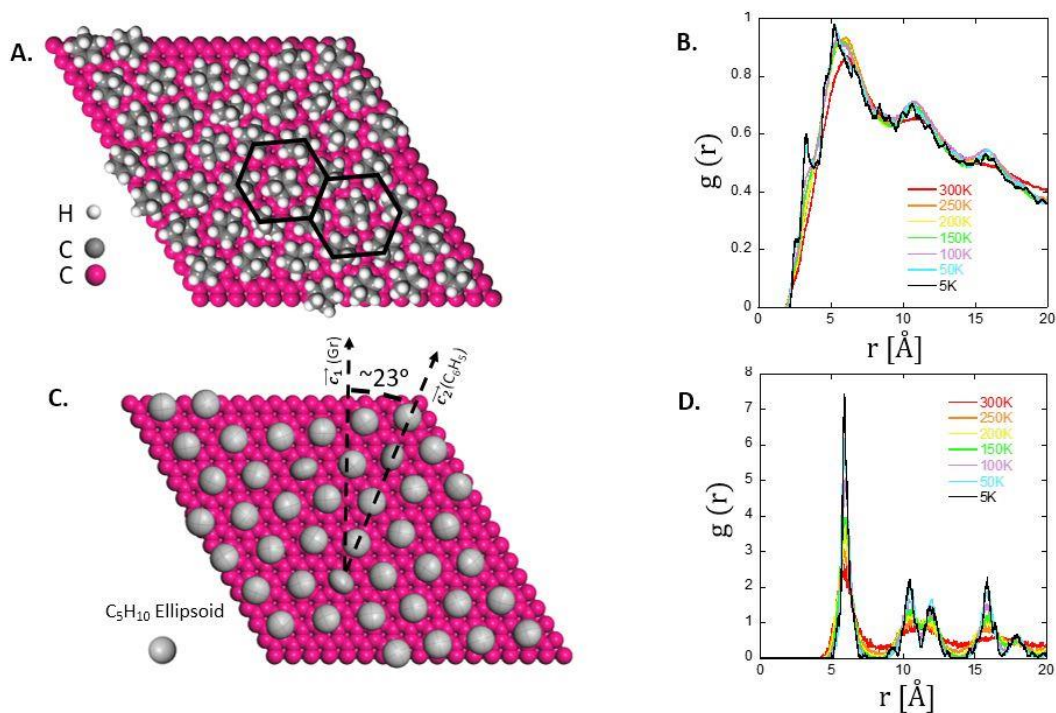


Figure 3.18 Monolayer structure on graphite basal plane from the analysis of the trajectory files. (A) Snapshot from the dynamics simulation at 5K, (B) intermolecular components of the RDF, (C) molecules were represented as ellipsoid for a better demonstration of the lattice. The lattice vector, $\vec{b}_1$ of cyclopentane lattice is at an angle of $\approx 23^\circ$ with graphite basis vector $\vec{c}_1$, (D) RDF of the centroids of the cyclopentane molecules.

several hexagonal lattice domains on hBN (Figure 3.17C) rather than a single domain on MgO and graphite. The more structured peak shapes of the (time averaged) RDF of monolayer cyclopentane on hBN may also be indicative of a slower rotational diffusion of the individual molecules in the monolayer cyclopentane on hBN than on MgO or graphite. Incommensurate lattices are frequently referred to as floating solids especially when the corrugation surface potential is weak because the solid adsorbed layer “slides” across the surface plane because the thermal motion is large enough to overcome the lateral energy barrier.

Molecular Behavior in Z-Direction from the Surface

Monolayer Regime

Beyond the behavior of the monolayer film, it is useful to explore the microscopic film wetting properties at higher coverages (e.g. two and three) using MD simulations. Concentration profile analysis of the molecule has been used as a tool to investigate molecular orientation and interlayer diffusion on the surfaces. In previous studies of linear alkanes on MgO (100) the effect of molecule-substrate interaction on the spatial distribution of the molecules has been investigated [67-69, 91]. We note that in our non-bond energy calculation, the minimum energy configuration of an isolated molecule the cyclopentane was found to be in the “bent” or envelope configuration on all surfaces (Figure 3.13, Figure 3.14 and Figure 3.15). The concentration profile analysis discussed in this section provides a greater insight into the molecular distribution normal to the surface plane (i.e. the z direction). As noted earlier the molecular orientation of an adsorbed cyclopentane will be referred to as “parallel” when the plane of the four carbon atoms on the four “envelope” corners is horizontal and “perpendicular” when this plane is vertical with the substrate surface. Prior to monolayer completion almost all the molecules oriented parallel to the substrate surface. However, on MgO upon increasing the number of molecules needed to complete the layer, in addition to occupying the second layer some of the added molecules are “pulled” into the layer closest to the surface causing some of the first layer “parallel” molecules to reorient into a “perpendicular” orientation. The fraction of “perpendicular” molecules grows to about ~20%. This reorientation behavior is not observed at or above the monolayer completion region on hBN and graphite. The added molecules beyond layer completion remain in the second layer on these two surfaces. The concentration profile analysis of a single molecule in the parallel and perpendicular orientation on MgO(100) is shown in Figure 3.19A which can be used as a measure to

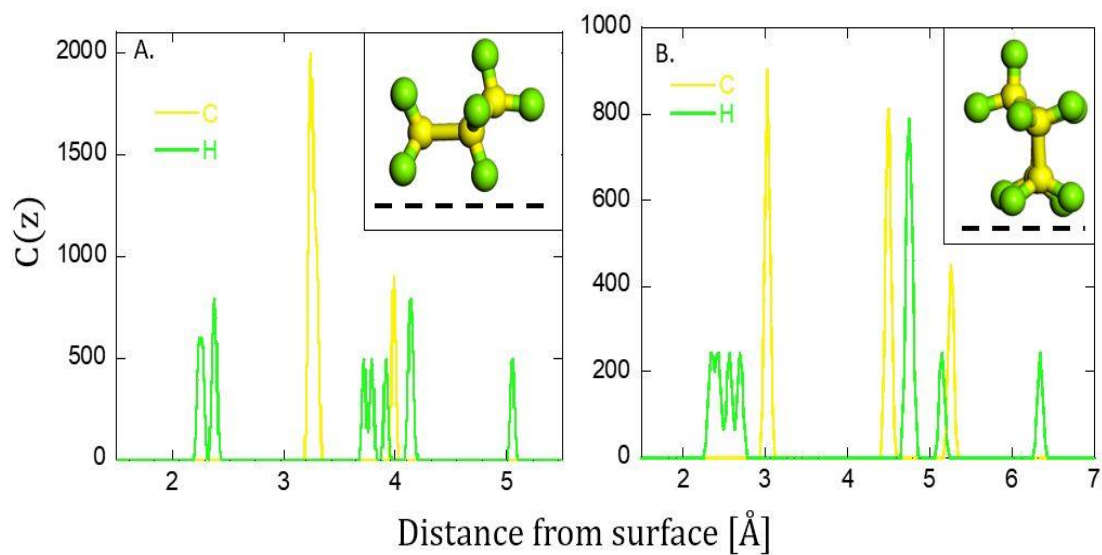


Figure 3.19 Concentration profiles of the carbon and hydrogen atoms of cyclopentane as a function of the distance from the surface of MgO(100). The $C(z)$ of the molecules adsorbed (A) parallel to the surface and (B) perpendicular to the surface are particularly distinguished by the single hydrogen peak at $\sim 6.3\text{\AA}$.

determine the orientation of the molecules in the adsorbed layers. The most distinguishable $C(z)$ peak of a perpendicularly oriented molecule is the peak from H atom at $\sim 6.3\text{\AA}$ (Figure 3.19B). This peak is not present when the molecule is parallel to the surface (Figure 3.19A). The other two peaks that distinguish perpendicular orientation are the carbon peak at $\sim 4.5\text{\AA}$ and the hydrogen peak at $\sim 4.7\text{\AA}$. Figure 3.20 displays the snapshots from the molecular trajectory files on MgO at 0.8ML, 1.0 ML and 1.1ML have been shown. Corresponding concentration profiles with these coverages demonstrate that with increasing coverage the peaks resulted from a perpendicular orientation become discernible particularly at low temperatures (Figure 3.20F). The molecules in the vertical orientation are highlighted in yellow (see Figure 3.20C). The $C(z)$ of the isolated molecules were also compared with that of the monolayer on hBN (Figure 3.21 and Figure 3.22) and graphite (Figure 3.23 and Figure 3.24) where only a negligible amount of the molecules is oriented perpendicular to the surface.

Multilayer Regime

The MD simulations were performed at greater film thicknesses to explore the wetting and microscopic interlayer mobility of the cyclopentane film as a function of temperature. The predominant peaks in $C(z)$ for the layer nearest to the surfaces remained centered at essentially the same distance from the surface even as a function of temperature (albeit the peaks broadened as the thermal motion in the perpendicular direction increased) and the peaks from the second and third layers significantly broadened. The snapshots from the trajectories of the bilayer coverages on the surfaces at different temperatures ($0.2\times$ and $1.52\times$ of the bulk triple point) show the roughness of the second layer and the interlayer mobility between the first and second layer at higher temperatures (subfigures B and C of Figure 3.25, Figure 3.26 and Figure 3.27). The $C(z)$ plots show the increase in interfacial spreading with increasing temperatures. The third layer simulation suggest that there may be a possibility of a third layer formation at even lower temperatures. Note that the difference in the order in molecular orientation in z direction in the third layer on graphite with those on MgO and hBN. This behavior agrees with our experimental finding where the cyclopentane molecules formed three layers on graphite and two layers on the other surfaces at our experimental temperature range. The structural order in the first and second layer increases with the increase in coverage (Figure 3.28, Figure 3.29 and Figure 3.30). The interlayer mobility becomes higher in the upper layers which was observed in molecular trajectories and the concentration profile analysis which shows the broadening of the interlayer region.

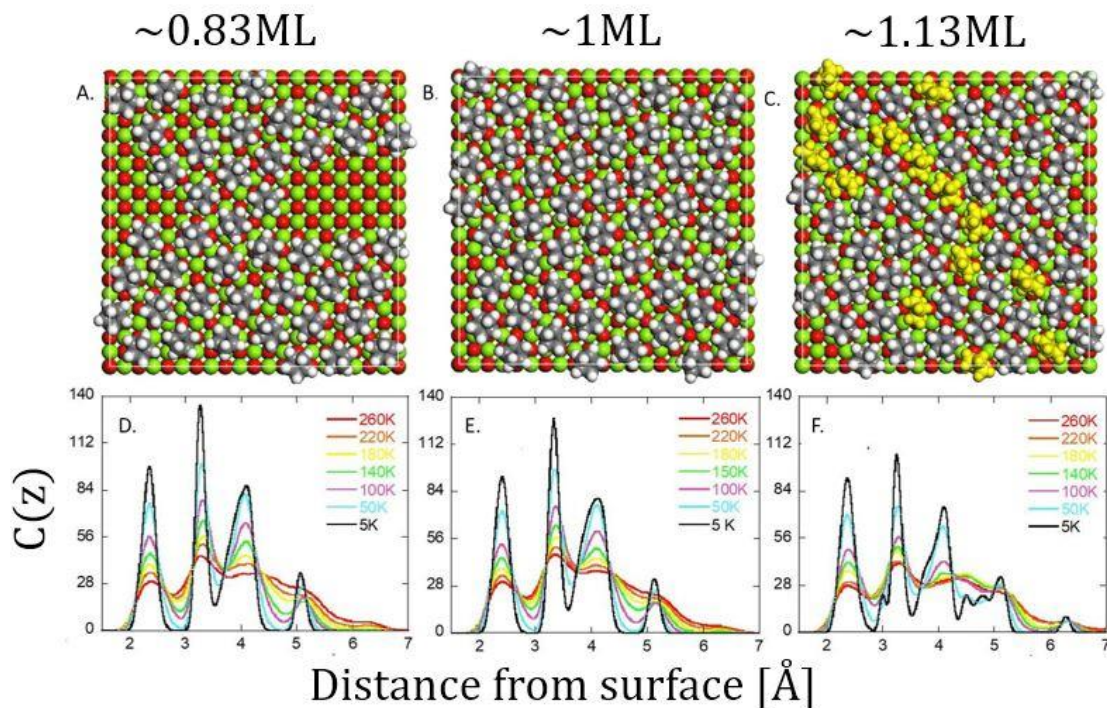


Figure 3.20 Adjustment in molecular orientation with increasing surface coverage. Snapshot at 5K at nominal coverages of (A) 83% of a monolayer, (B) one monolayer, and (C) 13% higher than a monolayer. The corresponding concentration profiles of the layers as a function of temperature are shown in the plots D, E, and F respectively. Obvious change in peak shape occurs in the region beyond $\sim 4.5\text{\AA}$ due to an accommodation of molecules in perpendicular orientation

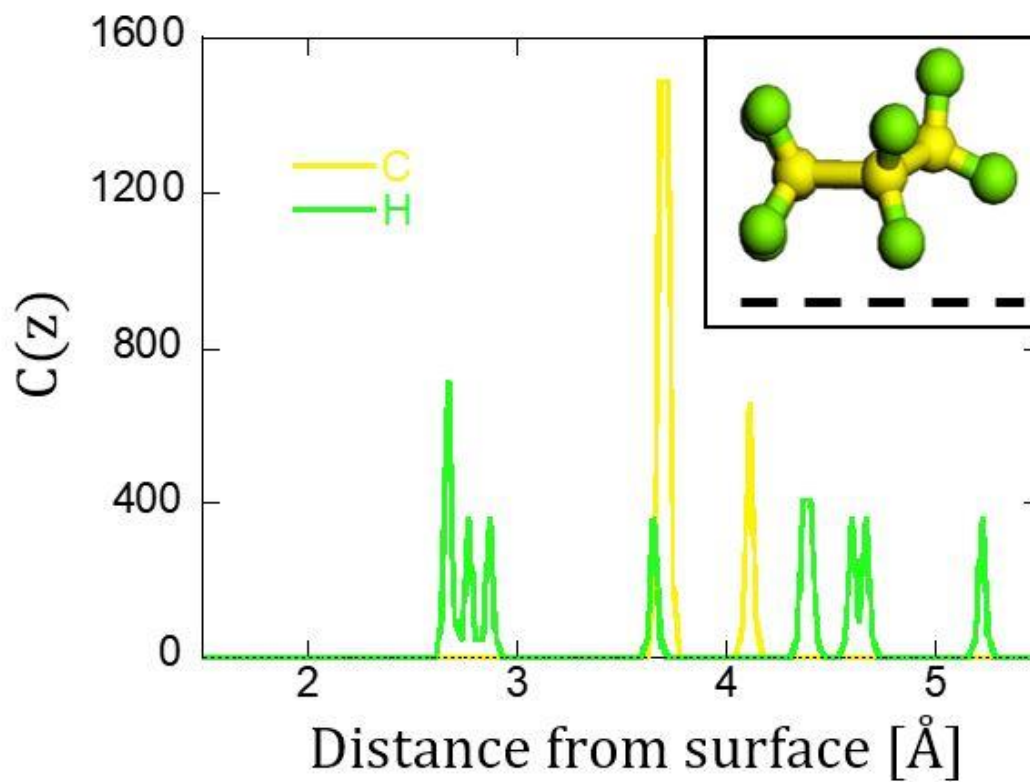


Figure 3.21 Concentration profiles of the carbon and hydrogen atoms of a cyclopentane molecule adsorbed in parallel as a function of the distance from hBN surface.

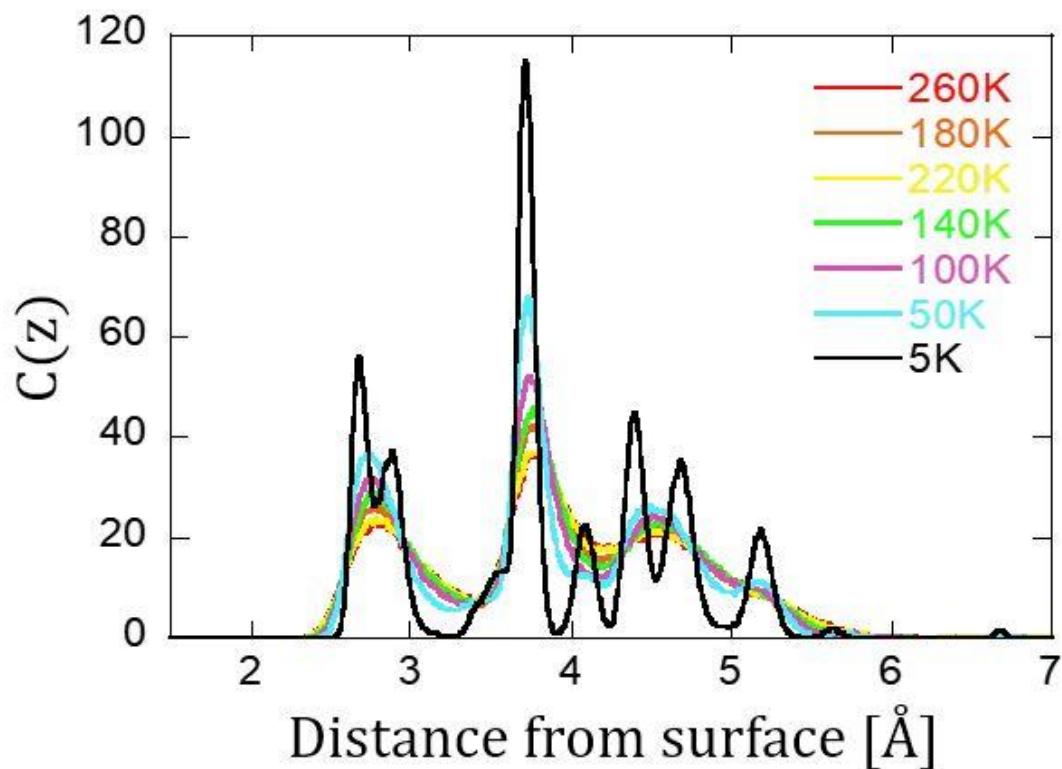


Figure 3.22 A representative selection of the concentration profiles, $C(z)$ at nominal monolayer coverage in the z -direction for cyclopentane molecules on hBN. The appearances of the peaks at similar distances from the surface as in the $C(z)$ of an isolated molecule adsorbed in parallel verifies the preference in parallel orientation of the molecules to the surface at higher coverage.

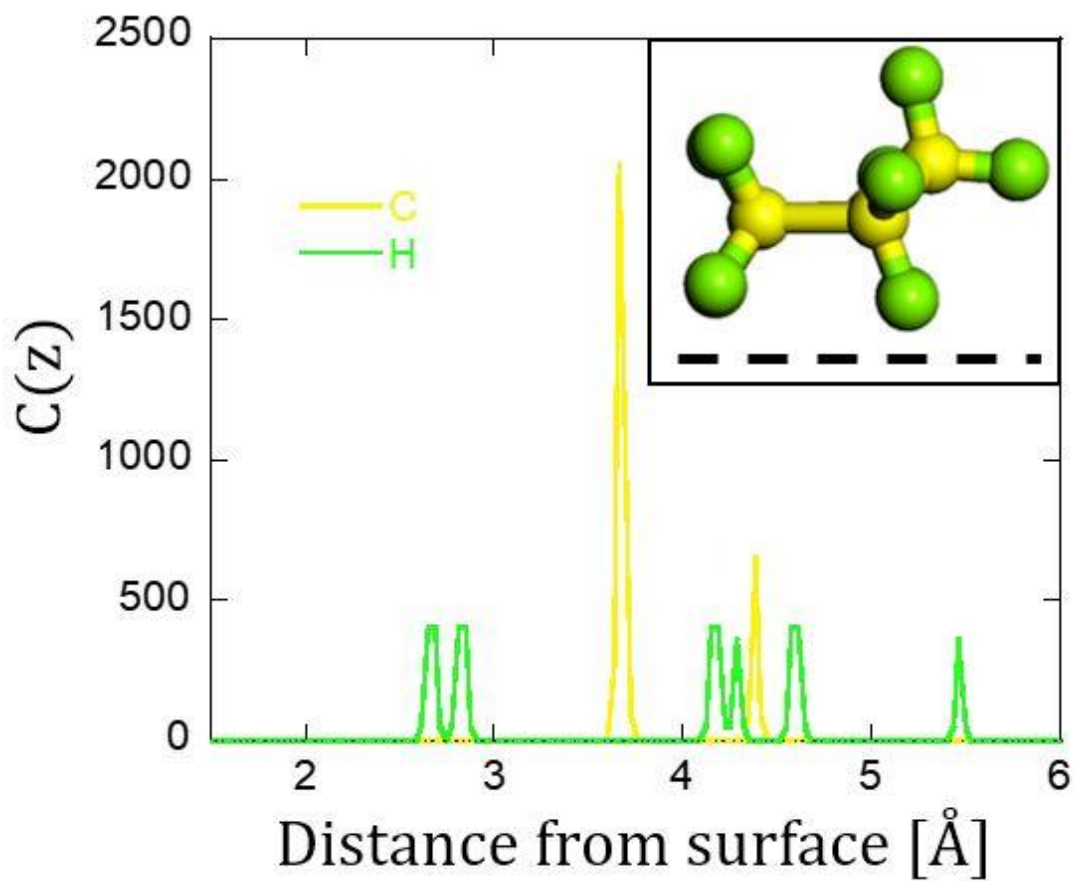


Figure 3.23 Concentration profiles of the carbon and hydrogen atoms of cyclopentane molecule adsorbed in parallel as a function of the distance from graphite basal plane.

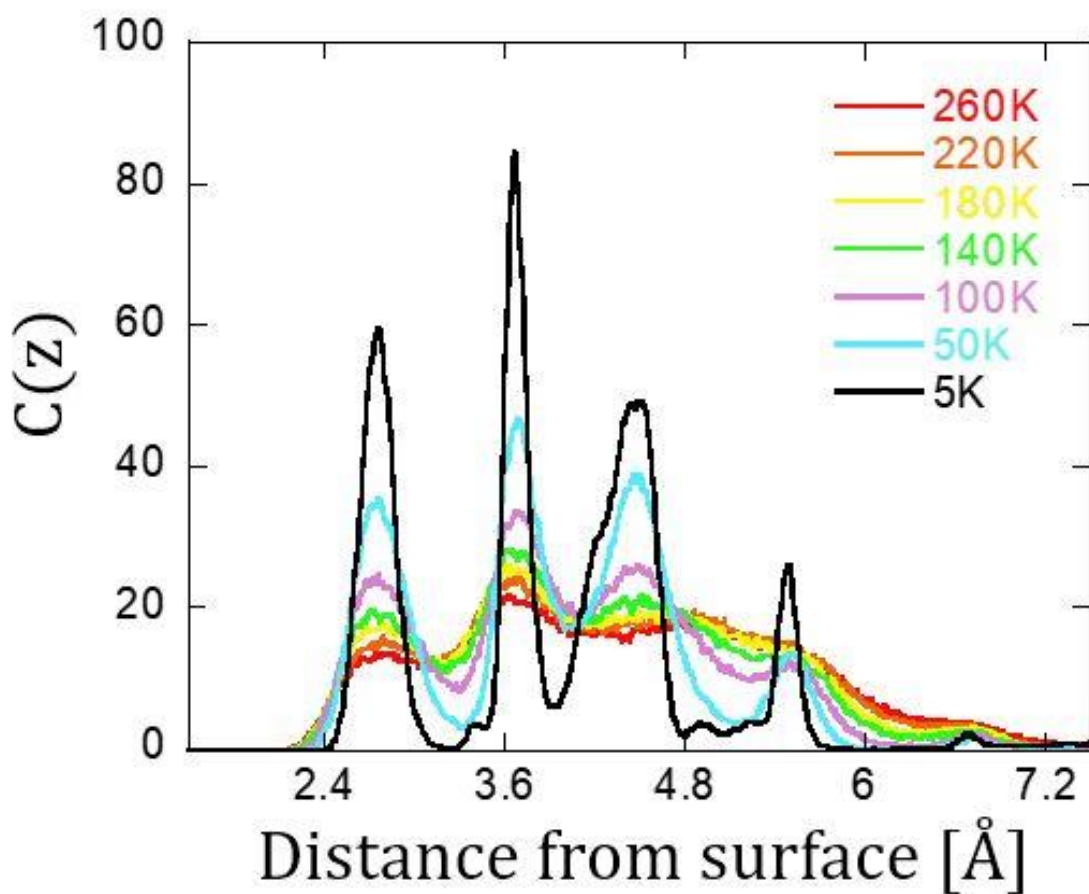


Figure 3.24 A representative selection of the concentration profiles, $C(z)$ at nominal monolayer coverage in the z -direction for cyclopentane molecules on graphite basal plane. The appearances of the peaks at similar distances from the surface as in the $C(z)$ of an isolated molecule adsorbed in parallel verifies the preference in parallel orientation to the surface at higher coverage.

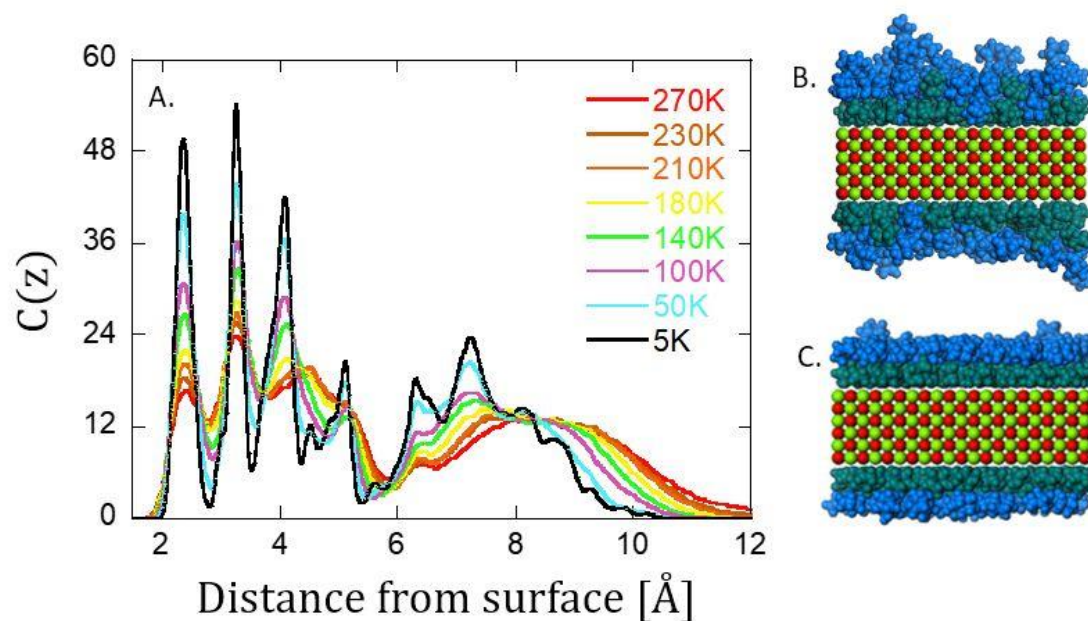


Figure 3.25 A representative selection of the concentration profiles, $C(z)$ at nominal bilayer coverage in the z -direction for cyclopentane molecules on MgO. The molecules in the first and second layers are highlighted in teal and royal blue colors to show the interlayer molecular mobility with the change in temperature. The subfigures in B and C are the snapshot from molecular trajectories at 270K and 40K respectively.

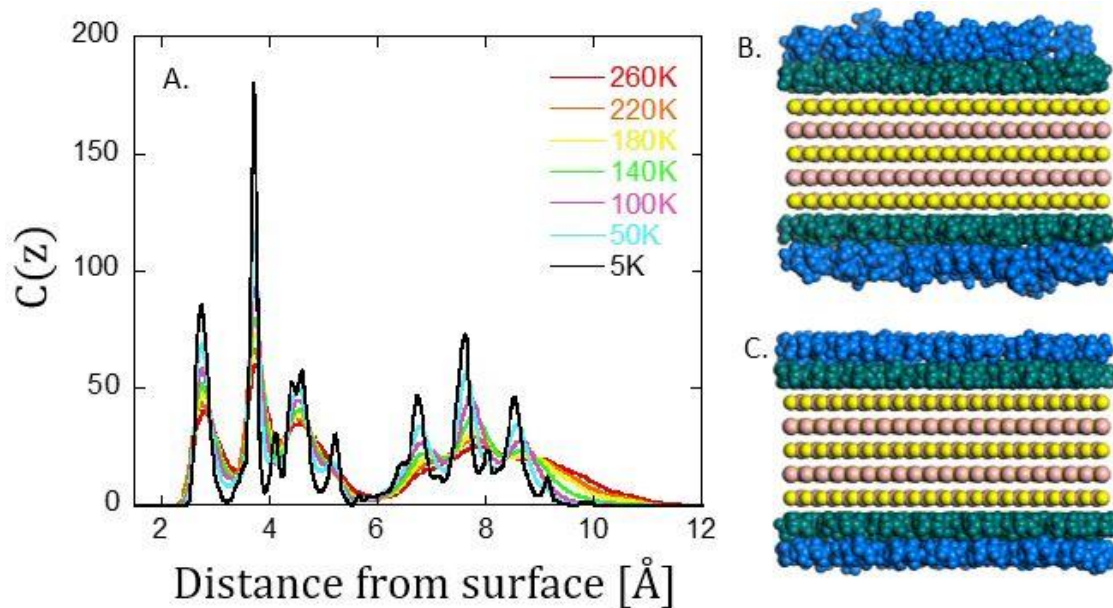


Figure 3.26 A representative selection of the concentration profiles, $C(z)$ at nominal bilayer coverage in the z -direction for cyclopentane molecules on hBN. The molecules in the first and second layers are highlighted in teal and royal blue colors to show the interlayer molecular mobility with the change in temperature. The subfigures in B and C are the snapshot from molecular trajectories at 270K and 40K respectively.

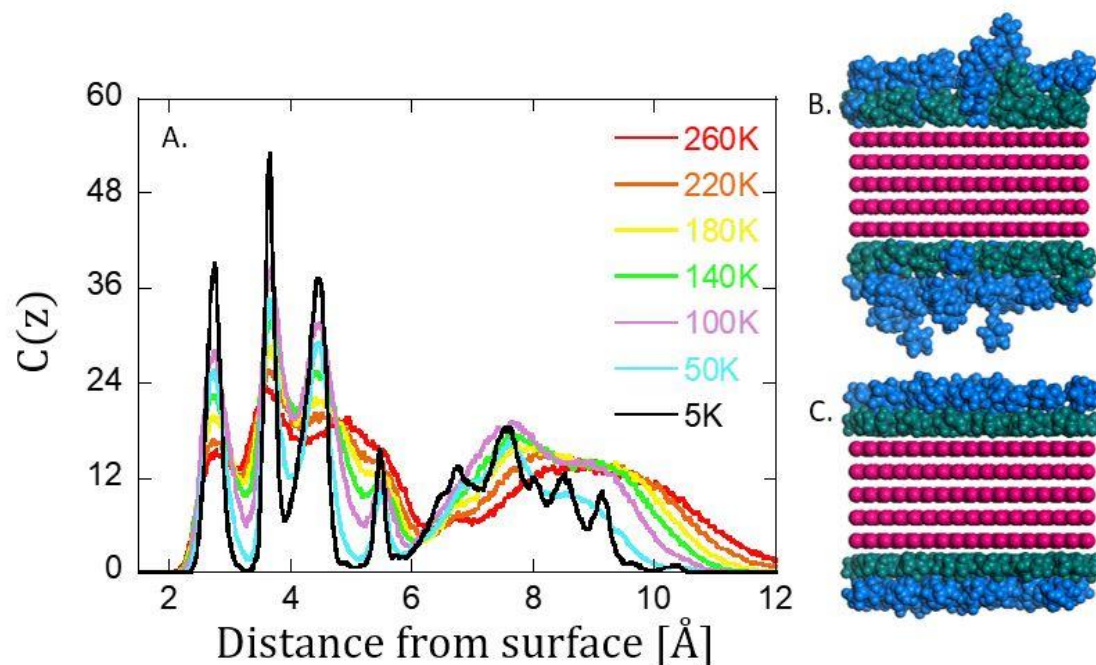


Figure 3.27 A representative selection of the concentration profiles, $C(z)$ at nominal bilayer coverage in the z -direction for cyclopentane molecules on graphite surface. The molecules in the first and second layers are highlighted in teal and royal blue colors to show the interlayer molecular mobility with the change in temperature. The subfigures in B and C are the snapshot from molecular trajectories at 270K and 40K

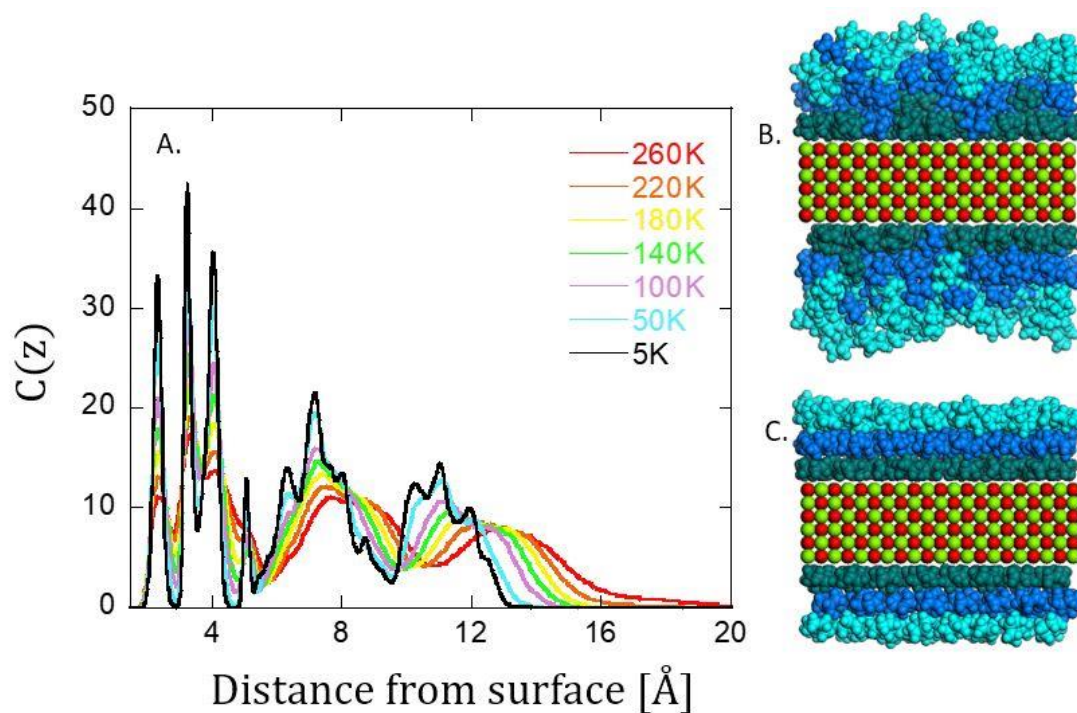


Figure 3.28 A representative selection of the concentration profiles, $C(z)$ at nominal tri-layer coverage in the z -direction for cyclopentane molecules on MgO(100). The molecules in the first, second and third layers are highlighted in teal, royal blue and cyan colors to show the interlayer molecular mobility with the change in temperature. The subfigures in B and C are the snapshots from molecular trajectories at 270K and 40K respectively.

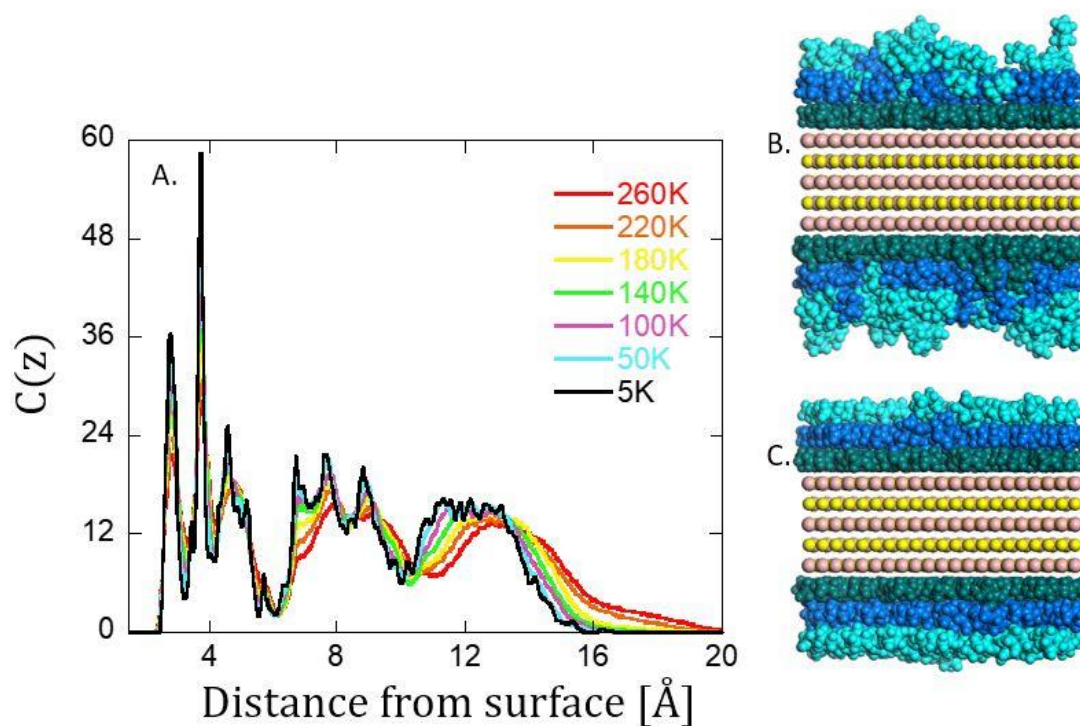


Figure 3.29 A representative selection of the concentration profiles, $C(z)$ at nominal tri-layer coverage in the z -direction for cyclopentane molecules on hBN. The molecules in the first, second and third layers are highlighted in teal, royal blue and cyan colors to show the interlayer molecular mobility with the change in temperature. The subfigures in B and C are the snapshot from molecular trajectories at 270K and 40K respectively.

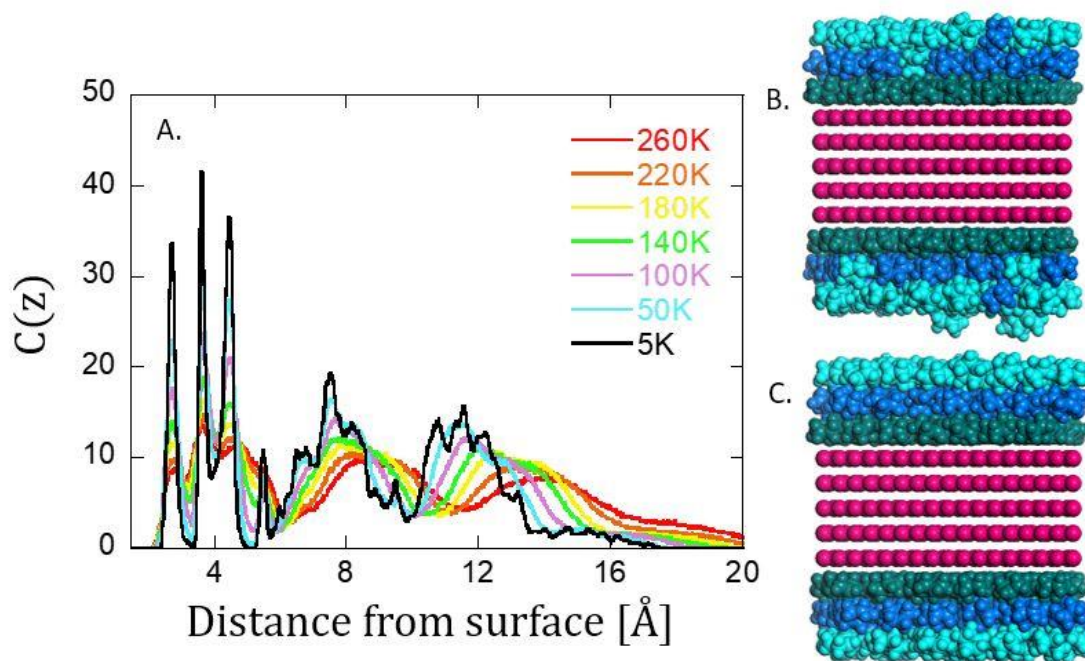


Figure 3.30 A representative selection of the concentration profiles, $C(z)$ at nominal tri-layer coverage in the z -direction for cyclopentane molecules on graphite. The molecules in the first, second and third layers are highlighted in teal, royal blue and cyan colors to show the interlayer molecular mobility with the change in temperature. The subfigures in B and C are the snapshot from molecular trajectories at 270K and 40K respectively.

3.5 Conclusion

The layering properties of cyclopentane on MgO (100), hexagonal boron nitride and graphite have been investigated and compared using volumetric adsorption isotherm data within the temperature range of 195K to 264K. Two layering transitions were identified on MgO(100) and hBN basal plane while three layers were detected on graphite basal plane. The thermodynamic properties such as heat of adsorption, differential enthalpy and entropy of all the layers as well as the bulk cyclopentane vapor were determined. As the film thickness increases these thermodynamic values exhibit behavior that converges toward the published bulk thermodynamic values. The location of potential phase transitions within the temperature regime of this study have been identified as a liquid to hypercritical fluid phase using changes in two-dimensional compressibility. Classical MD simulation and geometry optimization of the adsorbate-adsorbent systems were used to characterize the microscopic structure of the adsorbed layers. The energy minimization of the isolated molecules suggests that the molecules are adsorbed in "bent" (envelop) configuration and "parallel" orientation to the surface planes. Analysis of the intermolecular radial distribution function (RDF) indicates that a hexagonal solid form at the lower temperatures and suggests that there is a distinct difference in the nature of the crystal structure of the adsorbed layer on hBN (i.e. formation of an incommensurate hexagonal lattice). The lattice constant of cyclopentane monolayer at 5K on hBN (5.76Å) was determined to be less than that on MgO (100) (6.04Å) and on graphite basal planes (5.91Å). The analysis of molecular distribution perpendicular to the surface reveals that the layer nearest to the surface remained more ordered (and planar) even at the higher temperatures due to the effective pressure from the molecular dynamics in the upper layers which appear to be more liquid-like, a finding consistent with the thermodynamic isotherm measurements. The findings of this study form a suitable basis for future studies of the structure of the adsorbed layer using x-ray and neutron diffraction and dynamics using inelastic neutron scattering.

CHAPTER 4 ADSORPTION OF CYCLOHEXANE ON MGO, HBN, AND GRAPHITE BASAL PLANE

4.1 Introduction

This chapter discusses the adsorption behavior of cyclohexane on MgO, hexagonal boron nitride and graphite basal plane. Cyclohexane differs from previously discussed cyclopentane in its symmetry and rotational vibrational behaviors. The ring strain in cyclohexane is the lowest among all cycloalkanes. Furthermore, cyclohexane molecule has a three-fold symmetry in its minimum energy chair conformation. On the other hand, graphite and hBN basal planes have similar three-fold symmetry while MgO exhibits a four-fold symmetry. For this reason, the adsorption of cyclohexane on these surfaces offers a scope to study the effect of symmetry and composition of the surfaces on the wetting properties. The adsorption behavior was investigated by a combination of thermodynamic study and molecular dynamics (MD) simulations. The volumetric adsorption isotherm experiments demonstrated the thermodynamic properties of the adsorbed layer on these surfaces. These results were compared to probe the effect of surface and molecular symmetry on the macroscopic physicochemical properties of the adsorbed layers.

Furthermore, molecular dynamic (MD) simulations were presented to investigate the microscopic aspects of cyclohexane adsorption on these adsorbate surfaces. The preliminary analysis of these MD studies indicates that cyclohexane on graphite forms a commensurate $\sqrt{7} \times \sqrt{7}$ solid with molecular lattice rotated by $\sim 19.1^\circ$ from the surface lattice. While on MgO, in the liquid phase the simulations suggest that the molecules roll across the surface like a wobbly tire. Evidence have been recorded suggesting that as the temperature is increased the interface between layers broadens with subsequent decrease in orientational order. However, with the increase in temperature the near surface layer of cyclohexane on the surfaces remain ordered even when the layers above it exhibits liquid-like behavior at higher temperature.

4.2 Experimental Methods

A series of high-resolution volumetric adsorption isotherms were recorded within the range of 204K-292K. The temperature range was limited by the resolution limit of the pressure transducer at low temperatures and above by the room temperature . The details of experimental methods have been discussed in Chapter 2. The modeling investigation have been performed using the molecular dynamics option within the Forcite environment of Accelrys' Materials Studio software suite. The simulations were performed over a broad

range of temperature of 5K to 264K. The MD simulations were used to evaluate the distribution of the molecules both in plane of the adsorbed layers and perpendicular to the surfaces as a function of temperature and nominal surface coverage. More details of simulation and analysis methods were explained in Chapter 2.

4.3 Results and Discussion

4.3.1 Thermodynamics of Adsorption

Adsorption isotherms of cyclohexane show at least two layers on each of the substrates suggesting a delicate interplay in the molecule-molecule (MM) and molecule-surface (MS) interactions that underpins this behavior. However, there are at least three distinct steps formed on graphite which are identified more clearly using numerical derivatives. On MgO the isotherms show an incomplete wetting behavior at higher temperatures with two layering transitions. The incomplete wetting is indicated by the asymptotic approach toward saturated vapor pressure (SVP) as the pressure increases. However, at low temperature this behavior changes to non-wetting behavior where the pressure increases to SVP abruptly after the completion of monolayer. A subset of isotherms measured on MgO illustrate this behavior in Figure 4.1. The second layer on MgO vanishes below 232K and above 281K.

The other distinct feature is the shape of the monolayer adsorption region. At low coverage the isotherms exhibit linear adsorption region. This behavior becomes more pronounced with decrease in temperature. Beyond this linear portion the shape of isotherms become vertical indicating the formation of the first layer. The second layer transitions are also very subtle for cyclohexane on MgO systems. The layering transitions are more clearly observed in the numerical derivative plots. Three representative adsorption isotherms of cyclohexane on MgO, graphite and hBN are shown in Figure 4.2, Figure 4.3 and Figure 4.4 respectively.

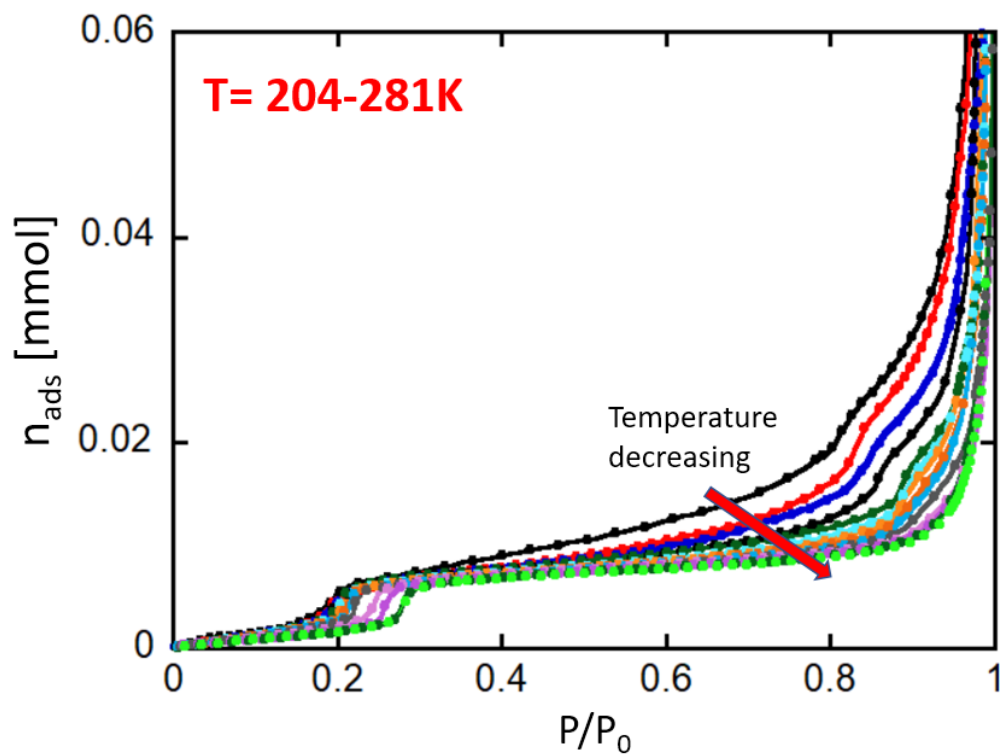


Figure 4.1 Select adsorption isotherms of cyclohexane on MgO within 204-288K.

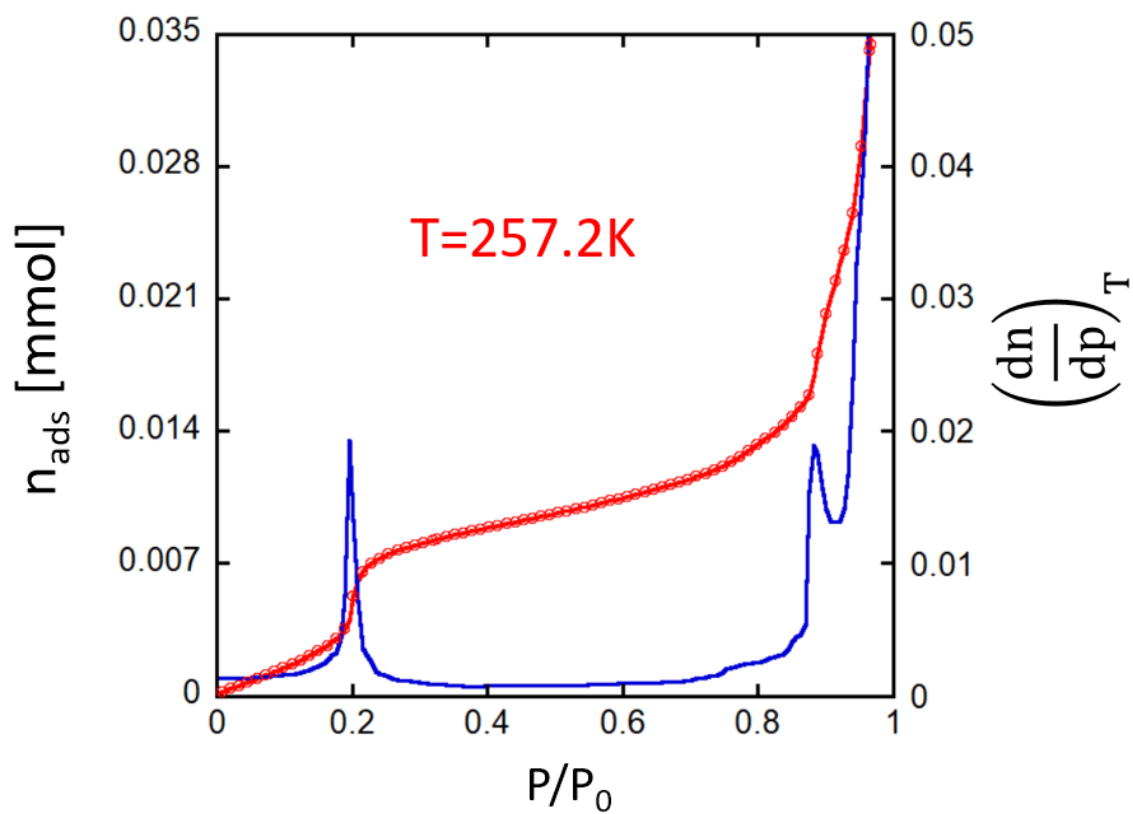


Figure 4.2 Adsorption isotherm of cyclohexane on MgO at 257.2K (red) with corresponding numerical derivative (blue).

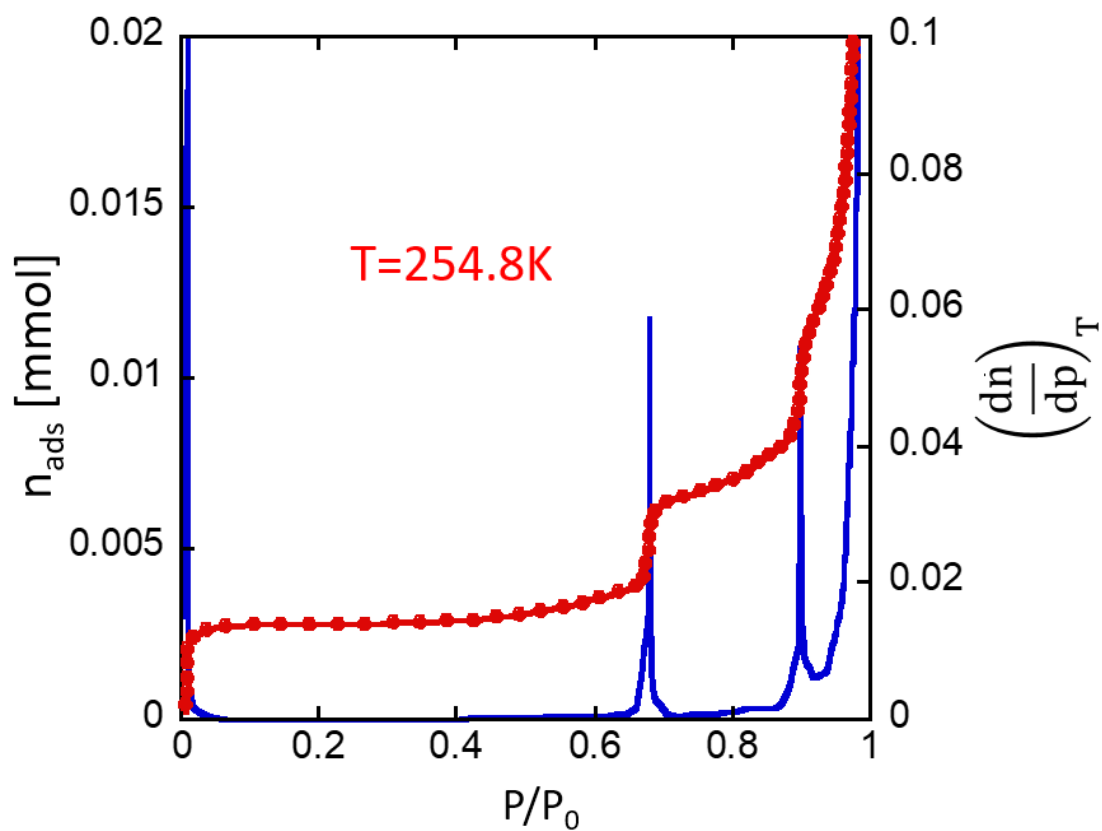


Figure 4.3 Adsorption isotherm of cyclohexane on graphite at 254.8K (red) with corresponding numerical derivative (blue).

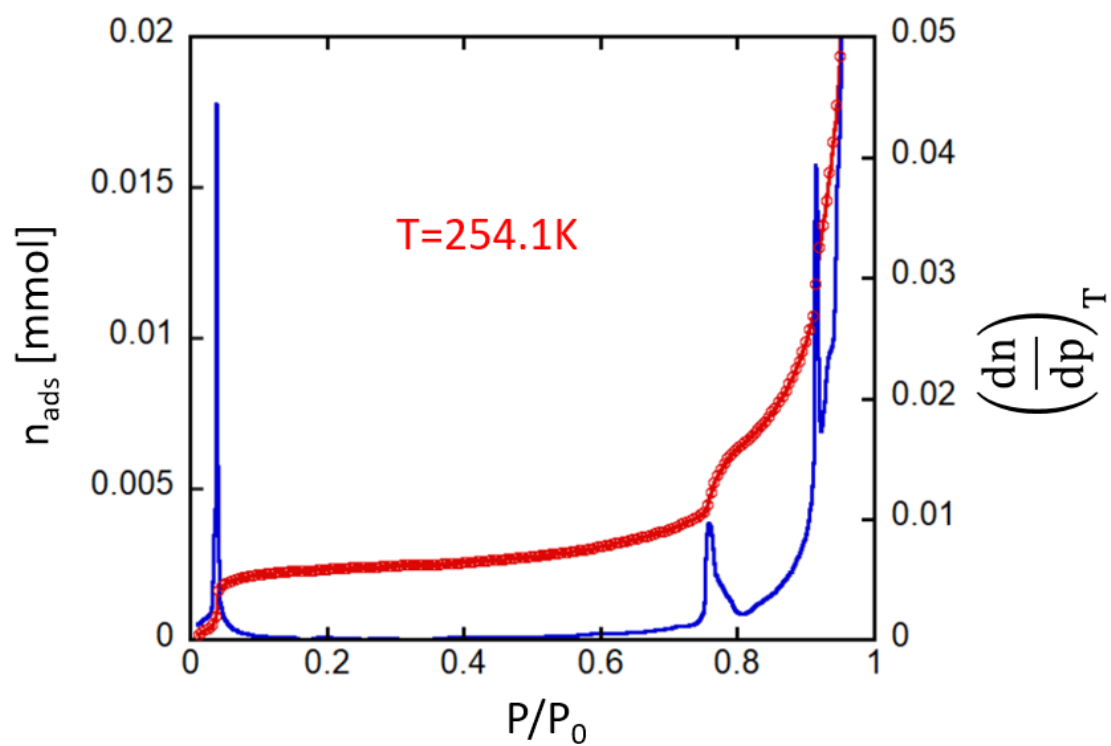


Figure 4.4 Adsorption isotherm of cyclohexane on hBN at 254.1K (red) with corresponding numerical derivative (blue).

The derivatives have been used to identify the location of layering transitions on the isotherms and used with modified Clausius-Clapeyron equation to obtain the P-T diagram of the adsorbed and bulk cyclohexane. The layering transitions on each surface are shown in the Clausius-Clapeyron in Figure 4.5, Figure 4.6, and Figure 4.7. The lines on the Clausius-Clapeyron plots from bottom to top represent the first (red), second (blue), third (green) steps and the topmost line in black represent the change in saturated vapor pressure with temperature. The evolution of the second layer on MgO can be clearly observed as the second layering line merges into the bulk line at 232K (Figure 4.5).

Three distinct layering transitions on graphite were found over the whole temperature range under study. The shape of cyclohexane on graphite isotherms differs drastically than that on MgO. On graphite the formation of monolayer is instantaneous, and the layering steps are nearly vertical for both the first and second layers (Figure 4.3). The isotherms show an asymptotic approach to saturated vapor pressure indicating a complete and incomplete wetting. The third layer is present throughout the entire temperature range 292-208K indicated by the green line in Figure 4.6.

On hBN three layering transitions were found within the range of 290-250. The second layer appears below 273K and the third layer below 263K. There is a linear adsorption region before the formation of monolayer step indicating a weaker interaction between cyclohexane and hBN basal plane than that between cyclohexane and graphite surface (Figure 4.4). Using the location of layer formation into modified Clausius-Clapeyron relation the thermodynamic quantities such as heat of adsorption, differential enthalpy and entropy have been calculated. These values are tabulated in Table 4.1.

The two-dimensional isothermal compressibility, K_{2D} was used to identify the locations of layer formations and potential phase transitions. The full width at the half maximum (FWHM) of the compressibility peaks of first layer on MgO do not changes significantly until 264K with increasing temperature (Figure 4.8). The FWHM values increases sharply above this temperature indicating a possible phase transition in the first layer. For the second layer this temperature has been identified by 264K. On graphite the shape of first layer on the isotherms is too steep to calculate 2D compressibility (Figure 4.9). The potential phase transition temperatures obtained for the second and the third layers on graphite are 269K and 272K respectively. For cyclohexane on hBN, these temperatures are 266.8K and 268.4K for the first and second layer respectively. The shape of third layer on hBN are too unpronounced to clearly predict a phase transition (Figure 4.10).

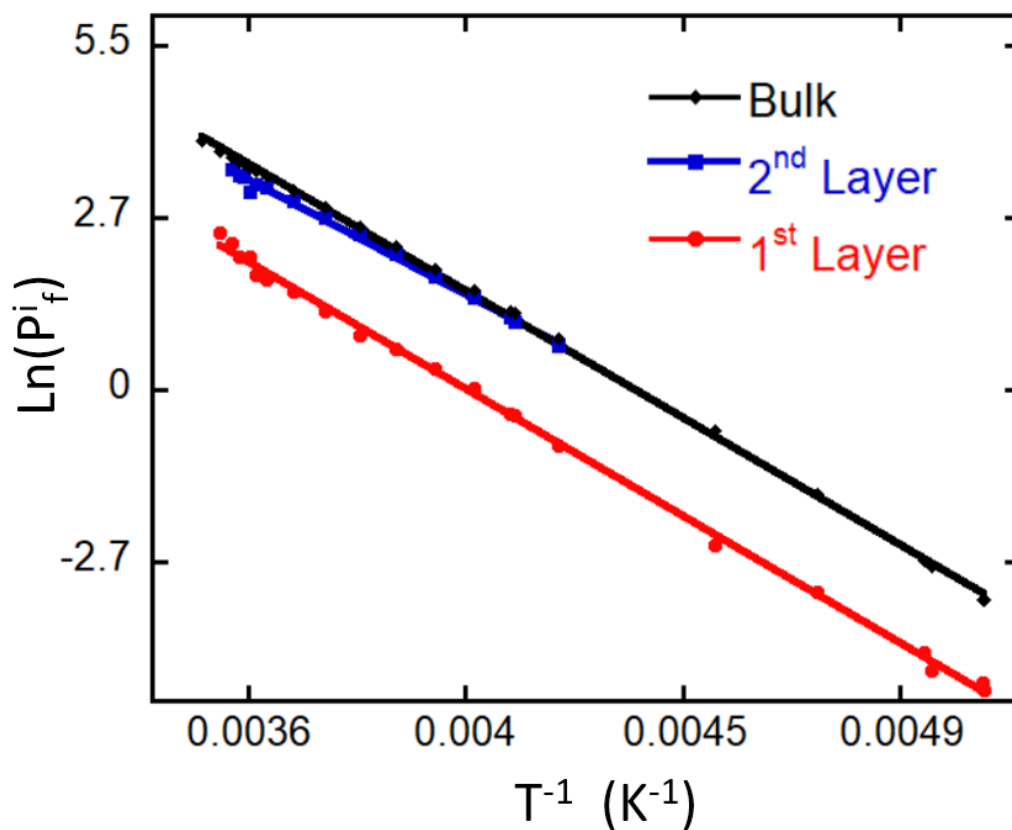


Figure 4.5 Clausius-Clapeyron plot for cyclohexane adsorbed on the surface of MgO. The individual layers are represented by red circles (1st layer) and blue squares (2nd layer), and saturated vapor pressure is represented by black diamonds.

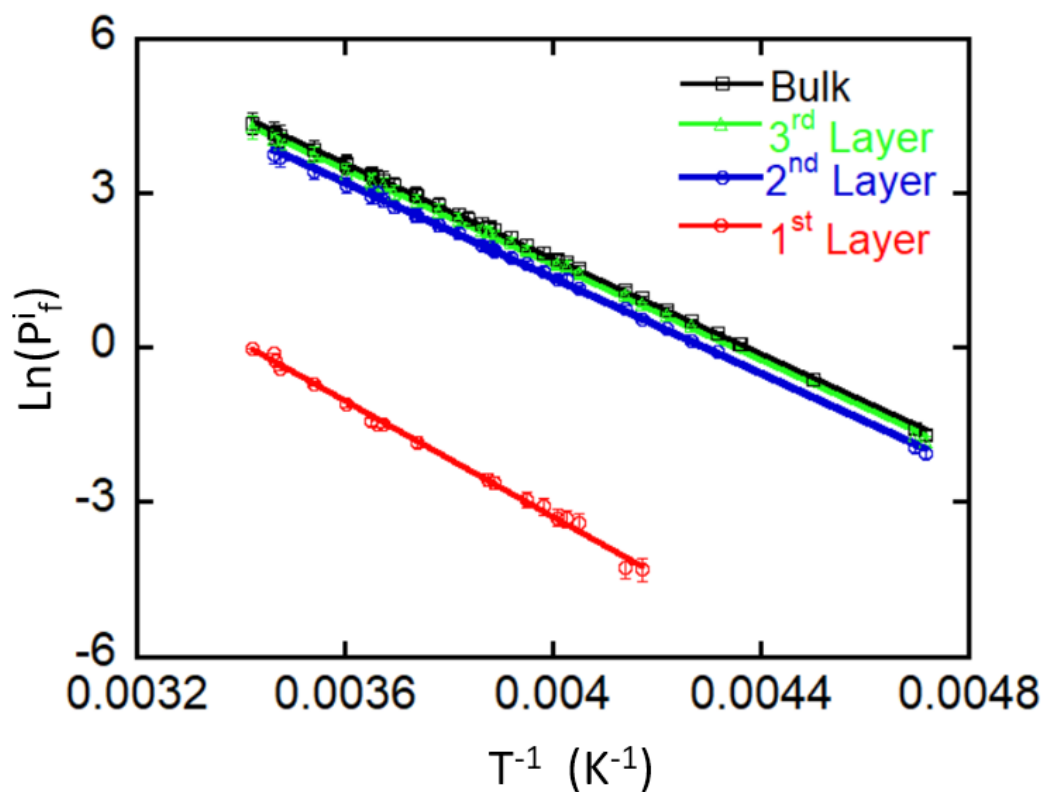


Figure 4.6 Clausius-Clapeyron plot for cyclohexane adsorbed on the surface of graphite. The individual layers are represented by red circles (1st layer) and blue squares (2nd layer), green triangles (3rd layer) and black squares (SVP).

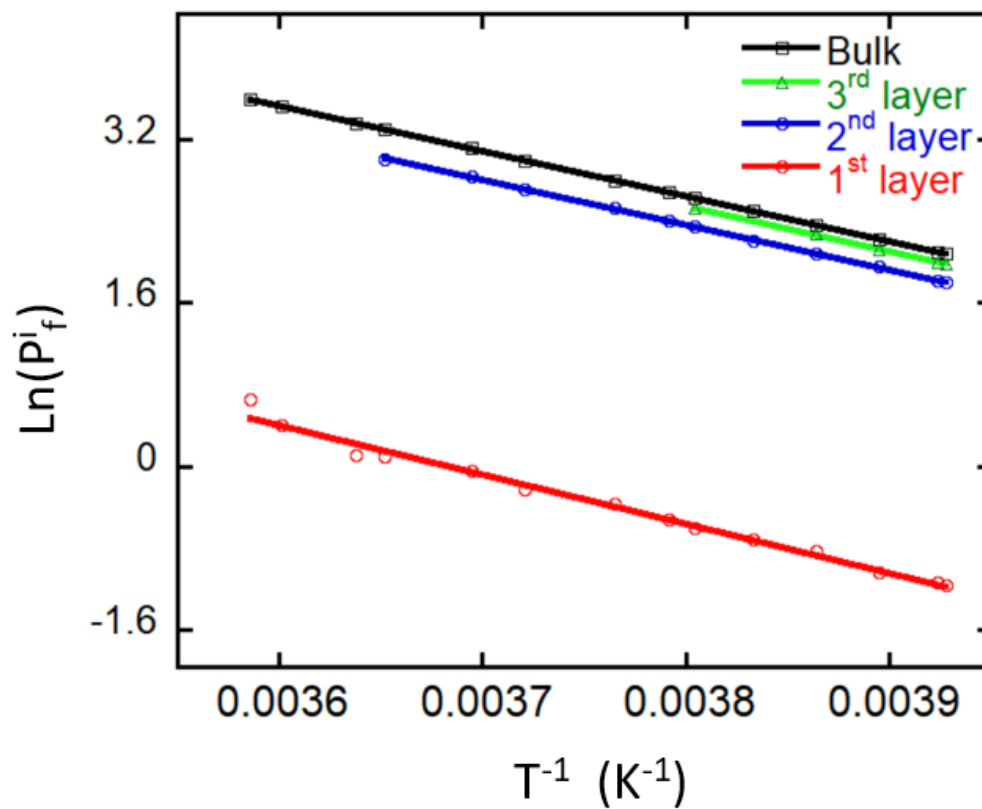


Figure 4.7 Clausius-Clapeyron plot for cyclohexane adsorbed on the surface of hBN. The individual layers are represented by red circles (1st layer) and blue circles (2nd layer), green triangles (3rd layer) and black squares (SVP).

Table 4.1 Thermodynamic values calculated from the cyclohexane adsorption isotherms using equation and Clausius-Clapeyron plot (Figure 4.5, Figure 4.6 and Figure 4.7).

Surface	n	$A^{(n)}$ (K)	$B^{(n)}$	$Q_{\text{ads}}^{(n)}$ (kJmol ⁻¹)	$\Delta H^{(n)}$ (kJmol ⁻¹)	$\Delta S^{(n)}$ (JK ⁻¹ mol ⁻¹)
MgO	1	4559.1	18.33	37.90	-0.31	12.97
	2	4524.1	18.98	37.61	-0.02	7.96
	∞	4521.5	19.89	37.59	0	0
hBN	1	4906.7	18.08	40.79	-3.47	13.81
	2	4479.0	19.42	37.24	0.08	2.64
	3	4529.5	19.79	37.65	-0.34	-0.50
	∞	4489.2	19.74	37.32	0	0
Graphite	1	5441.0	18.56	45.24	-6.86	13.65
	2	4633.4	19.89	38.52	-0.15	2.51
	3	4632.8	20.16	38.52	-0.14	0.29
	∞	4615.4	20.19	38.37	0	0

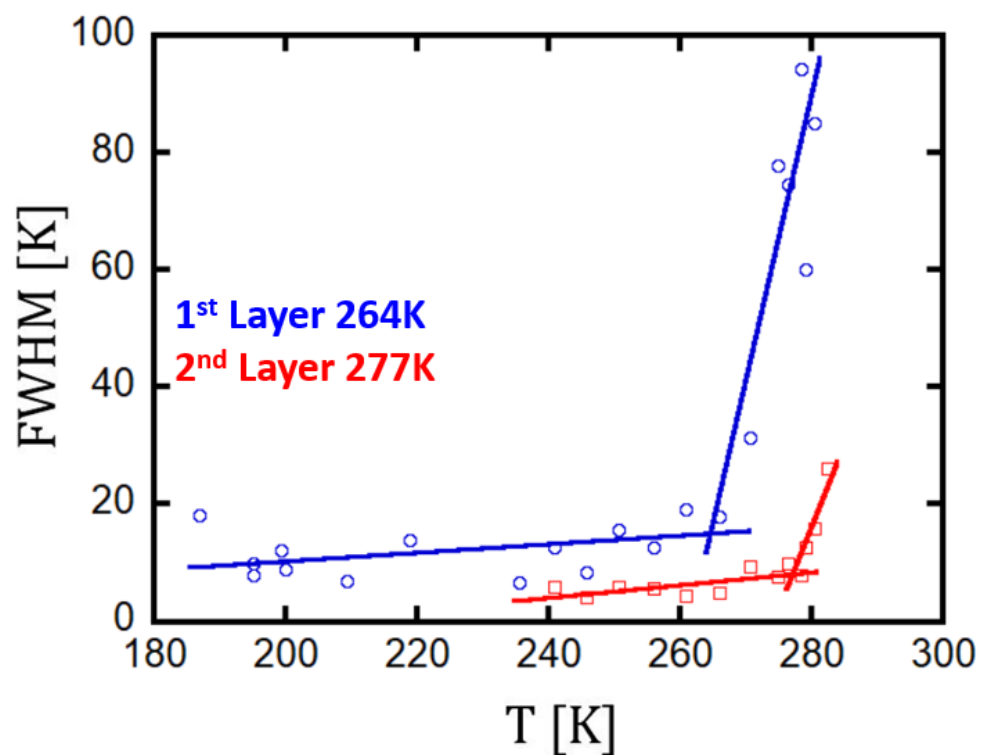


Figure 4.8 The full-width at the half maximum of the fitted Lorentzian function to the 2D compressibility of the cyclohexane layers on MgO (100) against the temperatures of the isotherms. Sharp changes in the slope suggest phase transition for the first and the second at 264K and 277K respectively.

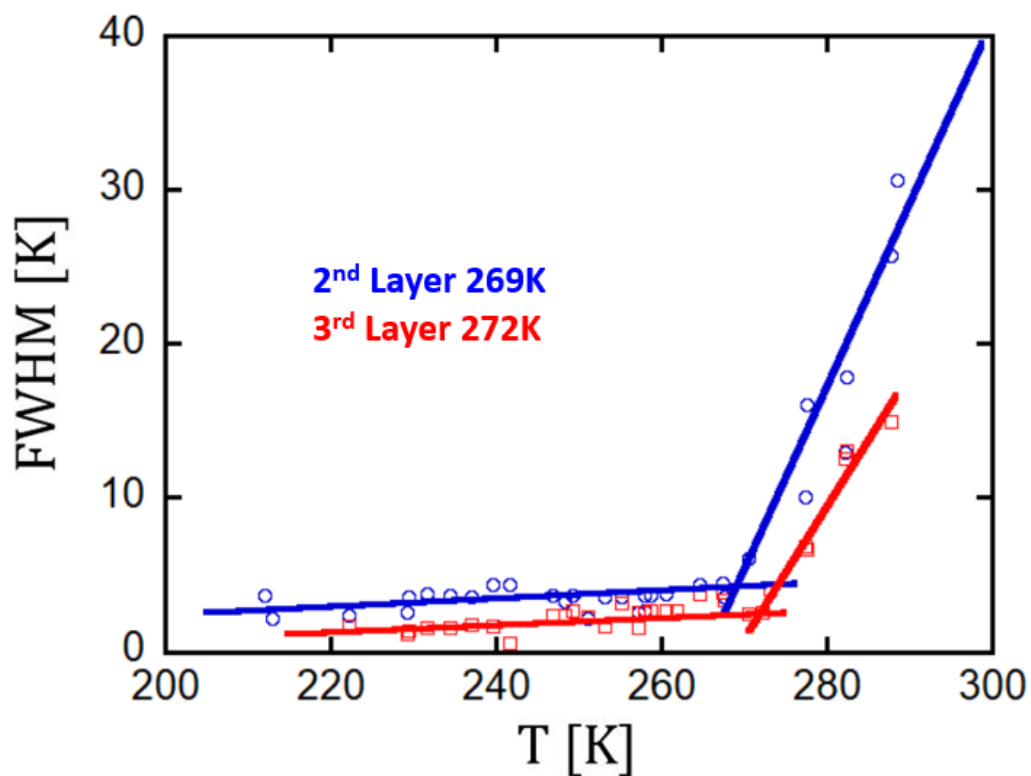


Figure 4.9 The full-width at the half maximum of the fitted Lorentzian function to the 2D compressibility of the cyclohexane layers on graphite against the temperatures of the isotherms. Sharp changes in the slope suggest phase transition for the second and the third adsorbed layers at 269K and 272K respectively.

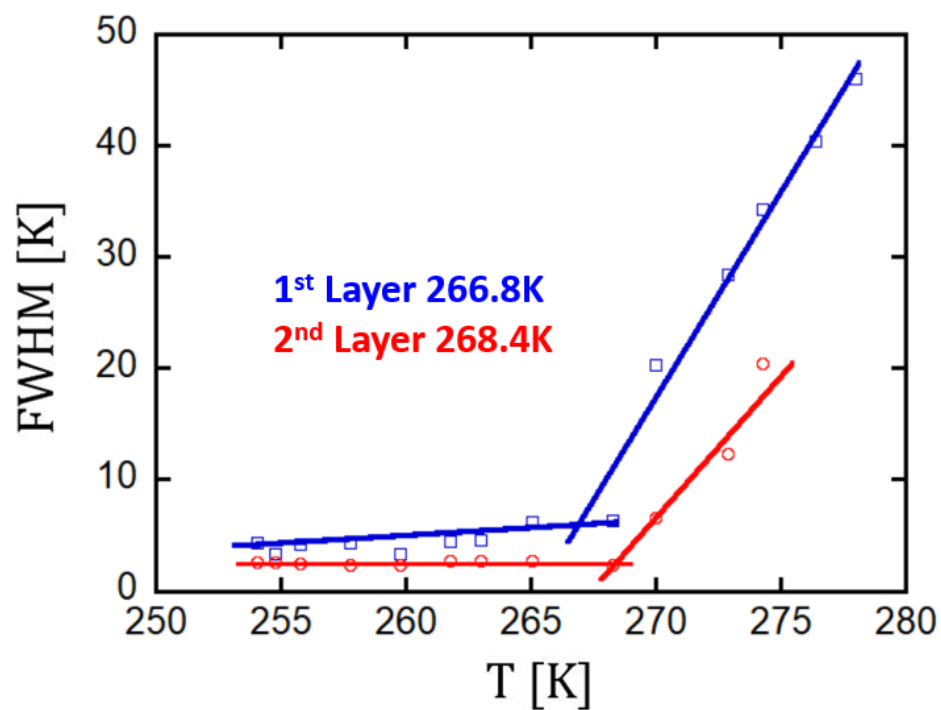


Figure 4.10 The full-width at the half maximum of the fitted Lorentzian function to the 2D compressibility of the cyclohexane layers on hBN against the temperatures of the isotherms. Sharp changes in the slope suggest phase transition for the second and the third adsorbed layers at 266.8K and 268.4K respectively.

4.3.2 MD Simulations

Minimum Energy Structure on Surfaces

To obtain the minimum energy molecular structure of cyclohexane on the substrate surface the isolated molecules were geometrically optimized on the high symmetry adsorption sites using the method mentioned in Chapter 2. On all surfaces the optimized final structure adopted parallel orientation to the surface irrespective of the initial location and orientation of the simulation. In all cases the lowest energy structure was a D_{3d} chair structure with three-fold symmetry. In this structure there are six hydrogens on axial position of the carbon ring: three below the plane of the molecule and three above. Figure 4.11 shows the result of the energy minimization calculation. On all cases the minimum energy molecular structure was resulted with the center of mass (COM) of the molecule located on the atom sites. On MgO more than one minimized structure were obtained with negligible difference in final energy. Two such structures that were frequently obtained in a number of simulations are shown in Figure 4.11A. This behavior reflected the mismatch in molecular and surface symmetry indicating a frustration to find an absolute minimum on the potential energy surface. However, an exciting behavior was obtained on graphite and hBN. In all the simulations on these two surfaces, the molecule returned a structure with its COM located on atom site and its three axial hydrogens located toward the three adjacent hollow sites. Figure 4.1 B and C show the optimized cyclohexane structure on graphite and hBN respectively. On hBN, the difference in the energy on B and N atom sites were very little (compared to structures located anywhere else on the hBN surface). The absolute minimum energy structures on graphite and hBN basal planes were favored by the molecular symmetry and dimension being similar to the symmetry and lattice constants of the surfaces. Figure 4.12 A shows a perspective side view of the molecule on graphite surface to illustrate the minimum energy structure on surfaces with threefold symmetry. Table 4.2 shows the calculated energy values for minimum energy configurations of isolated cyclohexane molecule on the surfaces.

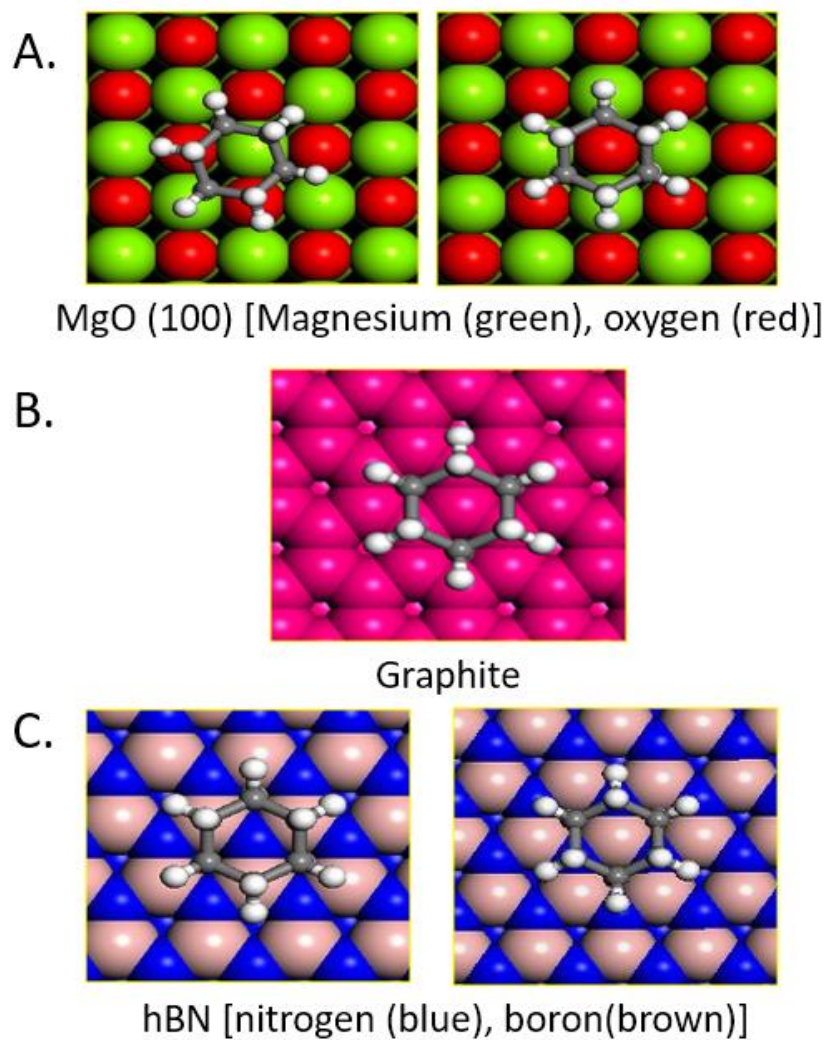


Figure 4.11 Minimum energy structure of isolated cyclohexane molecule A. on MgO, B. on graphite, C. on hBN

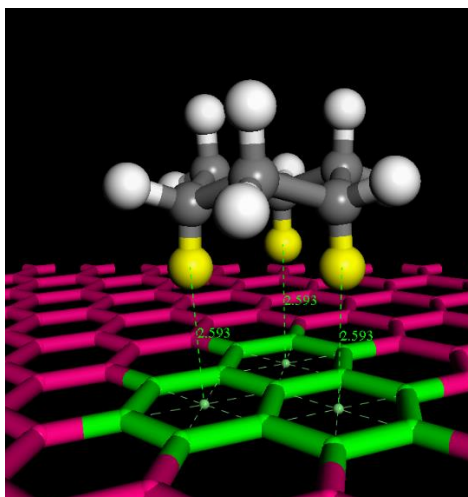


Figure 4.12 A perspective side view of cyclohexane molecule on graphite shows the position of axial hydrogens (yellow) with respect to the surface hollow sites (green).

Table 4.2 Non-bond energy of isolated cyclohexane molecule on the surfaces

Adsorbate	Surface	Non-bonding Energy kcal/mol	Total Energy kcal/mol
Cyclohexane	Graphite	-10.46	-27.43
	hBN	-9.81	-27.01
	MgO	-9.35	-26.33

Monolayer structure from RDF analysis

Unlike the isolated molecular structure where only molecule-substrate (M-S) interaction determines the minimum energy adsorption sites and molecular configuration, in a monolayer structure the molecule interaction also plays a major role in determining the structure of the molecular layer. A competition between M-M and M-S interactions is responsible for the structure of the layers on the surface. At lower temperature, on all surfaces cyclohexane formed a hexagonally packed layer. On MgO, the molecular lattice is rotated by an angle of approximately 14° from the substrate $\langle 10 \rangle$ direction. The lattice constant on MgO is obtained as $6.71 \text{ \AA}$ (Figure 4.13). On graphite a solid commensurate layer has been found from the lower temperature simulations. The lattice constant of graphite, $2.46 \text{ \AA}$ and that of the cyclohexane layer is $\sim 6.52 \text{ \AA}$. The molecular lattice (AC) is rotated by 19.1° from the surface lattice direction (AB) (Figure 4.14). These measurements along with the observation of the location of COM of the molecules throughout the entire monolayer agree with $(\sqrt{7} \times \sqrt{7}) R 19.1^\circ$ commensurate solid layer on the surface. Hexagonal structure is also observed on hBN where the molecular lattice constant is found to be $6.62 \text{ \AA}$ which is slightly higher than that on graphite (Figure 4.15).

Molecular distribution in Z-direction

The orientation of cyclohexane molecules with respect to the surface are clearly realized from the concentration profile ($C(z)$) analysis of the adsorbed molecules in the direction perpendicular to the surface. To calculate the concentration profile, the total volume of supercell and vacuum slab is divided into 3000 equivalent bins. Concentration profile of a particular atom is determined from the atomic fraction in a bin (atoms in bin/total atoms) multiplied by the total volume (total number of bins). By averaging the calculated $C(z)$ over the total simulation time, the probability density function of an atom at a position z on the surface normal vector can be found. The COM of the top molecular layer of the adsorbent surface is set as the reference zero plane.

The change in molecular orientation and dynamics in the adlayers with surface coverage and temperature are visible in the $C(z)$ plots. Figure 4.16, Figure 4.17, and Figure 4.18 show the contribution from hydrogen and carbon atoms to the concentration profile of an isolated cyclohexane molecules adsorbed in a minimum energy configuration on MgO, graphite and hexagonal BN. The orientation of molecule changes with respect to the surface which was also found from the minimum energy structure.

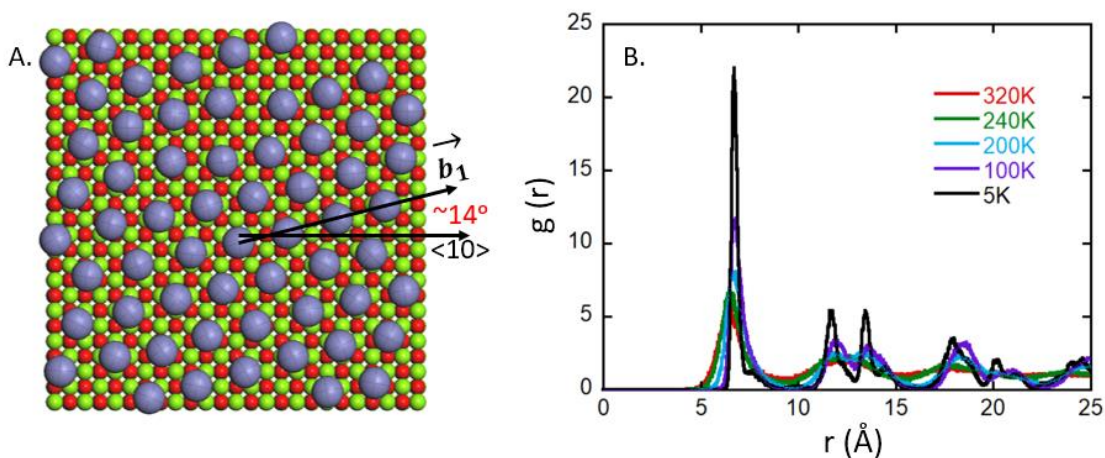


Figure 4.13 Monolayer structure of cyclohexane on MgO. A. Molecules are depicted as centroids for a clear demonstration of the hexagonal structure B. In-plane RDF calculated using the center of the mass of the molecules.

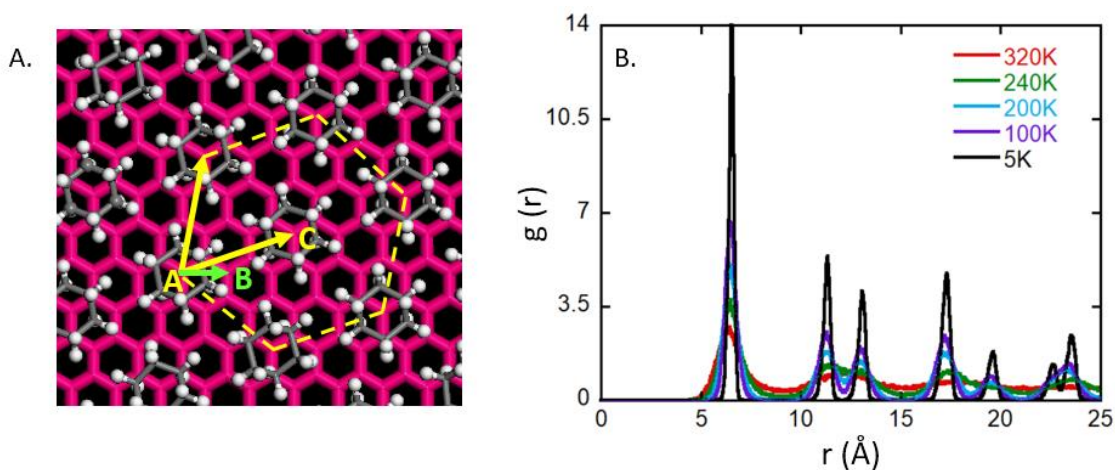


Figure 4.14 Monolayer structure of cyclohexane on graphite. A. Molecules and the substrates are depicted using balls-and-stick model to show the commensurability of the structure of cyclohexane on graphite. B. In-plane RDF calculated using the center of the mass of the molecules.

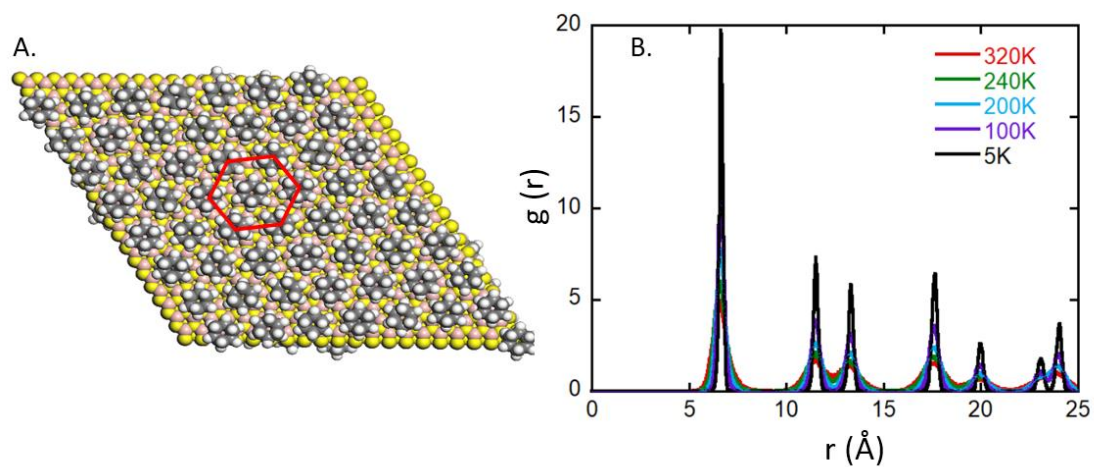


Figure 4.15 Monolayer structure of cyclohexane on hBN. A. Molecules and the substrates are depicted using balls-and-stick model to show the commensurability of the structure of cyclohexane on graphite. B. In-plane RDF calculated using the center of the mass of the molecules.

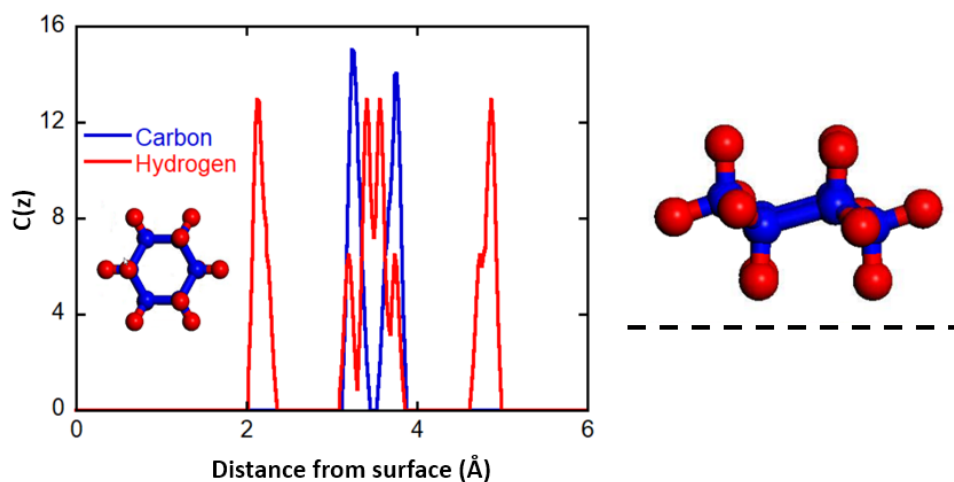


Figure 4.16 Concentration profile of H (red) and C (blue) atoms of a single cyclohexane molecule on MgO (100) surface.

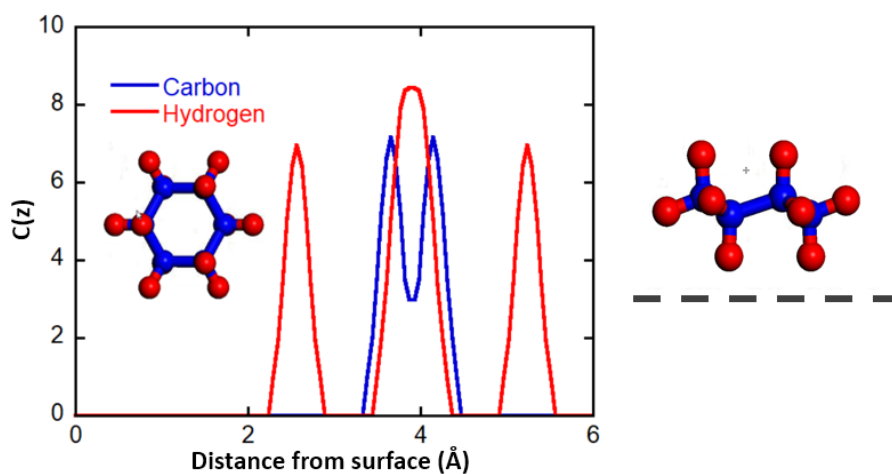


Figure 4.17 Concentration profile of H (red) and C (blue) atoms of a single cyclohexane molecule on graphite surface

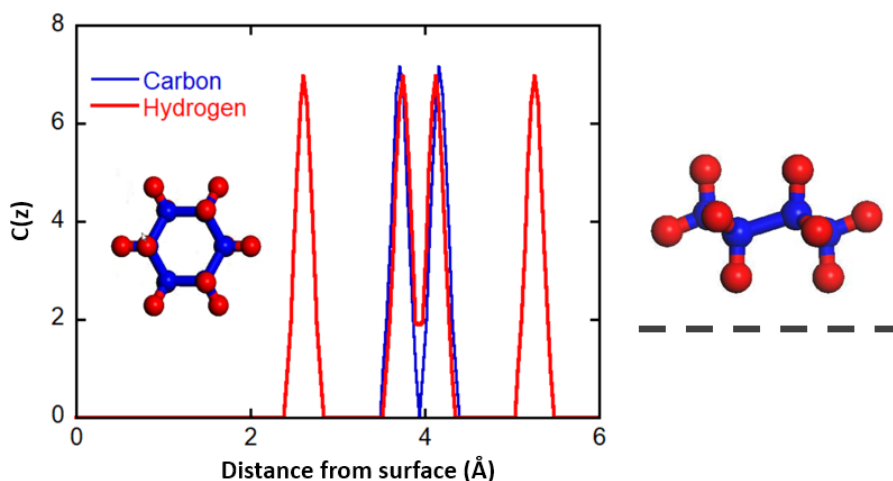


Figure 4.18 Concentration profile of H (red) and C (blue) atoms of a single cyclohexane molecule on hBN surface

Cyclohexane molecule on both Gr and hBN are adsorbed completely parallel to the surface. However, on MgO the molecule is slightly tilted which is clearly distinguished in the peak shape found on $C(z)$ (Figure 4.16). At a monolayer coverage the molecular orientation changes from that of an isolated molecule since at higher coverage molecule-molecule interaction also play a major role in addition to the molecule-surface interaction. Figure 4.19, Figure 4.20 and Figure 4.21 show the z -distribution of the molecules at a nominal monolayer coverage. On each surface all the molecules are lying parallel to the surface. Adsorption study at a monolayer coverage gives the scope to appreciate how the behavior of matter differs in two dimensions than from its 3D counterpart. Previous adsorption studies showed that the surface melting is much lower than bulk melting temperature due to the reduced coordination in 2D, however at higher coverage the melting of a nearest surface layer is much higher. This phenomenon has been observed for cyclohexane adsorption on all three surfaces. The $C(z)$ peaks become narrower with increase in surface coverage to nominal bi- and trilayer. This behavior indicates the compression of the nearest adsorbed layer in z direction which occurs as a result of the effective pressure from the dynamics of molecules in the second and third layers. As a result, the nearest surface layer is stabilized and retains its structure even above the bulk melting point. Figure 4.22, Figure 4.23 and Figure 4.24 display the $C(z)$ of bi- and tri-layer coverages on MgO, graphite and hBN respectively.

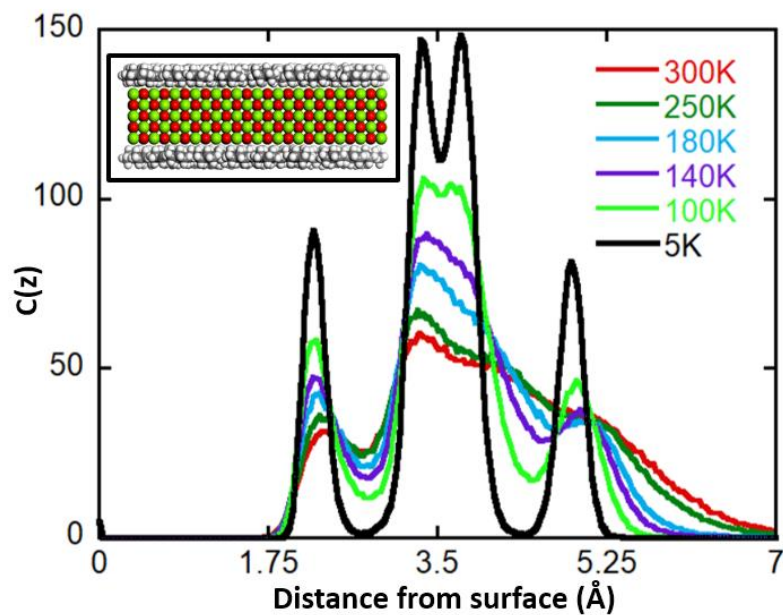


Figure 4.19 Molecular $C(z)$ calculated for nominal monolayer coverage of cyclohexane on MgO as a function of temperature (300K-5K). Bulk triple point of cyclohexane is 279.48K. Side view of a monolayer coverage on surface are shown inset.

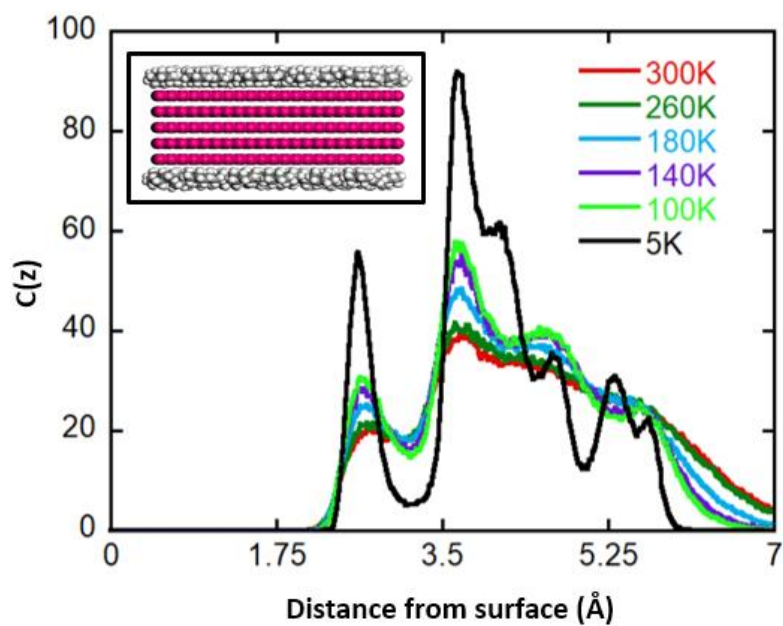


Figure 4.20 Molecular $C(z)$ calculated for nominal monolayer coverage of cyclohexane on graphite as a function of temperature (300K-5K). Side view of a monolayer coverage on surface are shown inset.

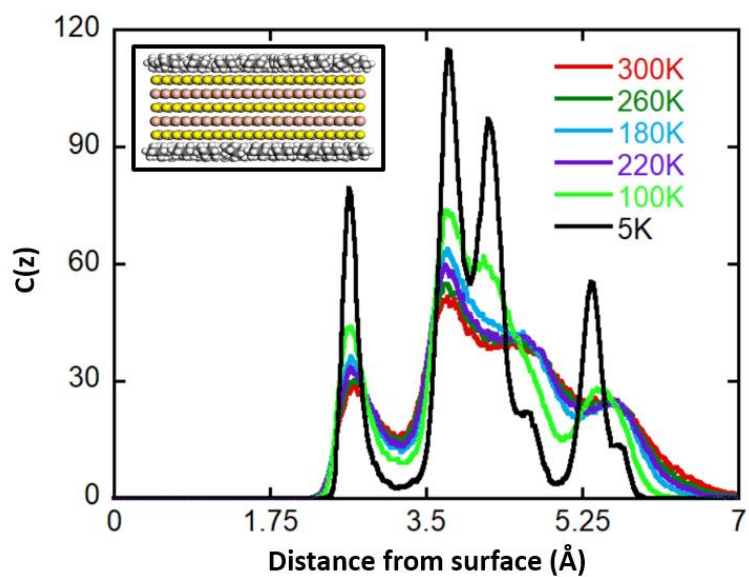


Figure 4.21 Molecular $C(z)$ calculated for nominal monolayer coverage of cyclohexane on hBN as a function of temperature (300K-5K). Side view of a monolayer coverage on surface are shown inset.

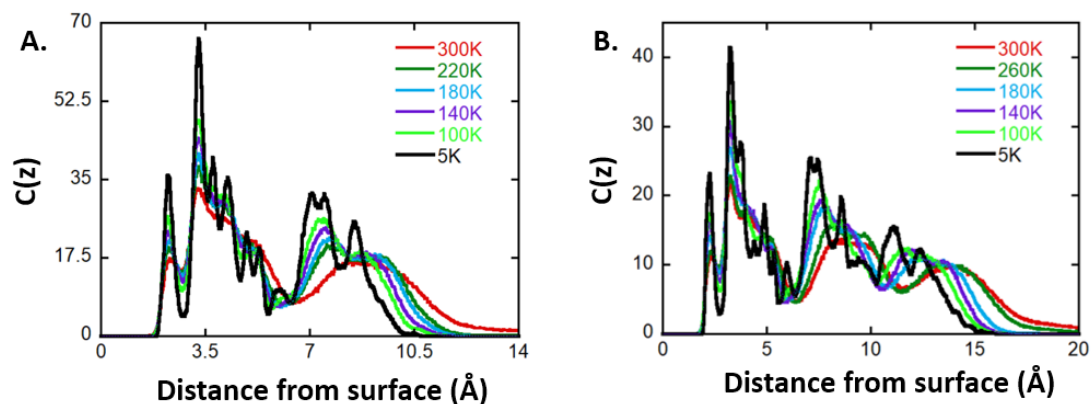


Figure 4.22 Molecular $C(z)$ calculated for nominal A. bilayer and B. trilayer coverage of cyclohexane on MgO as a function of temperature (300K-5K).

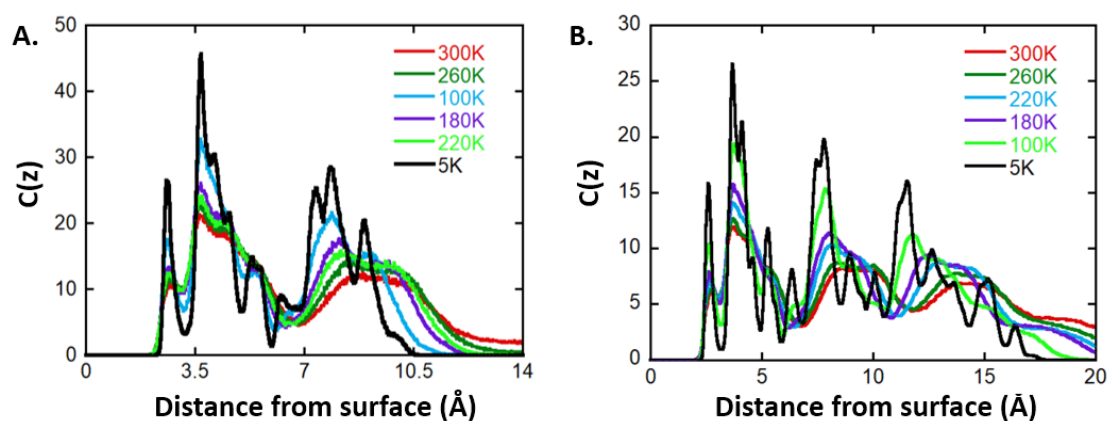


Figure 4.23 Molecular $C(z)$ calculated for nominal A. bilayer and B. trilayer coverage of cyclohexane on graphite as a function of temperature (300K-5K).

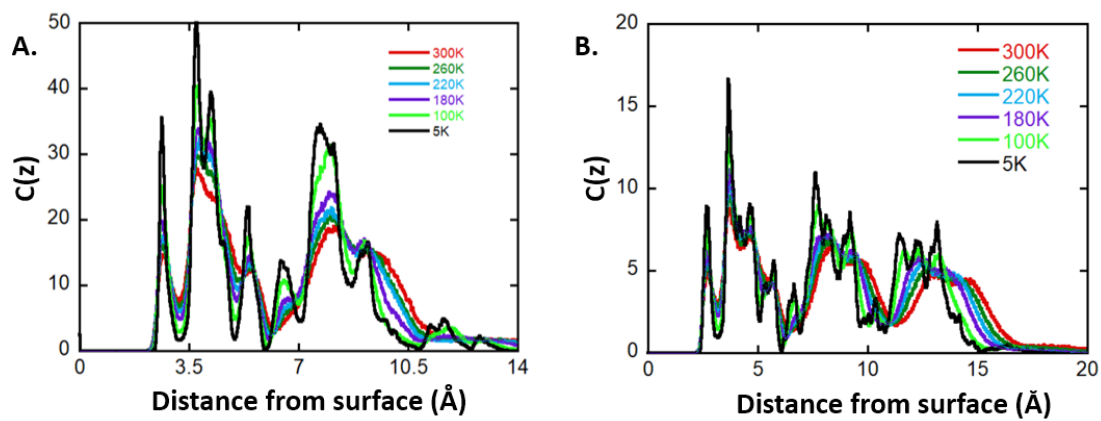


Figure 4.24 Molecular $C(z)$ calculated for nominal A. bilayer and B. trilayer coverage of cyclohexane on hBN as a function of temperature (300K-5K).

4.4 Conclusions

Adsorption behavior of cyclohexane has been examined through the measurement and analysis of volumetric adsorption isotherms and molecular dynamics simulation. From the isotherms recorded over the temperature range of 204-292K three layering transitions were found on both graphite and hBN and only two found on MgO. Thermodynamic analysis of the recorded isotherms was used to obtain heats of adsorption on the all surfaces. The highest heat of adsorption was found for graphite surface, while the lowest was found for MgO. This trend in surface molecule interaction is also reflected in the monolayer absorption region of the isotherms. The linear adsorption at a very low reduced pressure (p/p_0) before monolayer step is longest on MgO, and substantial in case of hBN, while this region is almost absent on graphite. The molecular dynamics simulation and analysis over a broad range of temperature (600K-5K) have been used to obtain microscopic insight of the structure and dynamics of the adsorbed layers. The geometry optimization calculation has been used to obtain the minimum energy structure of isolated molecules on the surface. Monolayer and multilayer coverages have also been carefully examined using the simulated molecular trajectories. Radial distribution function analysis has indicated a commensurate ($\sqrt{7} \times \sqrt{7}$) R19.1° layer formation on graphite. Concentration profile analysis have indicated nearest layer stabilization on the surfaces at temperatures above bulk melting point. This thermodynamic and modeling investigations can be used as a prelude to future elastic and inelastic neutron scattering investigation into the structure and dynamics of the adsorbed layer.

**CHAPTER 5 ADSORPTION OF CYCLOHEPTANE AND
CYCLOOCTANE ON MGO, HBN, AND GRAPHITE BASAL
PLANE**

5.1 Thermodynamics of Adsorption on hBN and Graphite

Cycloheptane forms two distinct layers on graphite and hBN within the temperature range under study. Two representative plots of volumetric adsorption isotherms of cycloheptane on graphite and hBN are shown in Figure 5.1 and Figure 5.2 respectively. The sharp increase in the number of molecules adsorbed with a small change in chemical potential indicates the formation of monolayer at a low P/P_0 . After the completion monolayer, another sharp increase indicates the formation of the second layers on both the surfaces. However, very shallow “bump” like features indicating a third layer were also observed in the cycloheptane isotherms on graphite surface. This feature appears right before reaching saturated vapor pressure and was consistently detected in the derivative plots of cycloheptane on graphite. The steps on graphite are sharper while the layering transitions on hBN are smoother. By comparing the monolayer adsorption capacity for cycloheptane on graphite with that of methane adsorption isotherms the area occupied by a single cycloheptane molecule on graphite has been determined using point B method. An example of area per molecule calculation is shown in Figure 5.3. The APM of cycloheptane on graphite is calculated as $\sim 122 \text{ \AA}^2$ at 254K and on hBN is $\sim 130 \text{ \AA}^2$.

A variation of the Clausius-Clapeyron equations developed by Larher [85] were used to calculate the thermodynamics of adsorption. The numerical derivative of raw isotherm plot was used to obtain the location of equilibrium vapor pressure associated with each layer formation. The natural logarithm of these pressures was plotted against inverse temperatures. The Clausius-Clapeyron plots of cycloheptane adsorption on graphite and hBN are shown in Figure 5.4 and Figure 5.5. The slope and intercept of these plots were used in a variety of thermodynamic equations to obtain the heats of adsorption, differential entropy, enthalpy. Cyclooctane forms two layers on graphite and hBN in the temperature range of 254-290K. Two representative plots of cyclooctane adsorption on graphite and hBN are shown in Figure 5.6 and Figure 5.7 respectively. The wetting behavior of cyclooctane on these two surfaces are quite similar to that of cycloheptane except only two distinct layers were observed on graphite. The Clausius-Clapeyron plots for graphite (Figure 5.8) and hBN (Figure 5.9) show the P-T relationship for the two layering transitions. Due to very low equilibrium pressure at the monolayer region the P-T lines for the equilibrium associated with monolayer formation could only be detected accurately for the isotherms at higher temperature. The thermodynamic values obtained for cycloheptane and cyclooctane on graphite and hBN are tabulated in Table 5.1 and Table 5.2.

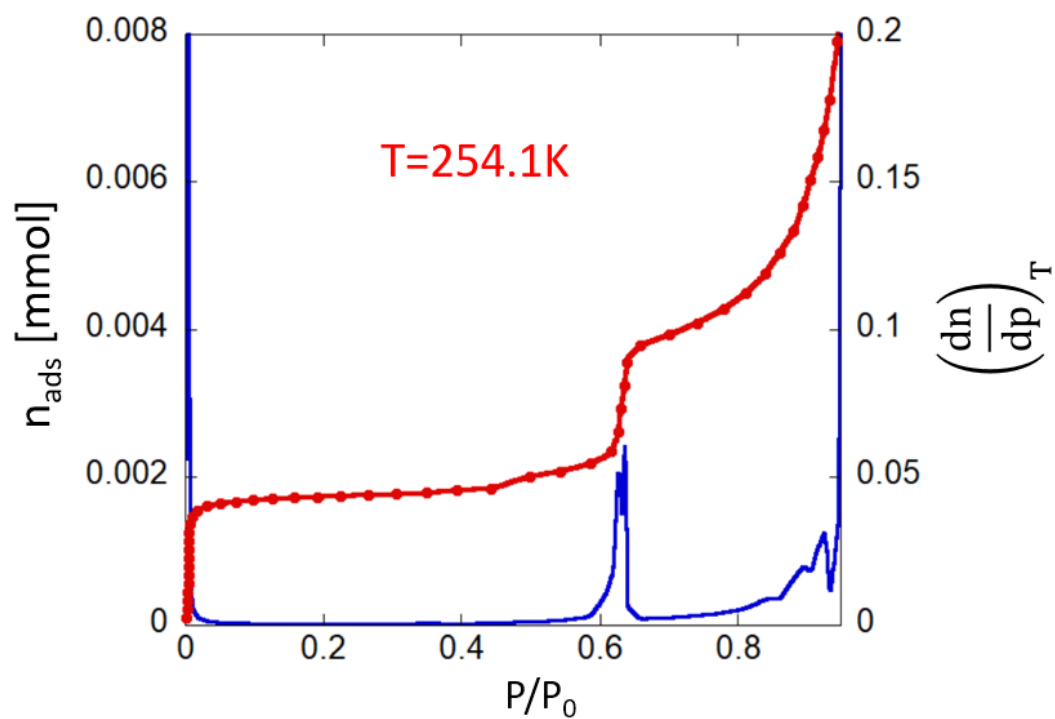


Figure 5.1 Representative adsorption isotherm of cycloheptane on graphite at 254.1K with corresponding derivative plot.

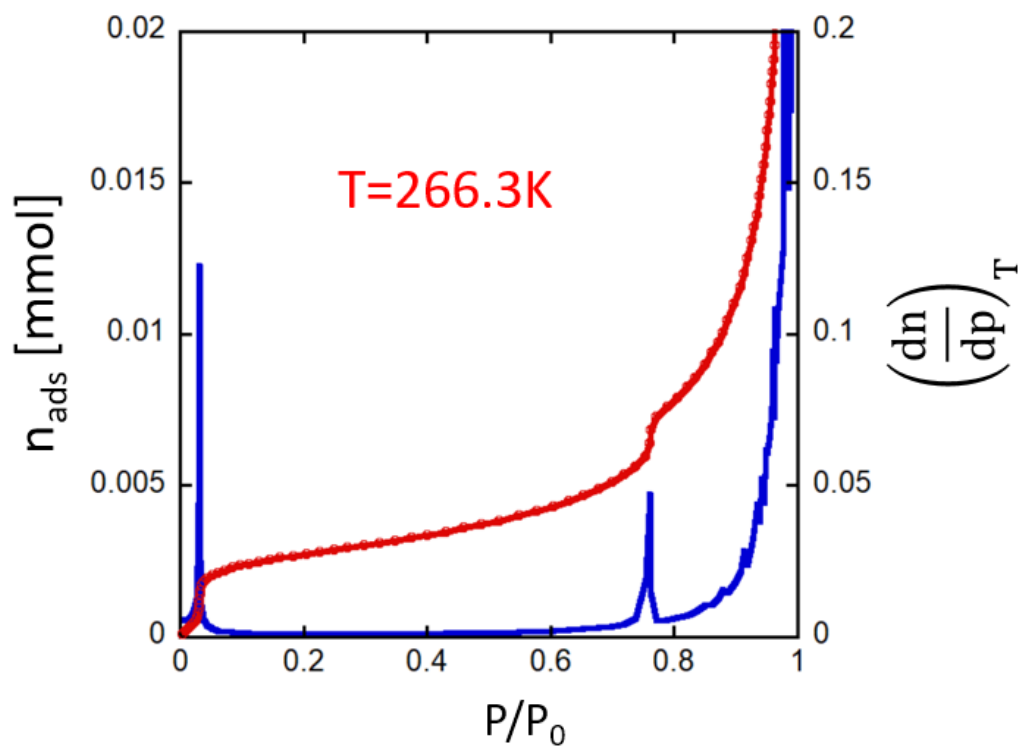


Figure 5.2 Representative adsorption isotherm of cycloheptane on hBN at 266.3K with corresponding derivative plot.

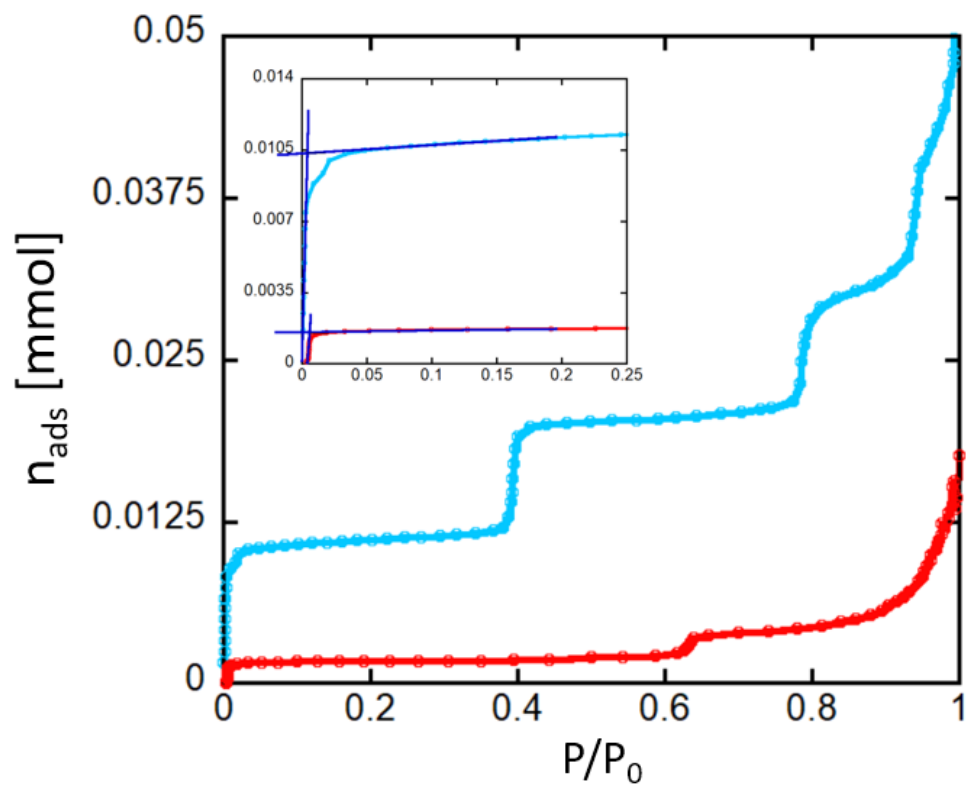


Figure 5.3 Example of an area per molecule (APM) calculated for cycloheptane on graphite.

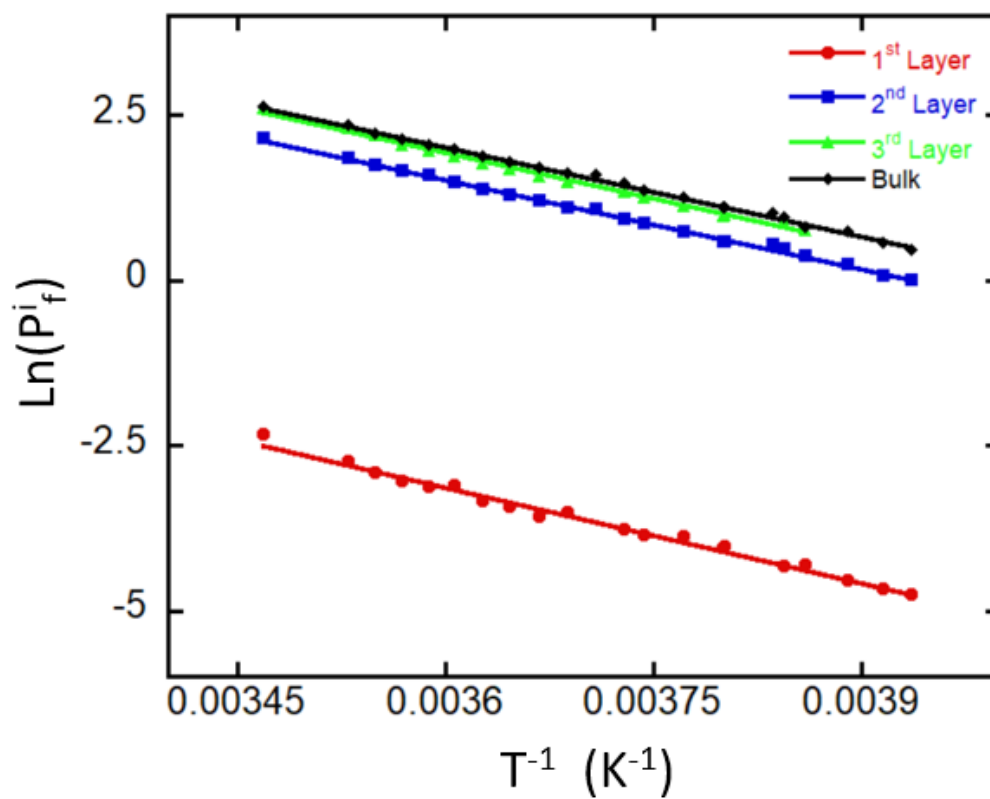


Figure 5.4 Clausius-Clapeyron analysis of cycloheptane on graphite

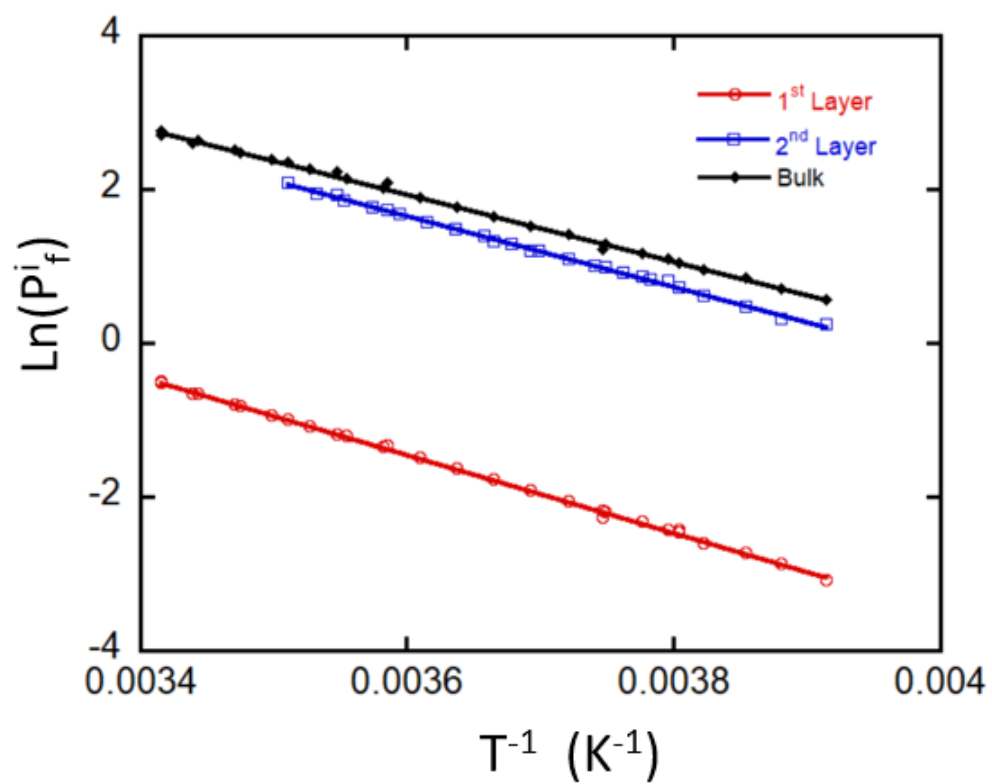


Figure 5.5 Clausius-Clapeyron analysis of cycloheptane on hBN.

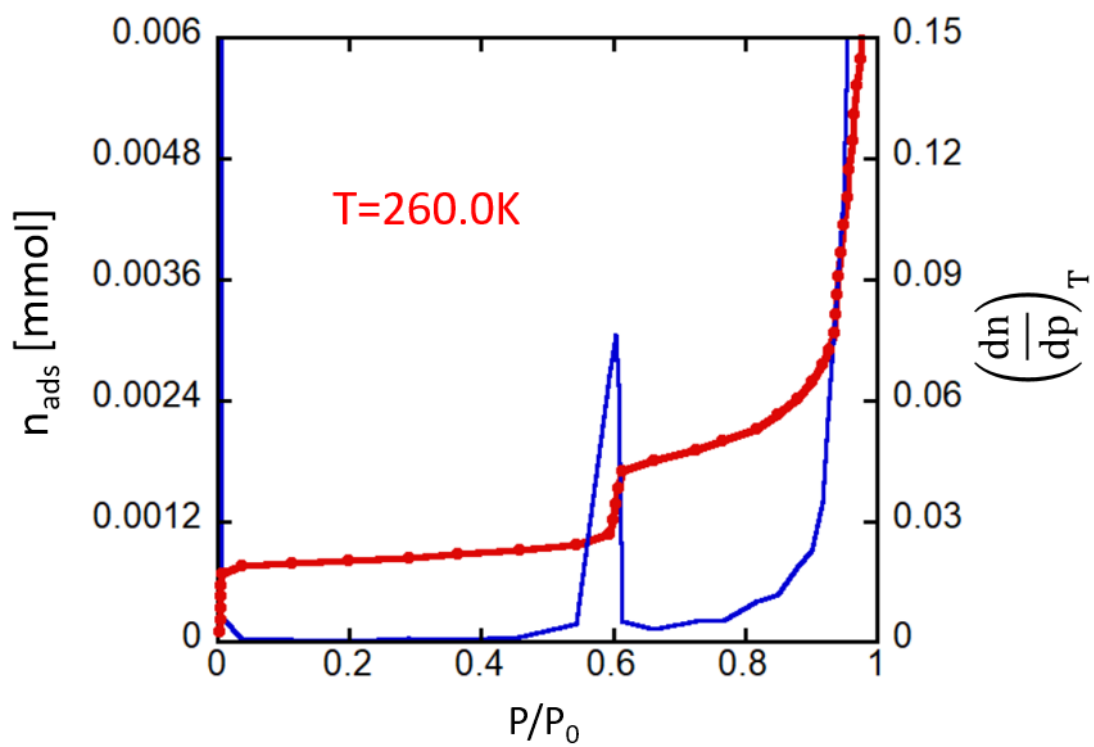


Figure 5.6 Representative plot of cyclooctane on graphite at 260.0K

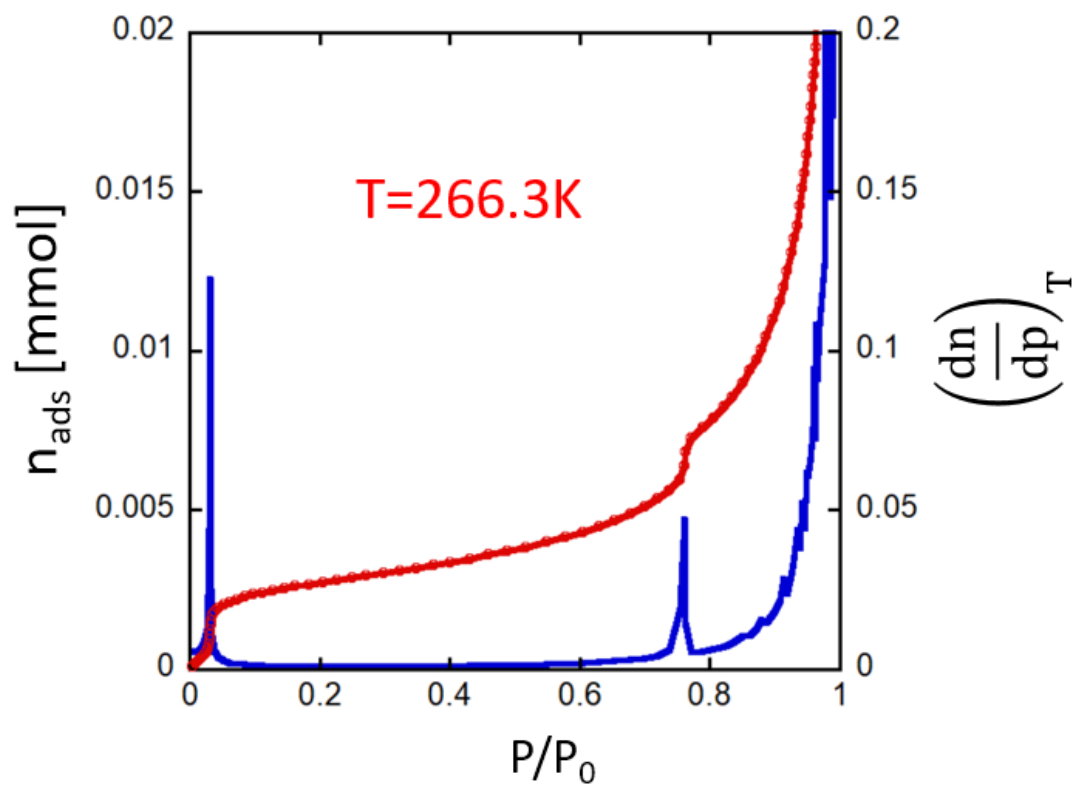


Figure 5.7 Representative plot of cyclooctane on hBN at 260.0K.

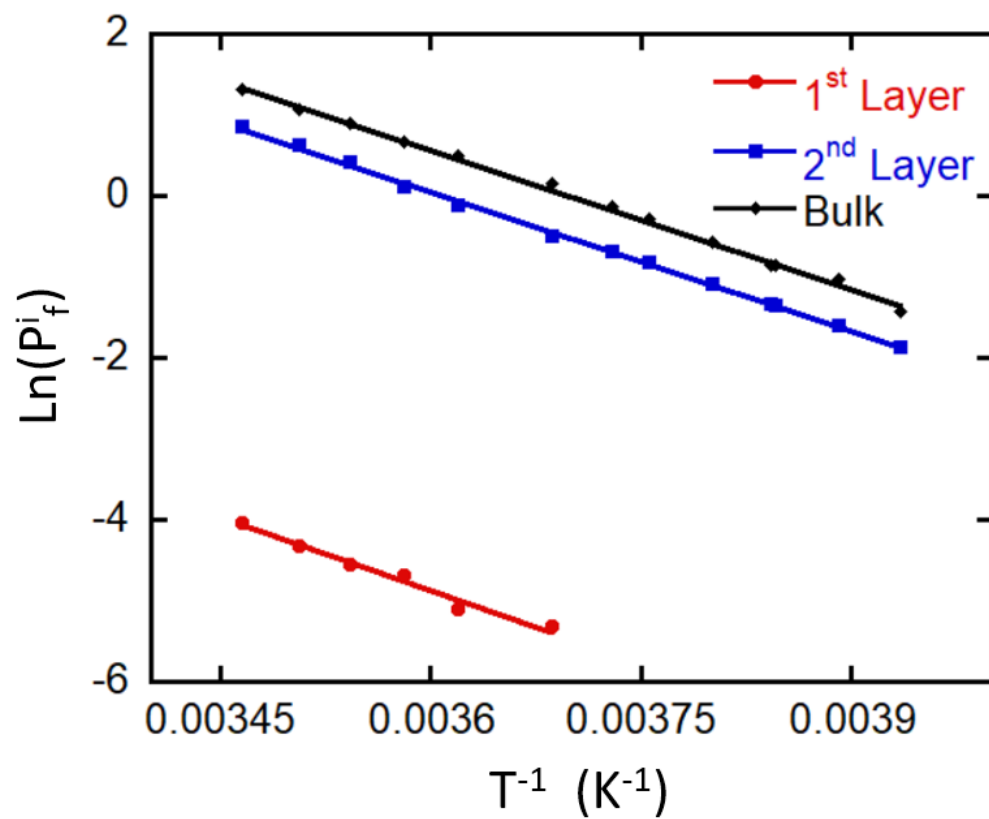


Figure 5.8 Clausius-Clapeyron analysis of cyclooctane on graphite

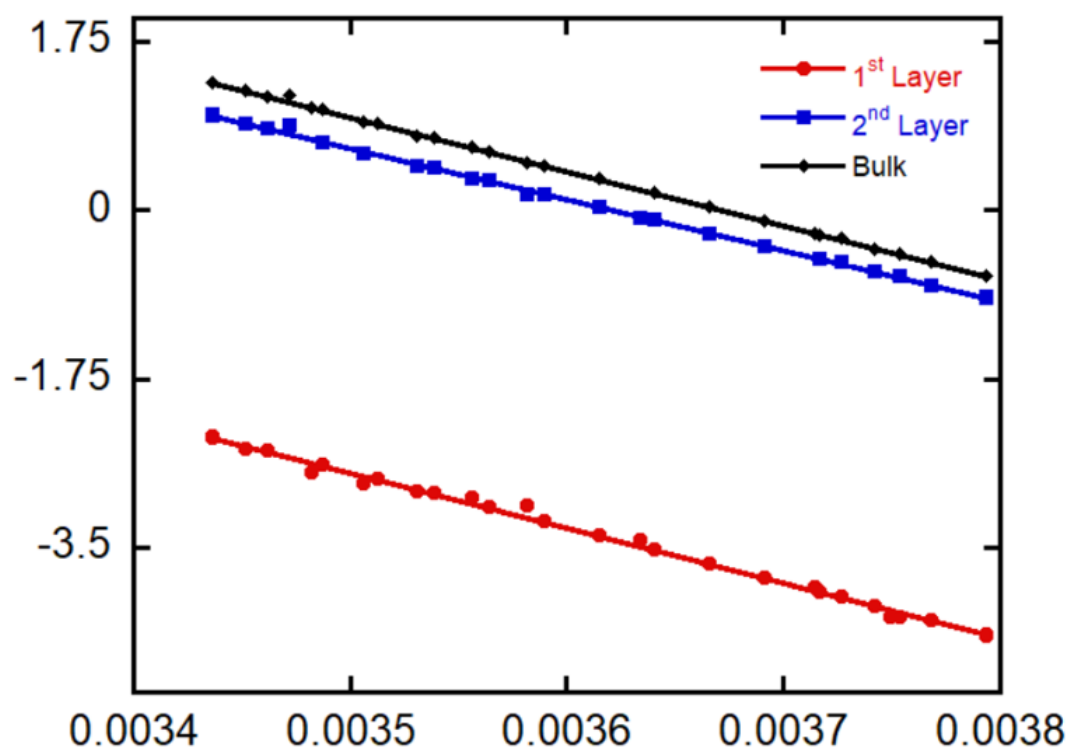


Figure 5.9 Clausius-Clapeyron analysis of cyclooctane on hBN

Table 5.1 Thermodynamic properties of cycloheptane on graphite and hBN surfaces.

Surface	n	$A^{(n)}$ (K)	$B^{(n)}$	$Q_{\text{ads}}^{(n)}$ (kJmol ⁻¹)	$\Delta H^{(n)}$ (kJmol ⁻¹)	$\Delta S^{(n)}$ (JK ⁻¹ mol ⁻¹)
Graphite	1	5134.0	14.28	42.68	-5.22	32.94
	2	4603.9	17.75	38.28	-0.81	4.12
	3	4619.4	18.17	38.41	-0.94	0.66
	∞	4506.0	18.24	37.46	-----	-----
hBN	1	5031.7	16.67	41.83	-5.23	9.28
	2	4518.3	17.12	37.57	-0.96	5.57
	∞	4403.3	17.79	36.61	-----	-----

Table 5.2 Thermodynamic properties of cyclooctane on graphite and hBN surfaces.

Surface	n	$A^{(n)}$ (K)	$B^{(n)}$	$Q_{\text{ads}}^{(n)}$ (kJmol ⁻¹)	$\Delta H^{(n)}$ (kJmol ⁻¹)	$\Delta S^{(n)}$ (JK ⁻¹ mol ⁻¹)
Graphite	1	5976.0	14.34	49.68	-2.13	56.73
	2	5752.1	19.95	47.82	-0.27	10.14
	∞	5720.1	21.17	47.56	0	0
hBN	1	5740.2	17.38	47.72	-0.90	27.51
	2	5689.9	19.18	47.31	-0.48	12.55
	∞	5632.6	20.69	46.83	0	0

5.2 Modeling

Cycloheptane and cyclooctane molecules have been geometrically optimized on all three surfaces in a method previously described. Figure 5.10 and Figure 5.11 show the lowest energy configurations of cycloheptane and cyclooctane on hBN, graphite and MgO. With increased number of carbons in the ring these two molecules are more flexible than previously discussed cyclohexane and cyclopentane. In the lowest energy structure, the molecules return puckered structures anchoring the hydrogen that are facing the surface toward hollow sites of the surface. Interestingly, cyclooctane on MgO returned a puckered structure that has a four-fold symmetry (Figure 5.11C). This conformation is known as the crown structure [36]. In bulk condition, this structure has slightly higher energy than the boat-chair conformation. The non-bond energy of the cycloheptane and cyclooctane are listed in Table 5.3.

The in-plane monolayer structure of cycloheptane and cyclooctane on hBN and graphite have been studied using the radial distribution function and concentration profile analysis of the trajectory files generated in MD simulations over a temperature range of 650K-5K. The molecules are more flexible, and the layers appeared to be more dynamic at the lower temperature range of the simulation. The RDF analysis of the COM of the molecule shows hexagonal structure formation on all three surfaces. The lattice constants obtained from the RDF analysis are listed in Table 5.4. Figure 5.12, Figure 5.13 and Figure 5.14 show the RDF analysis of the COM of the cycloheptane molecules on graphite, hBN and MgO respectively. Figure 5.15, Figure 5.16 and Figure 5.17 show the RDF analysis of the COM of the cyclooctane molecules on graphite, hBN and MgO respectively. The monolayer structures of both molecules show similarities in RDF peak structures.

The molecular distribution of cycloheptane and cyclooctane on the surfaces show the stabilization of nearest surface layer at temperatures above the bulk melting points. Comparative plots of monolayer and nominal trilayer coverages for cycloheptane on graphite, hBN and MgO are provided in Figure 5.18, Figure 5.19 and Figure 5.20 respectively. The $C(z)$ plots for mono- and trilayer of cyclooctane on graphite, hBN and MgO are shown in Figure 5.21, Figure 5.22 and Figure 5.23 respectively. The layer compression at higher coverage indicate restricted dynamics of the molecules in the nearest surface layer.

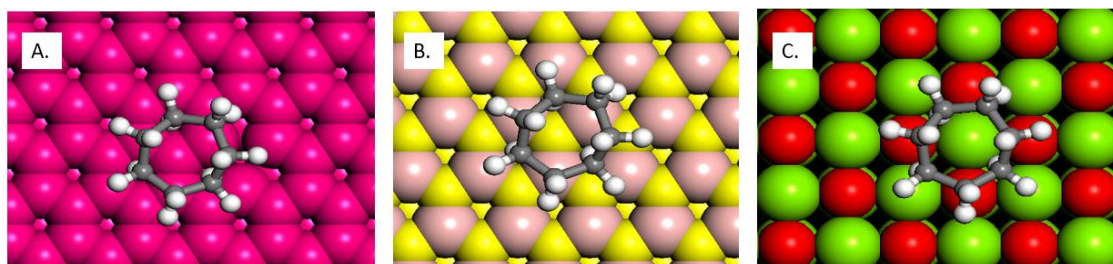


Figure 5.10 Minimum energy structures of cycloheptane on A. graphite, B. hBN and C. MgO (100) surfaces.

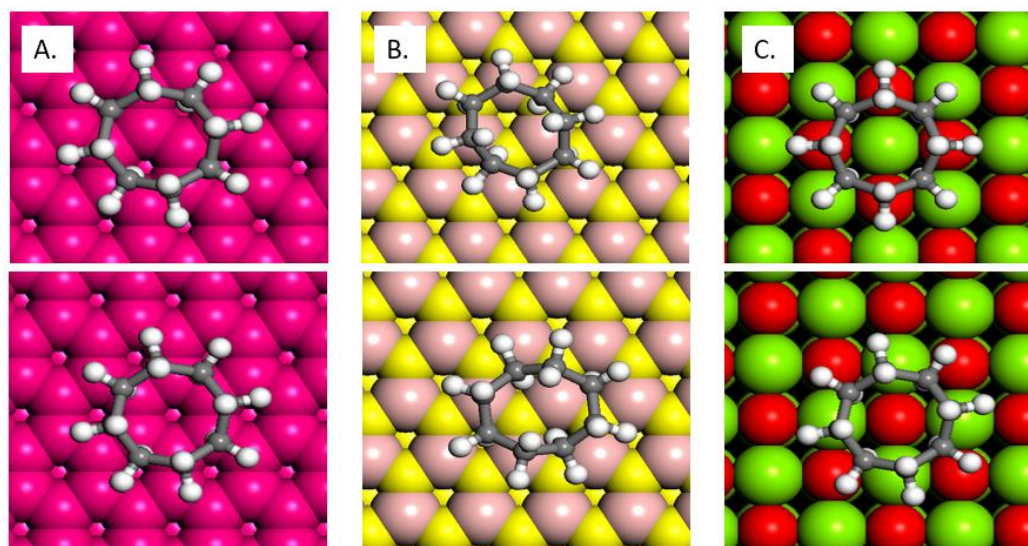


Figure 5.11 Minimum energy structures of cyclooctane on A. graphite, B. hBN and C. MgO (100) surfaces.

Table 5.3 Minimum non-bond energy of cycloheptane and cyclooctane on the surfaces

Cycloalkane	MgO (kJmol ⁻¹)	Graphite (kJmol ⁻¹)	hBN (kJmol ⁻¹)
Cycloheptane	-54.2271	-47.6018	-49.203
Cyclooctane	-64.644 (Mg) -63.2267 (O)	-55.6316	-52.442

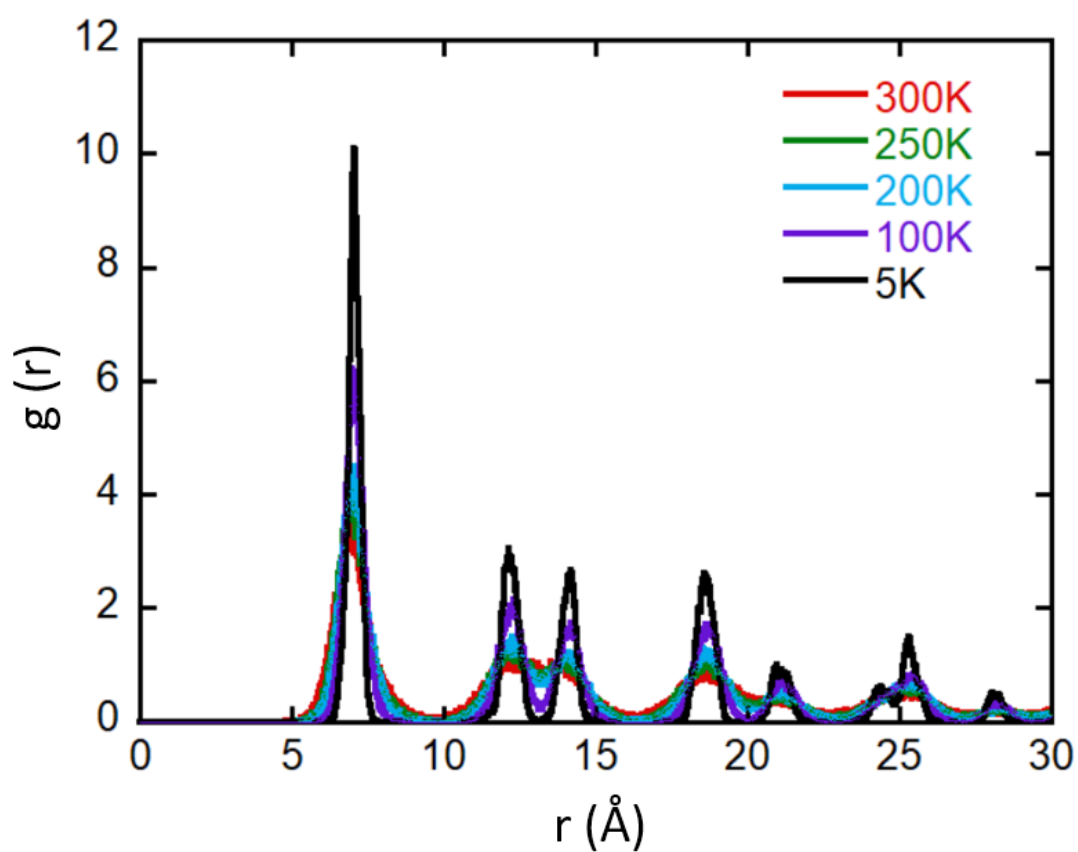


Figure 5.12 In-plane radial distribution function of the COM of cycloheptane molecules in a monolayer on graphite surface

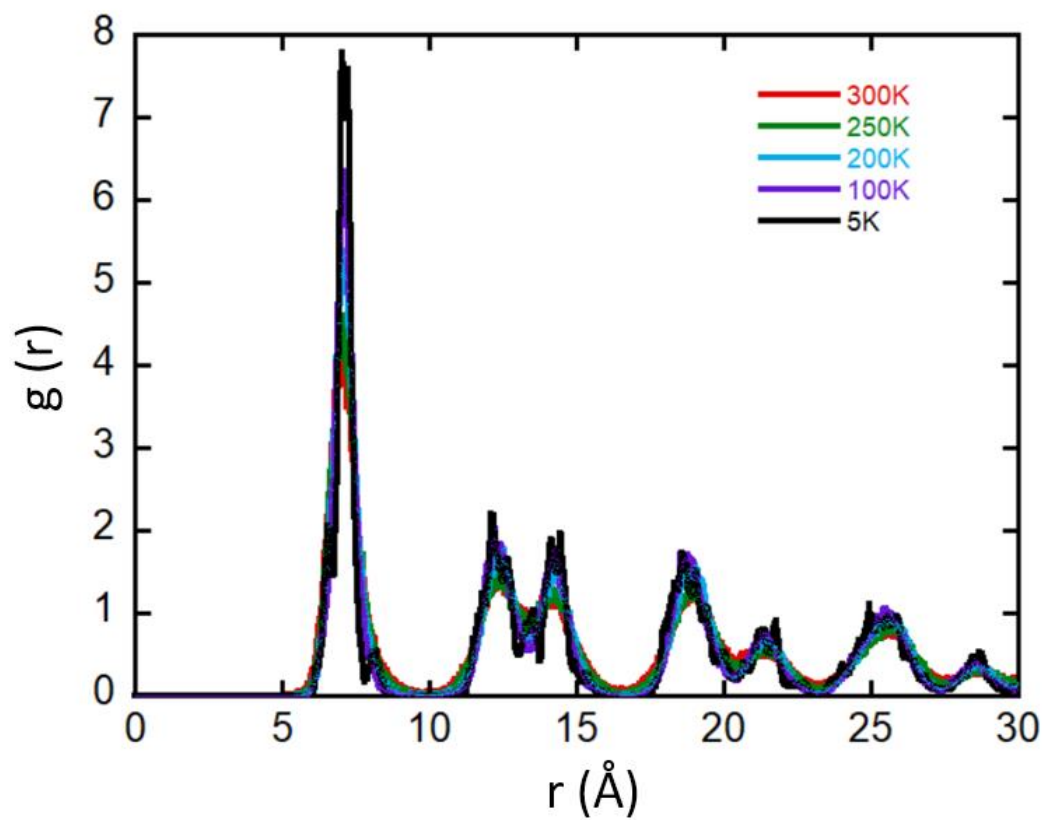


Figure 5.13 In plane RDF of the COM of cycloheptane molecules in a monolayer on hBN surface

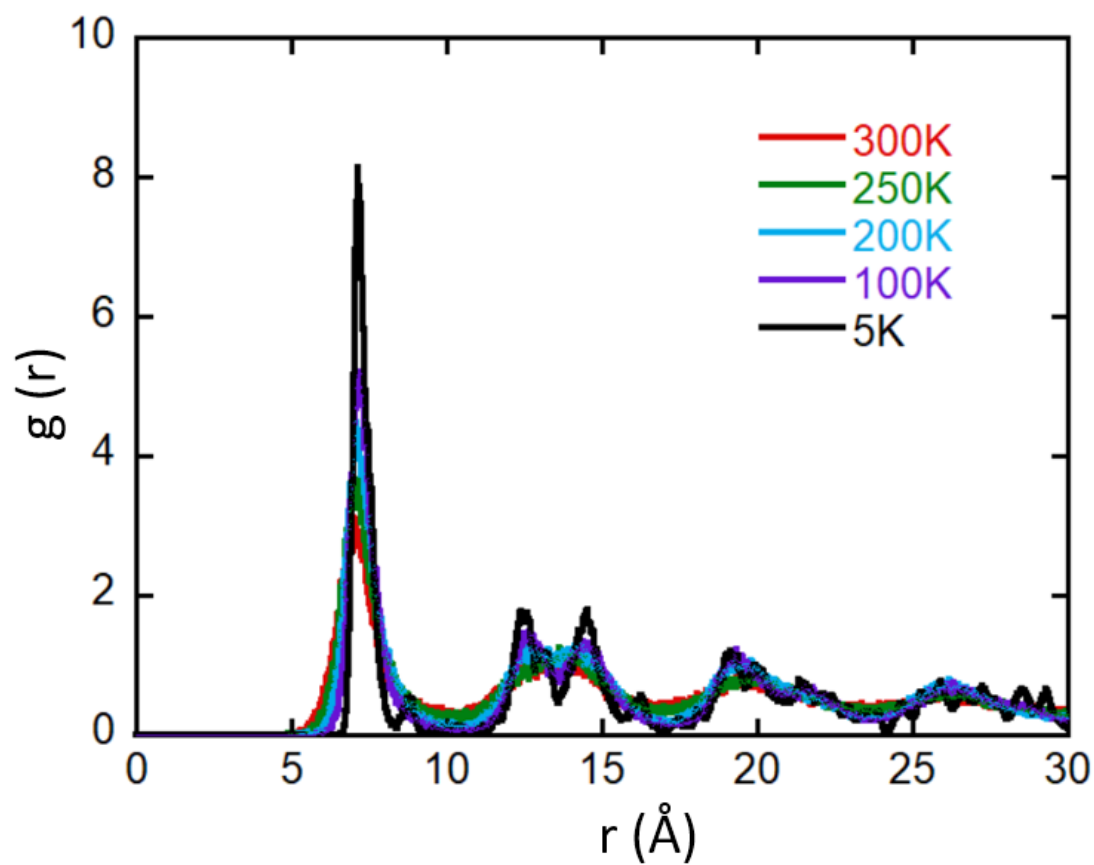


Figure 5.14 In plane RDF of the COM of cycloheptane molecules in a monolayer on MgO surface

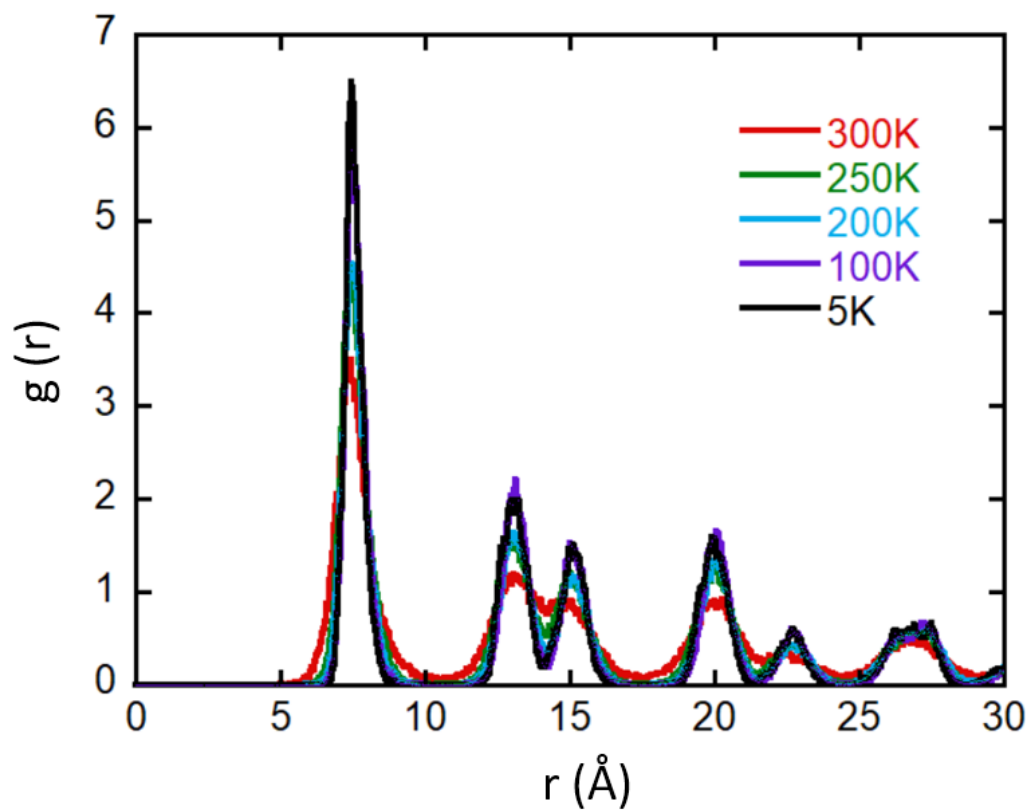


Figure 5.15 In plane RDF of the COM of cyclooctane molecules in a monolayer on graphite surface.

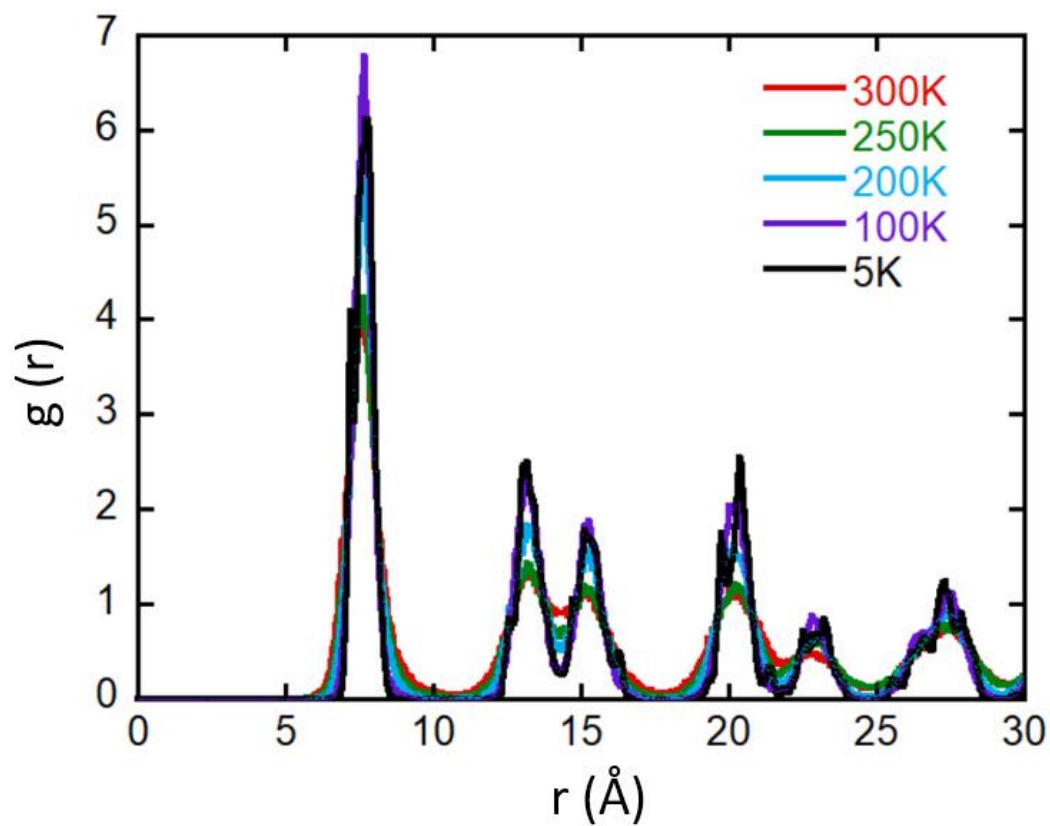


Figure 5.16 In plane RDF of the COM of cyclooctane molecules in a monolayer on hBN surface.

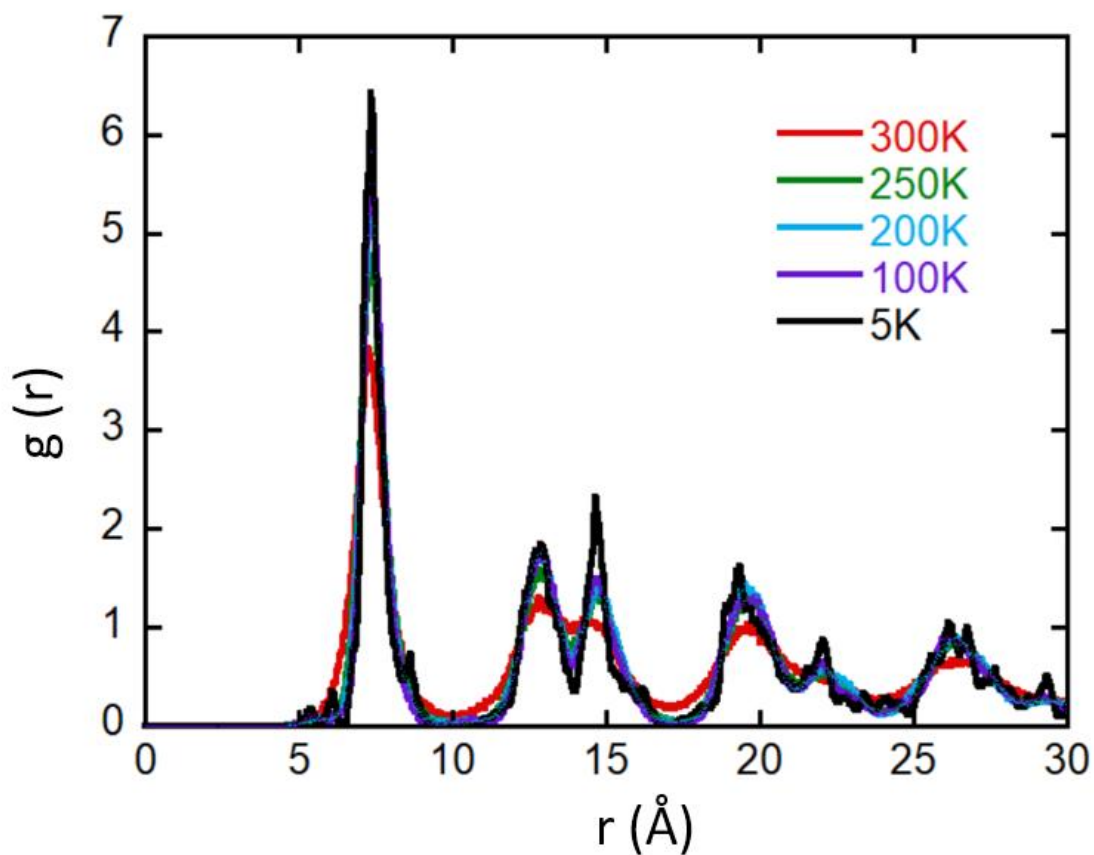


Figure 5.17 In plane RDF of the COM of cyclooctane molecules in a monolayer on MgO surface

Table 5.4 Lattice constants of cycloalkanes obtained on all the surfaces

	MgO	Graphite	hBN
Cyclopentane	5.8556	5.8611	5.7720
Cyclohexane	6.7097	6.5301	6.6298
Cycloheptane	7.1500	7.0495	7.1232
Cyclooctane	7.3251	7.3250	7.6750

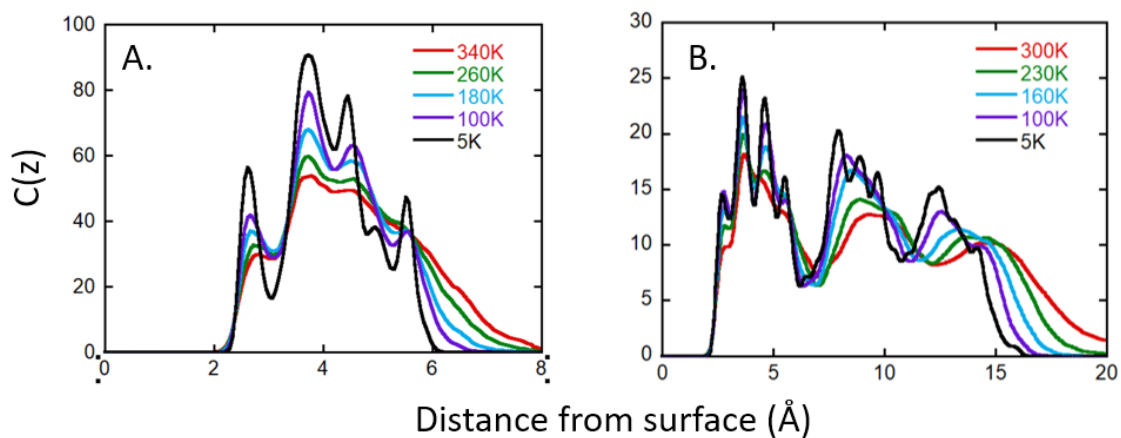


Figure 5.18 Concentration profile of cycloheptane on graphite. Molecular distribution in A. monolayer vs B. at nominal trilayer coverage.

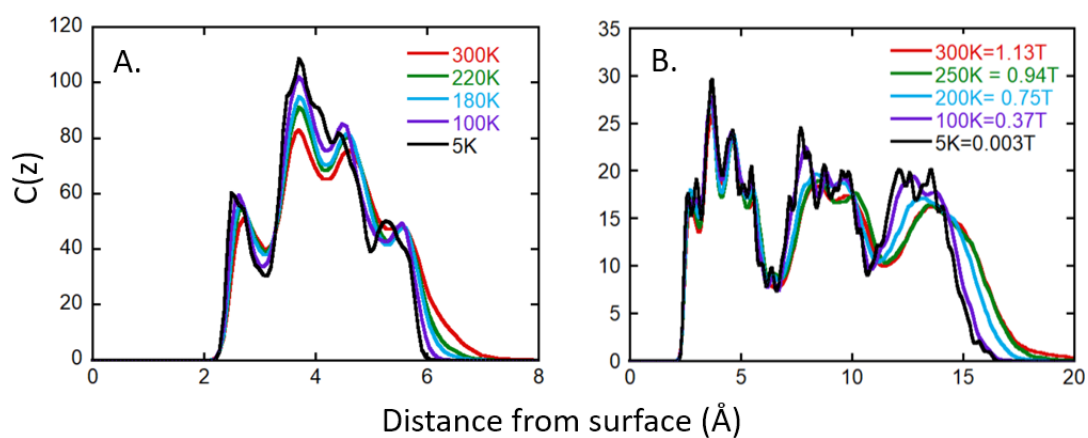


Figure 5.19 Concentration profile of cycloheptane on hBN. Molecular distribution in A. monolayer vs B. at a nominal trilayer coverage.

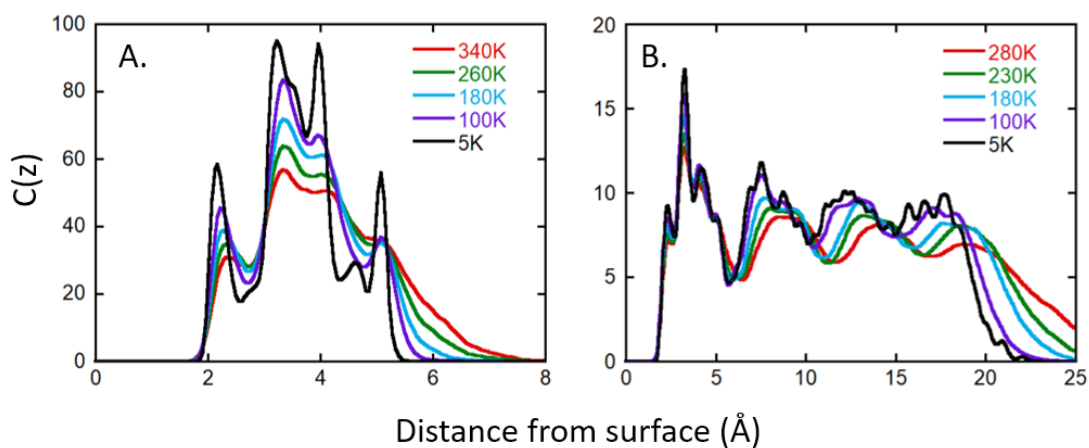


Figure 5.20 Concentration profile of cycloheptane on MgO. Molecular distribution in A. monolayer vs B. slightly above a trilayer coverage.

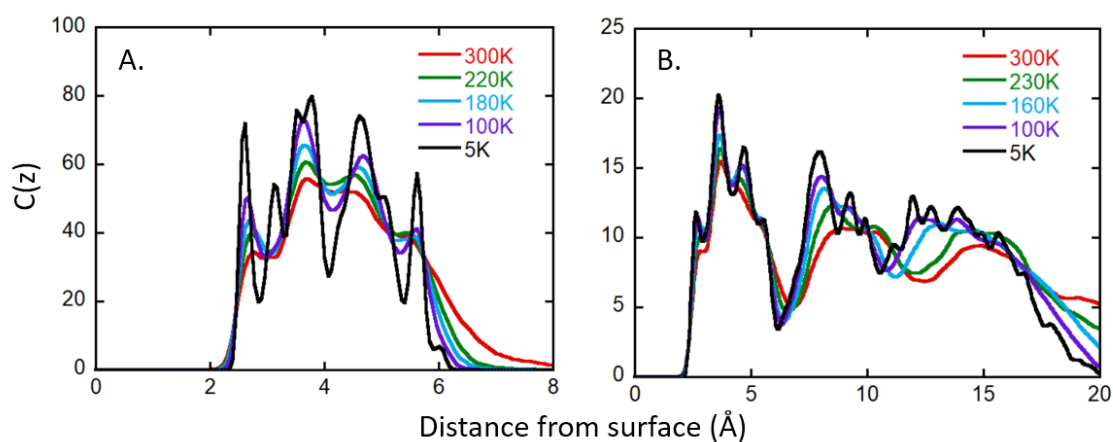


Figure 5.21 Concentration profile of cyclooctane on graphite. Molecular distribution in A. monolayer vs B. at nominal trilayer coverage.

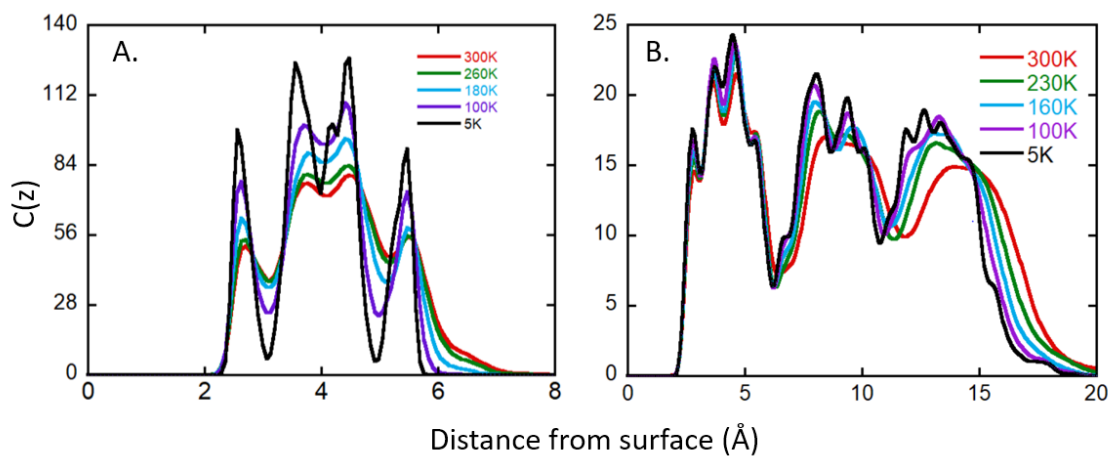


Figure 5.22 Concentration profile of cyclooctane on hBN. Molecular distribution in A. monolayer vs B. at nominal trilayer coverage.

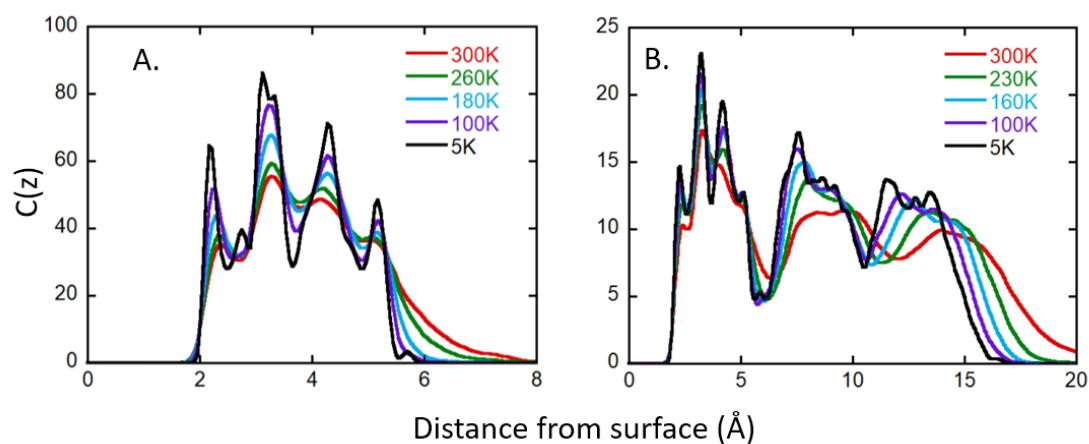


Figure 5.23 Concentration profile of cyclooctane on hBN. Molecular distribution in A. monolayer vs B. at nominal trilayer coverage.

CHAPTER 6 CONCLUSIONS AND FUTURE WORK

The goal of this dissertation was to understand the adsorption of cycloalkanes on MgO(100), hexagonal boron nitride and graphite basal plane by a combination of thermodynamic experiments and molecular dynamics simulations. The novel findings from this study provide insight into the role of substrate symmetry and chemical composition on the adsorption behavior of cycloalkanes on the surface of MgO, hBN and graphite basal planes. The adsorption behavior suggested that, the heats of adsorption of cycloalkanes with substrates maintains following order:

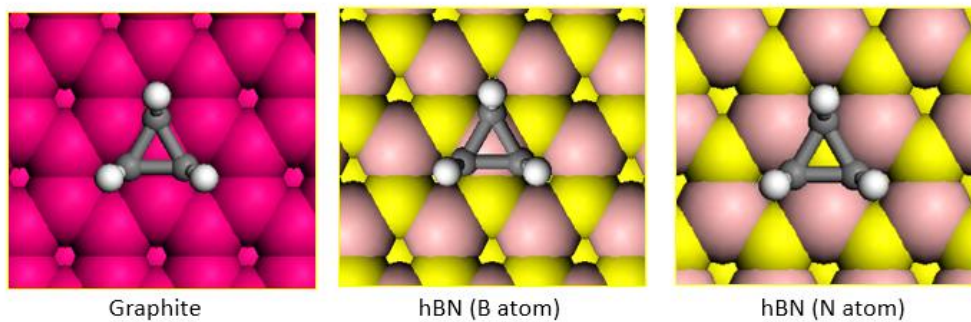
$$\text{graphite} > \text{hBN} > \text{MgO}$$

Which indicates the physisorbed layers of cycloalkanes adheres most strongly to graphite. The layering transitions have been identified using a series of adsorption isotherms of cycloalkanes on each surface.

Furthermore, classical molecular dynamics simulations were employed to characterize the microscopic structure of the adsorbed layer. The monolayer and multilayer molecular distribution analysis shows the hexagonal structure and nearest layer stabilization. In future, isotherm experiments can be carried out to study the behavior of smaller cycloalkanes such as cyclopropane and cyclobutene on these substrates. Cyclopropane is of relevance because it represents the only planar structure among the cycloalkane homologous series due to their torsional strain. They also offer a matching symmetry with graphite and hBN. Preliminary molecular dynamics simulations for cyclopropane indicated minimum energy structure of cyclopropane is similar to that of cyclohexane on the three-fold surface, while that of cyclobutane on MgO shows the orientation of molecules in $\langle 11 \rangle$ direction (Figure 6.1).

To confirm the structure and dynamics obtained from modeling future neutron scattering experiments can be performed using the results of thermodynamics experiments and molecular modeling as a prelude. To understand behavior such as structural changes in the adsorbed layer and critical phase transition points neutron scattering techniques will be extremely useful. The structure of solid adlayers can be identified using neutron diffraction. Furthermore, the effect of surface on the vibrational and rotational dynamics of these cycloalkanes can be investigated using inelastic and quasielastic experiments.

Cyclopropane on graphite and hBN



Cyclobutane on MgO

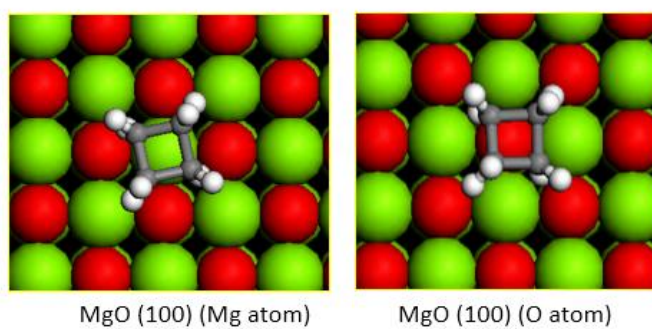


Figure 6.1 Preliminary investigation of the minimum energy structure of cyclopropane and cyclobutane

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APPENDICES

A.1 Physical and chemical properties of the surfaces

	MgO	hBN	Graphite
Crystal Structure	Cubic (fcc)	Hexagonal	Hexagonal
Lattice Constant	4.212	$a = b = 2.502 \text{ nm}$, $c = 6.617$	$a = 2.461$, $c = 6.708$
Melting Point ($^{\circ}\text{C}$, K)	2,852 3,125	2,973 $^{\circ}\text{C}$ 3,246 K	4600 K, 10,800 kPa
Boiling Point	3600 3870	-----	-----
Chemical Bonding	ionic	Covalent in basal plane, weak vdW interlayer => anisotropic properties	Covalent, vdW
Surface Symmetry	Four-fold	Three-fold	Six-fold
Bond Distance	2.106	1.449	1.420
Electronic nature	insulator	Wide bandgap semiconductor	metallic
Bandgap (eV)	7.8	5.2	0
Space Group	Fm $\bar{3}$ m	P6 $_3$ /mmc	P6 $_3$ /mmc
Co-ordination geometry	Octahedral (Mg^{2+}); octahedral (O^{2-})	B- trigonal N- trigonal	C- trigonal
Thermal conductivity ($\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$)	45–60	600 $\parallel$, 30 $\perp$	200–2000 $\parallel$ 2–800 $\perp$ 119–165
Dipole Moment (D=Debye)	$6.2 \pm 0.6 \text{ D}$	-----	-----
Bond Disso. Energy, $\Delta H_{298}^{\text{f}}$, kJ/mol	394(35)	389(21)	607(21)

**C-H bond dissociation energy $338.4 \pm 1.2 \text{ kJ/mol}$

A.2 Physical properties of Cycloalkanes (C3- to C8-)

Cycloalkane	C3	C4	C5	C6	C7	C8
Mol. Wt. (amu)	42.08	56.11	70.13	84.16	98.19	112.21
$\angle$ C-C-C angle (°)	60.0	88.3	102.9 105.0 105.9	109.5	113.5 116.5	118.1
C-C bond length (Å)	1.505	1.543	1.531 1.541 1.553	1.520 1.560	1.535 1.536 1.543	1.533
Symmetry	D _{3h}	---	C _s , C ₂	Boat- C _{2v} , Chair- D _{3d}	---	---
Min. Energy Configuration	planar	puckered	Bent, twist	Chair	Chair, twist chair, boat, twist boat	*boat-chair, crown
Triple point (K)	145.80	182.40	179.71	279.62	265.12	287.97
Vapor Pressure at T _{trip} (Torr)	~0.53	~1.30	0.19	39.56	~2.88	~2.93
Vapor Pressure at 298K (Torr)	5388.68	1170.17	315.52	96.98	21.50	~5.50
Strain energy (kcal/mol, kJ mol ⁻¹)	27.6 120	26.2 110	6.2 25	0.1 0.42	6.2 25	9.7 40.58

A.3 Number of layering transitions of cycloalkanes obtained on surface

Cycloalkane	Temperature Range (K)	Number of layering transitions		
		MgO (100)	hBN	Graphite
Cyclopentane	195-263	2	2	3
Cyclohexane	194-283	2	3	3
Cycloheptane	254-292	----	2	3
Cyclooctane	254-292	----	2	2

A.4 Thermodynamic properties calculated from cycloalkane isotherms on MgO

Cycloalkane	n	$A^{(n)}$ (K)	$B^{(n)}$	$Q_{ads}^{(n)}$ (kJmol ⁻¹)	$\Delta H^{(n)}$ (kJmol ⁻¹)	$\Delta S^{(n)}$ (kJmol ⁻¹)
Cyclopentane	1	3517.7	15.81	29.25	-0.67	11.12
	2	3459.9	16.96	28.77	-0.19	1.55
	∞	3437.2	17.16	28.58	—	—
Cyclohexane	1	4559.1	18.33	37.90	-0.31	12.97
	2	4524.1	18.98	37.61	-0.2	7.96
	∞	4521.5	19.89	37.59	—	—

A.5 Thermodynamic properties calculated from cycloalkane isotherms on hBN

Cycloalkane	n	$A^{(n)}$ (K)	$B^{(n)}$	$Q_{ads}^{(n)}$ (kJmol ⁻¹)	$\Delta H^{(n)}$ (kJmol ⁻¹)	$\Delta S^{(n)}$ (kJmol ⁻¹)
Cyclopentane	1	3904.9	15.80	32.47	-3.89	11.21
	2	3464.3	16.80	28.80	-0.23	2.86
	∞	3437.1	17.14	28.58	—	—
Cyclohexane	1	4906.7	18.08	40.79	-3.47	13.81
	2	4479.0	19.42	37.24	0.08	2.64
	3	4529.5	19.79	37.65	-0.34	-0.50
	∞	4489.2	19.74	37.32	—	—
Cycloheptane	1	5031.7	16.67	41.83	-5.23	9.28
	2	4518.3	17.12	37.57	-0.96	5.57
	∞	4403.3	17.79	36.61	—	—
Cyclooctane	1	5740.2	17.38	47.72	-0.90	27.51
	2	5689.9	19.18	47.31	-0.48	12.55
	∞	5632.6	20.69	46.83	—	—

VITA

Fatema Wahida was born in Kushtia, Bangladesh. She grew up in Jhenaidah, Bangladesh where she attended the Jhenaidah Govt Girls High School. Fatema attended University of Dhaka, Bangladesh, where she obtained a Bachelor of Science degree in Applied Chemistry & Chemical Engineering. After finishing her undergraduate study, she joined the graduate program in Fall 2013 at the Chemistry department of University of Nebraska – Lincoln where she worked with Dr. Stephen A. Morin as a graduate assistant for a year. She joined University of Tennessee in Fall 2014 and started her Ph.D. in physical chemistry where she performed her doctoral research under the supervision of Dr. John Z. Larese. After finishing PhD, she will be joining Intel Corporation at Hillsboro, Oregon, as a Process Engineer.