Thermodynamic modelling of adsorption isotherms and kinetics for gas storage and cooling applications

Sun, Baichuan

2015

Sun, B. (2015). Thermodynamic modelling of adsorption isotherms and kinetics for gas storage and cooling applications. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/65837>

<https://doi.org/10.32657/10356/65837>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**THERMODYNAMIC MODELLING OF ADSORPTION
ISOTHERMS AND KINETICS FOR GAS STORAGE AND
COOLING APPLICATIONS**

SUN BAICHUAN

SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING

2015

Thermodynamic Modelling of Adsorption Isotherms and Kinetics for Gas Storage and Cooling Applications

Sun Baichuan

School of Mechanical and Aerospace Engineering

A thesis submitted to Nanyang Technological University
in partial fulfillment of the requirement for the degree of

DOCTOR OF PHILOSOPHY

July 2015

Abstract

Adsorption occurs due to force interactions between a solid adsorbent surface and gaseous phase molecules. With an effect of low or negligible carbon footprint, it is capable of performing gas storage and adsorptive chilling. Extensive works have been done in the literature to establish the knowledge of adsorption isotherms, kinetics, isosteric heat of adsorption and adsorbent + adsorbate thermodynamic properties. All these works laid a foundation for industrial applications of adsorption science.

Nevertheless, all existing classical adsorption models, as proposed by Langmuir, Tóth, Dubinin, Henry and others, are limited by their individual deficiencies from being valid within the complete temperature and pressure conditions. As a result, it is necessary to develop a consistent adsorption thermodynamic framework, for understanding its behaviours ranging from the Henry's region to the saturated pressures. From this motivation, this thesis presents the theoretical and experimental studies of the adsorbate + adsorbent thermodynamic frameworks, with prospective applications to natural gas storage and adsorptive cooling purpose.

Firstly, novel adsorption isotherm and kinetics equations are developed from the rigor of the partition distribution function of each adsorbate adsorptive site on adsorbents, and the condensation approximation of adsorptive molecules. The proposed models are thermodynamically connected with the pore structures of adsorbent materials. The kinetics theory is formulated with the analogy of Langmuir kinetics. It is found that the proposed models are thermodynamically consistent from the Henry's region to the saturated pressure.

Secondly, the thermo physical properties of adsorbents, including AQSOA-type

zeolites, HKUST-1 and MIL-101(Cr) metal-organic frameworks (MOFs), are verified and characterised by X-ray diffraction (XRD), scanning electron microscope (SEM), N_2 ad/desorption isotherms and thermo gravimetric analyzer (TGA). A constant volume variable pressure apparatus is designed, developed and fabricated to measure the amount of adsorbate uptakes for various pressures and temperatures onto these materials. The experimental setup is extensively utilised to measure the amount of methane uptake for the temperatures ranging from 120 K to 303 K and pressures up to 10 bar. The proposed isotherm model is validated with the experimental data of silica gel + water and AQSOA-Z01, Z02, Z05 + water systems, and explains the S-shaped isotherms within acceptable error ranges ($\pm 5\%$), as compared with Langmuir and Tóth isotherm equations.

Thirdly, the derived kinetics model is verified with the experimental data of silica gel + water systems, with respect to various size and grain layers configuration. The results are compared with Langumirian kinetics model and the Linear Driving Force model (LDF). It is found that the derived kinetics model provides better results when they are compared with the experimental data.

Besides the analytical and experimental studies, the Grand Canonical Monte Carlo simulation is performed and verified with the experimental results, in order to give an computational insight of CH_4 adsorption onto MOFs unit cells. From the computational simulations, it can be found that the guest CH_4 molecules favour the metal atom sites at lower pressure range, and then start to capture larger porous channels of the MOFs cell. Therefore, the adsorption of CH_4 inside MOFs can be concluded to be a heterogenous process.

Acknowledgements

I would like to express my sincere gratitude to my Ph.D. supervisor, Asst. Prof. Anutosh Chakraborty for his great patience, invaluable academic inspirations, and unyielding support to my study and research work. It has been a privilege, as well as a pleasure, to be able to discuss research with such a distinguished and enthusiastic scientist daily. It was my honour to be co-author with him in seven TIRE 1 journal papers and four international peer-reviewed conference papers. Without his instructions and effort by passing down the knowledge of adsorption and clarifying doubts during my studies, this thesis would be impossible to be accomplished.

I am also grateful to the technicians, Mr. Lee Keng Yuen Roger, Mr. Yeo Boon Chuan Edward, Mr. Ang Koon Teck Lawrence and all other collaborators in Energy Systems Laboratory for their assistance during my experiments.

I owe gratitude to our current group members: Yap Ken Shaun, Datta Nirmalya, Fan Wu, Sibnath Kayal, Syed Muztuza Ali. Those discussions and conversations were always helpful and fun. I would also like to emphasise my appreciation to the Nanyang Technology University, Singapore for the research scholarship during the course of candidature. This 4-year-time research period will be one of the highlights in my life.

I also dedicate this report to my family for their unconditional moral support and love throughout the process of the study and research. Finally, I wish to express gratitude to my fiancée, Dr. Shuang Yu, for being a constant source of mental support and companion in the past 7 years.

Contents

Abstract	i
Acknowledgements	iii
Table of Contents	iv
List of Figures	viii
List of Tables	xiv
Nomenclature	xvi
1 Introduction	1
1.1 Adsorption Process	1
1.2 Motivation	6
1.3 Research Objectives and Scopes	7
1.4 Layout of Report	8
2 Literature Review	10
2.1 Introduction	10
2.2 Driving Force for Physisorption	11
2.3 Adsorption Process	13
2.4 Adsorbent Material Properties	14
2.5 Adsorption Isotherms	18
2.5.1 Adsorption Equilibria and Isotherms	18
2.5.2 Classification of Adsorption Isotherms	19
2.5.3 Isosteric Heat of Adsorption	20

2.5.4	Surface Adsorption Isotherm	21
2.5.5	Microporous Adsorption Isotherm	22
2.5.6	Heterogeneous Adsorption Isotherm	22
2.6	Adsorption Kinetics	25
2.7	Milestones of Adsorption Researches	31
2.8	Summary	34
3	Thermodynamic Formulation of Adsorption Isotherms and Kinetics	35
3.1	Introduction	35
3.1.1	Isotherms	35
3.1.2	Kinetics	36
3.2	Thermodynamics of Adsorption Isotherms	37
3.2.1	Lattice Gas Statistics	37
3.2.2	Heterogeneity Factor	42
3.2.3	Isosteric Heat of Adsorption	45
3.2.4	Adsorption Isotherm Classifications	47
3.3	Kinetics with Lattice Statistics	49
3.4	Lattice Gas Cellular Automata	52
3.4.1	Rule Space and Boundary Condition	53
3.4.2	Porous Network	55
3.4.3	Virtualisation	56
3.5	Summary	59
4	Characterisation of Adsorbent Structures and Measurements of Adsorption Isotherms	61
4.1	Introduction	61
4.2	Characteristics of Adsorbent Materials	62
4.2.1	Zeolites	62
4.2.2	Carbonaceous adsorbents	65
4.2.3	Metal-organic Frameworks	66

4.3	Experimental Investigation for Adsorbate Uptakes	77
4.3.1	Volumetric Apparatus	77
4.3.2	Cryostat Setup	81
4.4	Calculations of Adsorbate Uptakes	83
4.5	Summary	85
5	Results and Discussion: Adsorption Isotherms	86
5.1	Various Adsorbents and Water Isotherms	86
5.2	Isotherm of MOFs + Methane Systems	91
5.3	Summary	105
6	Results and Discussion: Adsorption Kinetics	107
6.1	Silica gel and Water Adsorption Kinetics	109
6.2	Summary	115
7	Conclusions and Recommendations	117
	References	120
	Appendices	147
A	Calibration of Pressure Transducer	148
B	Cryostat Standard Operating Procedure	151
B.1	Experimental Apparatus Components	151
B.2	Operating Procedures	153
B.2.1	Disassemble and Sample Preparation	153
B.2.2	Void Volume Calibration and Regeneration	154
B.2.3	Adsorption Cycle	154
B.2.4	Housekeeping	156
C	Experimental Data Processing	157
D	Configurations for Grand Canonical Monte Carlo Simulation	164

List of Figures

Chapter 1

1.1	Working procedure of a typical adsorption chiller.	2
1.2	Scheme of coupling of LNG re-gasification and filling of the ANG vessel.	5

Chapter 2

2.1	The dispersion-repulsion potential.	12
2.2	Adsorbate behaviour in an adsorption process.	14
2.3	Adsorbent structure.	16
2.4	Adsorbent structure of (a) zeolite ACO, (b) activated carbon, (c) carbon nanotubes, and (d) MOF-5.	17
2.5	IUPAC classification of five types of adsorption isotherm	20
2.6	Molecular diffusion controlling mechanisms	27

Chapter 3

3.1	The high order curves from numerator and denominator of equation (3.17) and their corresponding shortcuts.	42
3.2	The population distribution of adsorption uptakes with different Boltzmann levels.	44
3.3	Langmuir adsorption coverage θ for temperature 10K, 80K, 150K, 220K, 290K, and 360K, with Φ_G^* ranging from -10 to 10 kJ/mol.	46
3.4	Isotherm behaviours of Equation (3.21).	48

3.5	The hexagonal lattice of the FHP model. Lattice particles are represented by arrows, and surface with adsorption force field is represented by dashed line. The adsorbed particles are represented by point at the centre.	53
3.6	The FHP lattice with hexagonal symmetry. The lattice particles movements are represented by arrows	54
3.7	The evaluation rule of FHP model for 2 incoming particles onto 2 surfaces with 1 adsorbed particle. Lattice on the left with incoming state as 5225, will evaluates into lattice on the right as digit 5440. . .	55
3.8	Porous network within hexagonal lattice space by random surface of each cell.	56
3.9	LGCA evaluation for adsorption kinetics emulation.	57
3.10	LGCA adsorption kinetics with various emulation steps. The experimental data of silica gel + water are added herein for qualitative comparison purpose.	58

Chapter 4

4.1	X-ray diffraction (XRD) patterns of AQSOA-Z01 and AQSOA-Z02 adsorbents, peaks corresponding to reflection planes are indexed. . . .	63
4.2	SEM micrographs of (a) AQSOA-Z01, and (b) AQSOA-Z02 zeolite powders.	64
4.3	Weight loss versus temperature TGA curves of (a) AQSOA-Z01, and (b) AQSOA-Z02 zeolite powders heated up to 500 °C in air.	65
4.4	SEM Photographs and Pore Size Distribution of Maxsorb III.	67
4.5	SEM micrograph of HKUST-1 MOF showing particles having octahedral shape with average diameter of 5 μm	68
4.6	X-ray diffraction pattern of HKUST-1 MOF showing peaks corresponding to reflection planes are indexed. The inset shows the Rietveld refinement of this XRD pattern.	69

4.7	Unit cell crystallization structure of the HKUST-1 viewed from the [100] direction. (C, gray; H, white; O, red; Cu, pink)	70
4.8	Weight loss vs. temperature TGA curves of HKUST-1 MOF heated up to 550 °C in air. The initial weight loss (12 wt%) up to 150 °C due to desorption of physically adsorbed moisture and the sudden weight loss (51 wt%) at 330 °C due to the total degradation of BTC linker are observed.	71
4.9	X-ray diffraction pattern of MIL-101 (Cr) MOF, peaks corresponding to reflection planes are indexed.	73
4.10	SEM micrograph of MIL-101(Cr) (a) before and (b) after purification, showing particles having octahedral shape with average size of 1 μm	74
4.11	Weight loss vs. temperature TGA curve of MIL-101(Cr) heated up to 550 °C in air. The initial weight loss (45 wt%) up to 125 °C due to desorption of physically adsorbed water and the sudden weight loss (25 wt%) at 350 °C due to the total degradation of BDC linker of MOF are observed.	75
4.12	Fourier transform infrared (FTIR) spectra of MIL-101 (Cr) (a) before and (b) after CH_4 adsorption runs.	76
4.13	Unit cell crystallisation structure of the MIL101(Cr) viewed from the [100] direction, and its geometry size comparison with HKUST-1. (C, gray; H, white; O, red; Cu, pink; Cr, blue-gray)	77
4.14	Schematic of experimental apparatus.	78
4.15	Schematic diagram of cryogenic adsorption setup.	81
4.16	Pictorial view of cryogenic adsorption setup.	82

Chapter 5

5.1	Adsorption characteristics of various hydrophilic and hydrophobic porous adsorbents with adsorption cooling operation ranges.	87
-----	---	----

5.2	Water vapour uptakes on AQSOA-Z01 and AQSOA-Z05 with adsorption-desorption operating points.	89
5.3	Adsorption-desorption cycle of silica gel + water ($A'B'CD$) and AQSOA-Z01 + water ($ABCD$).	90
5.4	Gravimetric and volumetric adsorption isotherms of CH_4 on HKUST-1 MOF at 125 K, 130 K, 140 K, 200 K and 298 K. The logarithmic pressure scale is employed. The red lines show the fitting results with the proposed isotherm Equation (3.21).	92
5.5	Isosteric heat of adsorption for HKUST-1 + CH_4 against uptakes for 125 K and 140 K.	93
5.6	A comparison of various MOFs and Maxsorb III for gravimetric CH_4 uptakes at 130 K. The fitting results with the proposed isotherm Equation (3.21) are plotted.	94
5.7	A comparison of various MOFs and Maxsorb III for volumetric CH_4 uptakes at 130 K.	95
5.8	Gravimetric and volumetric uptake isotherms of CH_4 onto MIL-101(Cr) for the temperatures ranging from 130 K to 298 K. The fitting results from the proposed isotherm Equation (3.21) are shown in red lines. The Langmuir (blue line) and DA (green line) isotherms are also applied for comparison.	96
5.9	Isosteric heat of adsorption for MIL-101(Cr) + CH_4 against uptakes for 125 K, 130 K and 140 K.	96
5.10	Pressure benefits of CH_4 adsorption on MIL-101(Cr) MOF at 160 K. The discharge of CH_4 is shown at 298 K and 5 bar with net working or delivery capacity.	97

5.11	Comparison of excess volumetric and gravimetric uptakes of CH ₄ at 130 K onto eight adsorbent materials: MIL-101(Cr), HKUST-1, Ni-MOF-74, PCN-14, UTSA-20, NU-125, NU-111 and activated carbon (Maxsorb III). The results are fitted with the proposed isotherm Equation (3.21).	98
5.12	Verification of the GCMC simulated excess isotherm of CH ₄ on HKUST-1 with the reference results at ambient temperature 298 K.	103
5.13	Snapshots of CH ₄ (green spheres) in HKUST-1 MOF at 140 K for 1 kPa, 5 kPa, and 600 kPa	103
5.14	Density distribution of CH ₄ in HKUST-1 at 5 kPa and 140 K.	104
5.15	Snapshots view from [110] direction of CH ₄ (green sphere) in MIL-101(Cr) at 130 K for 1 kPa (Top), 5 kPa (Middle) and 100 kPa (Bottom).	106

Chapter 6

6.1	Schematic layout of a two-bed adsorption chiller with various configurations of adsorbent layer in the sorption beds.	108
6.2	Isosteric heat of adsorption for silica gel water system at zero surface coverage against pore widths of silica gels. Here Q_{st}^* for type RD silica gel and water is shown. Here, blue: 303.15 K, green: 308.15 K, red: 328.15 K, and black: 358.15 K.	110
6.3	The pore size distribution of type RD silica gel for its local maxima and minimum pore width information.	110
6.4	Isotherms of silica gel and water vapour for temperatures of 15 °C, 25 °C, 35 °C, 45 °C, 55 °C and 75 °C.	111
6.5	Dimensionless average adsorption kinetics behaviours of silica gel + water system from pre-cooling to adsorption stage (50 °C→30 °C) for experimentally measured 1 □, 4 ■ and 8 ○ layers configuration with grain sizes of 0.2-0.25 mm.	112

6.6	The dimensionless average adsorption kinetics behaviours with Langmuir Equation (2.17).	113
6.7	Dimensionless desorption kinetics behaviours of silica gel + water system ranging from pre-heating to desorption mode (58 °C→80 °C) of adsorption cooling cycle for experimentally measured 1 □, 4 ■ and 8 ○ layers configuration with grain sizes of 0.2-0.25 mm.	115
6.8	The dimensionless average desorption kinetics behaviours with Langmuir Equation (2.17).	116

Chapter A

A.1	Pressure transducer (Kyowa-PGS-200KA) calibration with the hydraulic deadweight tester.	148
A.2	Calibration and linear fitting analysis converting voltage to pressure value for Kyowa-PGS-200KA pressure transducers.	150

Chapter B

B.1	Experimental apparatus components.	152
-----	--	-----

Chapter C

C.1	Thermal property surface of adsorbate from REFPROP and reconstructed with Mathematica.	159
C.2	Information dialog.	160
C.3	Adsorption cell pressure profile.	160
C.4	Charging cell temperature profile.	160
C.5	Charging cell pressure profile.	161
C.6	Typical excess adsorption isotherm data processing result.	163

List of Tables

Chapter 2

2.1	Thermodynamic Properties of a Single Component Adsorbent + adsorbate System	15
2.2	Adsorption Characterization of Adsorbents	18
2.3	Ideal Monolayer Surface Isotherm Equations	21
2.4	Empirical Monolayer Surface Isotherm Equations	23
2.5	Ideal Microporous Isotherm Equations	24
2.6	Heterogeneous Adsorption Isotherm Equations	24
2.7	Diffusivity of Different Diffusion Mechanisms	26
2.8	Theoretical Work on Isotherm of Other Researchers	31

Chapter 3

3.1	Adsorption Isotherm Classification with Parameters K_h and m	47
-----	--	----

Chapter 4

4.1	Porous Properties of Maxsorb III	66
-----	--	----

Chapter 5

5.1	Fitting parameters with least squares from the proposed isotherm Equation (3.21) for cooling applications.	90
5.2	Fitting parameters from the proposed isotherm Equation (3.21) for CH_4 adsorption with HKUST-1.	93

5.3	Fitting parameters from the proposed isotherm Equation (3.21) for CH_4 adsorption with MIL-101(Cr).	95
5.4	Fitting parameters from the proposed isotherm Equation (3.21) for eight adsorbent materials at cryogenic 130 K.	99
5.5	Lennard-Jones (LJ) Potential Parameters for CH_4 with HKUST-1 and MIL-101(Cr)	101

Chapter 6

6.1	Model parameters of H_2O for slit-shaped nanopores theory	109
6.2	Parameters for adsorption isotherms and kinetics (303 K and 880 Pa) of type RD silica gel + water system	114

Nomenclature

Abbreviations

Abbreviation	Meaning
ACF	- Activated Carbon Fibre
ADC	- Adsorption Chiller
ANG	- Adsorbed Gas Storage
BAC	- Bead Activated Carbon
BET	- Brunauer-Emmett-Teller Theory
C-C	- Clausius-Clapeyron relation
CFD	- Computational Fluid Dynamics
CNT	- Carbon Nanotube
COP	- Coefficient of Performance
EAC	- Extruded Activated Carbon
FDM	- Finite Difference Method
FEM	- Finite Element Method
FVM	- Finite Volume Method
GAC	- Granular Activated Carbon
GCMC	- Grand Canonical Monte Carlo
IUPAC	- International Union of Applied Chemistry
LBM	- Lattice Boltzmann Method
LDF	- Linear Driving Force
LGCA	- Lattice Gas Cellular Automaton

MOF	- Metal-organic Framework
MWNT	- Multi-walled Carbon Nanotube
NG	- Natural Gas Storage
OFHC	- Oxygen-free High Thermal Conductivity
PAC	- Powdered Activated Carbon
RMSE	- Root-mean-square Error
SEM	- Scanning Electron Microscopy
SWNT	- Single-walled Carbon Nanotube
TEM	- Transmission Electron Microscopy
TGA	- Thermo-gravimetric Analyzer
XRD	- X-ray Diffraction

Greek Symbols

Symbol	Meaning	Unit
α	- Angle	$^{\circ}$
α_B	- Bragg's angle	$^{\circ}$
α_P	- polarizability	$\text{C}\cdot\text{m}^2/\text{V}$
β	- pre-exponential coefficient	$[-]$
β_{int}	- line broadening at half maximum intensity	nm
Δ	- separation between adsorbent planes	$\text{\AA}$
ϵ	- Lennard-Jones force constant	kJ/mol
η	- permanent dipole moment	$\text{C}\cdot\text{m}$
γ	- time constant	s
λ	- absolute activity	$[-]$
λ_{ray}	- X-ray wavelength	nm
μ	- chemical potential	kJ/mol
$\mu^{\ominus}$	- reference chemical potential	kJ/mol
μ_p	- viscosity in poise	$\text{Pa}\cdot\text{s}$

μ_{ext}	- external adsorbent wall potential	kJ/mol
μ_{gas}	- chemical potential of bulk phase	kJ/mol
ϕ	- adsorption potential energy	kJ
ϕ_G	- grand potential	kJ
Φ_G^*	- adsorption characteristics energy	kJ/mol
ϕ_μ	- field dipole energy	kJ
ϕ_D	- dispersion energy	kJ
ϕ_G^*	- adsorption characteristics energy	kJ/kg
ϕ_P	- polarization energy	kJ
ϕ_Q	- field gradient quadrupole energy	kJ
ϕ_R	- repulsion energy	kJ
ϕ_S	- sorbate-sorbate interaction energy	kJ
ψ_{ip}	- state of node at ip in lattice gas model	[-]
ρ	- density of gas	kg/m ³
ρ_l	- liquid density of adsorbate	kg
ρ_s	- density of solid adsorbent	kg/m ³
σ	- surface tension	N/m
σ_{sf}	- solid-fluid collision diameter	Å
τ	- residence time of migrating molecule	s
τ_{cry}	- mean crystallite size	nm
θ	- surface coverage	kg/kg
θ_t	- real time surface coverage	kg/kg
θ_{ini}	- initial adsorption fraction	kg/kg
ε_{sf}	- solid-fluid well depth potential	kJ
φ	- spreading pressure	kPa
ϖ	- partition function	[-]
ξ	- grand partition function	kJ/mol
ζ	- adsorbed phase area	m ²

Latin Symbols

Symbol	Meaning	Unit
d	- pore size of adsorbent	nm
b	- equilibrium constant	kPa ⁻¹
b_{∞}	- affinity constant	kPa ⁻¹
C	- number of components	[-]
c	- mass concentration	mol/m ³
C_r	- friction coefficient	[-]
c_p	- specific heat	kJ/kg·K
D	- diffusivity	m ² /s
E_a	- activated energy	kJ
E_0	- characteristic energy	kJ
F	- <i>Degree of Freedom</i>	[-]
h	- enthalpy	kJ/kg
I	- number of restricted phases	[-]
k	- Boltzmann constant	K·m ² kg/s ²
K_h	- Henry's coefficient	kPa·kg/kg
M	- molecular weight	kg
m	- adsorbed molecules maximum number	[-]
n	- adsorbed molecules number	[-]
P	- pressure	kPa
P_n	- number of phases	[-]
Q	- quadrupole moment	C·m ²
q	- local charge density	C/m ³
Q_{st}	- isosteric heat of adsorption	kJ/kg
r	- distance between molecules	m
R_p	- mean pore radius	m
R_g	- ideal gas constant	kJ/K·mol ⁻¹

s	- entropy	$\text{kJ/kg}\cdot\text{K}$
T	- temperature	K
u	- internal energy	kJ/kg
v_a	- specific adsorbed phase volume	m^3/kg
v_g	- specific gas phase volume	m^3/kg
x_a	- amount of adsorbate uptake	kg/kg
x_0	- adsorption uptake capacity	kg/kg
z	- coordination number	$[-]$

Chapter 1

Introduction

1.1 Adsorption Process

Adsorption phenomena are well-known to mankind and they are increasingly utilised to perform separation process [1, 2], purification of gases [3], adsorption chillers [2, 4–10], cryocoolers design, hydrogen driven vehicle [11–14] and more recently gas storage [15–21]. The physical adsorption process occurs mainly within the pores of adsorbent and the external adsorbent surface, and it requires the knowledge of the adsorption characteristics over wide ranges of pressures and temperatures. The amount of adsorbate uptake depends on the nature of adsorbates and the porous adsorbent structure. For higher adsorptive capacity, the adsorbents should have a very high surface area and high micropore volume with an optimum pore width that varies from super micropore to mesopores [9, 22]. The porous medium is naturally associated with very small pores and adsorbate molecules have to find their way to the interior surface area or micropore volume. This path-finding gives rise to the so called diffusional resistance towards molecular flow within the scope of adsorption kinetics. Understanding the thermodynamics of adsorptive capacity and the diffusional resistance within the adsorbents pore, a thermodynamic framework for the calculation of adsorbate uptake and kinetics is obliged to be developed and formulated. To properly understand an adsorption process, both the equilibria and

kinetics must be understood, the analysis of which is one of the main themes of this thesis.

In recent years, research efforts on thermally powered heat transmission systems such as the adsorption chiller have gained considerable interest for cooling applications [7, 23–44], due to its higher energy consumption (more than 50%) and considering CO₂ emissions generated from electrically driven mechanical compression chillers and heat pumps. The development of adsorption chiller (ADC) depends on the thermal compression and stability of adsorbent + adsorbate system with the unique features of (a) no risk of damage, (b) environmentally friendly (c) very low intrinsic electricity consumption, (d) no moving parts and (e) scalability with the potential of low maintenance effort and costs [39, 45, 46]. The ADC produces the useful cooling effects at the evaporator by the amalgamation of adsorption-triggered-evaporation and desorption-activated-condensation [9] as illustrated in Figure 1.1. The coefficient of

Figure 1.1: Water (has the highest evaporation enthalpy of all known fluids and is non-hazardous) is vaporized at a low pressure, taking up the heat of evaporation, Q_{evap} . The water molecules are then incorporated into AQSOA adsorbents, generating the heat of adsorption Q_{ads} . When the adsorbent material is completely loaded with water molecules, it is regenerated by applying driving heat Q_{des} for desorption. The water desorbs, condenses at a ambient temperature level releasing the condensation heat Q_{cond} , and is consequently available for the next cycle. Depending on the operation direction and therewith the heat sources and sinks, this heat transmission device can be used as the chiller or heat pump.

performance (i.e. the relation between useful cooling, Q_{evap} and driving heat energies, Q_{des} or Q_{evap}/Q_{des} in short), power density and operating lifetime of the ADC are governed by the adsorbent material and its figures of merit namely porosity, water

adsorption capacity, hydrophilicity and hydrothermal stability [9, 33]. The amount of water vapour per adsorption-desorption cycle and the required temperatures for adsorption and desorption directly depend on the hydrophilicity of the material, i.e. the shape of the adsorption isotherms. For the realistic performance characteristics of adsorption chiller, the relative pressure P/P_s of adsorbent-adsorbate system ranges from 0.05 to 0.25 [33], where P_s is the saturated pressure. Traditionally, inorganic porous substances such as silica gel, aluminophosphates, or zeolites have been investigated for cooling purposes. The key problem with silica gel/zeolite or aluminophosphates adsorbents for cooling applications is that most of the water adsorption occurs at too high relative pressures (P/P_s), this means that the working capacity (amount of adsorbate during uptake and offtake) over the cooling cycle (adsorption + desorption) is only a small part of the total adsorption capacity of the silica gel or zeolites. The adsorption isotherms of these materials may be tailored to a specific adsorbent by adjusting pore size, framework structure and composition. A new class of unique high-performance adsorbent materials such as aluminophosphate based AQSOA was developed for desiccant cooling and dehumidification applications [44] due to its ability for the adsorption and regeneration of water vapour efficiently at low temperature ranges. In this thesis, a detailed characterisation and property evaluation of AQSOA-Z01 and AQSOA-Z02 zeolites for adsorption cooling application will be reported.

Leading to global warming issues, CO₂ remains to be an important greenhouse gas with increasing concentration in the atmosphere. CO₂ capture through adsorption technology has become a significant research topic currently [3, 11, 47–53]. With over 85 % of the global energy demand supported by fossil fuels, concentration of CO₂ they release is growing rapidly in the atmosphere, and leads to over 60 % of global warming issues. As a result, CO₂ is referred as the "primary anthropogenic" greenhouse gas [3]. CO₂ emissions is expected to be reduced by 80-90 % for modern power plant equipped with suitable CO₂ capture and storage technologies [3].

The demand for alternative fuel is increasing due to concerns over national and

regional energy security, ground level air quality and climate change. Natural Gas (NG) containing mainly methane is the most prospective energy source in forthcoming decades as a potential fuel to the low carbon energy as methane delivers roughly twice the energy of coal in terms of the amount of CO_2 released [54].

NG is generally transported from the wellhead to the processing plant and consumers through high pressure gas pipelines. The transportation of NG to remote locations which are separated by large water reservoirs is conducted in its liquid form. Conventionally, there are three different methods of natural gas storage namely (i) compressed natural gas (CNG), (ii) liquefied natural gas (LNG), and (iii) adsorbed natural gas (ANG). CNG is limited to high-pressure facilities with its accompanied hazards. The disadvantages of LNG are; (i) the prolonged storage in an enclosed space is hazardous due to warming, and concomitant pressure build up in the cryogenic fuel tank and (ii) refuelling must be handled by trained personnel because of the danger of injury through contact with cryogenic CH_4 liquids.

As an alternative, ANG vessels can be designed to store NG at relatively low pressure, in a lightweight cylinder filled with porous adsorbents. The highest reported volumetric CH_4 capacities for activated carbons are in the range of 100-170 cm^3/cm^3 , which is well below the energy density of CNG. In 2012, the US Department of Energy set new CH_4 storage targets for adsorbents at 350 cm^3 (STP) per cm^3 adsorbent and 0.5 g CH_4 per g adsorbent at ambient conditions [55]. The storage of methane on adsorbents at ambient temperature requires (i) extra cooling energy due to higher enthalpy of adsorption, and (ii) higher time to reach thermal equilibrium during charging of CH_4 on porous adsorbents. Due to the availability of LNG and its re-gasification issues at comparatively lower pressures, the storage of methane at lower temperature is an important research area. A proposed solution as shown in Figure 1.2 is the coupling of LNG vaporization and ANG tank filling process [56], and utilizes the exergy of LNG by the direct usage of refrigeration power generated by LNG vaporization fluid. This method uses the latent heat of LNG vaporization for the pre-cooling of ANG adsorption bed. Due to a high temperature dependency of

adsorption phenomenon, the filling process of cold ANG can be performed with lower pressure in a well designed vessel. In that case, there is no need for the multi-stage gas compressor to pump the desired amount of gas in the vessel, which saves energy. Coupling of LNG and ANG helps the ANG technology due to high purity of methane (usually 94 to 98 %) i.e. the gas given to the adsorption process does not immediately cause bed degradation. This technique would help (i) to avoid the complexity of re-gasification of the LNG to ambient condition, and (ii) to use the cooling energy of LNG for district cooling applications. To implement this technique, the adsorption characteristics of CH_4 + porous adsorbent material must be well known for the temperatures ranging from 120 K to 303 K. However, major attention to ANG is put on its application at ambient conditions [16, 19, 20, 57–59]. Hence this thesis aspires to develop the theoretical and experimental studies of the adsorbate + adsorbent thermodynamic frameworks, with prospective applications to adsorptive chilling and natural gas storage.

Figure 1.2: Scheme of coupling of LNG re-gasification and filling of the ANG vessel.

From 2014, Singapore LNG Corporation has launched the Liquefied Natural Gas terminal program [60] for better energy security, cost effectiveness and environmental friendliness. By combining liquefied and adsorbed natural gas technologies, higher efficiency of energy usage is possible to be achieved in the future. The current obstacle for adsorbed natural gas technology popularization is that the ideal adsorbent material realizing the industrial storage target has yet been discovered. Therefore, much

research effort, including theoretical, experimental, and computational approaches, is desired for adsorbent material development, industrial thermodynamic process optimisations, etc.

1.2 Motivation

It is well known that the knowledge of adsorption isotherms and kinetics is needed for (1) the design and modelling of adsorbent reactors for gas storage, separation, purification and (2) cryo-cooling and most recently adsorption cooling applications. A number of adsorption isotherm equations have already been proposed and applied, these are [61]: Henry’s isotherm model, Langmuir equation [62, 63], Tóth model [22, 64], Frenundlich isotherm [64, 65], Dubinin-Astakhov or micropore filling equation [66–68] for calculating monolayer uptakes and Brunauer-Emmett-Teller Theory (BET) [69], for multi-layer adsorption uptakes. It should be noted here that all of these isotherm models are not complete in terms of applications that range from Henry’s ($P \rightarrow 0$) region to the saturated pressure ($P \rightarrow P_s$) region, whereas P is the adsorption equilibrium pressure, and P_s is the saturated pressure. As to conventional empirical isotherm models stemming from numerical analysis, they are unrelated to physical factors, which give rise to the result that these equations do not allow extrapolation out the range of variables for which the parameters have been determined, so that none of them is qualified with practical significance [65]. Furthermore, no existing adsorption isotherm is able to fit all five different adsorption isotherm types, as proposed by Brunauer et al. [69].

On the other hand, the adsorption rate or kinetic equations are widely used to describe adsorption data at non-equilibrium conditions, and it is of great significant to investigate the basic understanding of adsorption process that ranges from transient to the cyclic steady state. Current widely used adsorption kinetics includes: Langmuirian Kinetics model [70, 71], Fickian Diffusion model (FD) [72, 73], Linear Driving Force (LDF) model [73–75], Statistical Rate Theory (SRT) [76–78], etc. However, up to

now, no attempts are yet reported to explain the theoretical origins of adsorption rate equations for a single component adsorbent + adsorbate system in detail, and the current understanding of adsorption kinetics is not more established compared to the theoretical description of adsorption isotherm.

1.3 Research Objectives and Scopes

This research aims to develop a formalism of adsorption isotherms from the rigour of partition distribution function of each adsorptive site and the isosteric heat of adsorption at zero surface coverage for the calculation of adsorbate uptakes on various adsorbent materials. The proposed thermodynamic framework ranges from Henry’s to the saturated pressure and is applied to water vapor adsorption for the design and development into advanced materials for adsorption cooling applications, and to methane adsorption for the natural gas storage purpose. The proposed model is expected to be thermodynamically connected with the pore structures of adsorbent materials, and the guest molecules uptake highly depends on the isosteric heat of adsorption at zero surface coverage and the adsorptive sites of the adsorbent materials. Employing the proposed model, the thermodynamic trends of adsorbate uptakes on various adsorbents are estimated.

The research also attempts to focus more on the theoretical origins of the adsorption rate equation from the thermodynamics foundation of adsorption uptakes that varies from the Henry’s region (pressure $\rightarrow 0$). to the saturated pressure (P_s) values. The proposed adsorption kinetics formulation is connected with the pore structures or the heterogeneity factors of adsorbent materials and the isosteric heat of adsorption at zero surface coverage Q_{st}^* .

To experimentally measure the adsorption uptake of various adsorbate onto different adsorbent materials, under different temperatures (120 to 303 K) and pressures (up to 10 bar), a general volumetric apparatus incorporating with a cryostat is designed and fabricated. The amount of methane uptakes are computed in the unit

cell of Metal-organic Frameworks employing Grand Canonical Monte Carlo (GCMC) simulation and these results are compared with the experimental data. These research efforts provide necessary information and knowledge about adsorption cooling and gas storage system design and analysis.

1.4 Layout of Report

This report comprises seven chapters, and the arrangement is as follows:

Chapter 1: Introduction

Chapter 2: Literature Review

Chapter 3: Development of An Adsorption Isotherm and Kinetics Equation

Chapter 4: Experimental Investigation

Chapter 5: Results and Discussion: Adsorption Isotherms

Chapter 6: Results and Discussion: Adsorption Kinetics

Chapter 7: Conclusions

This report begins with an introduction from Chapter 1, which is followed by a literature review at Chapter 2. Brief description of the adsorption fundamentals is presented, including driving force field for adsorption phenomenon, typical adsorption processes, adsorption thermodynamical properties, adsorbent characteristics, various conventional adsorption isotherms, and their corresponding limitations, as well as adsorption kinetics theory. Advances of other researchers' distinguished works are also provided in this chapter.

Chapter 3 introduces the concepts of adsorption equilibrium as a function of pressure, temperature and the amount of adsorbate uptakes. This chapter mainly deals with the development of a novel adsorption isotherm equation from the rigor of statistical thermodynamics, which is valid from Henry's region to the saturated

pressure for various temperatures ranging from the subcritical to the supercritical regions. The proposed isotherm equation is expected to be applied to various isotherms according to IUPAC.

Chapter 3 also analyses the grand partition function within statistics lattice gas model, and an adsorption kinetics equation is formulated, which predicts the adsorption rate of adsorbate + adsorbent system thermo properties. It is found that the conventional kinetics theories overestimate the desorption rate under most cases, and the foundational physical evidences addressed to the Linear Driving Force (LDF) model are modified by the proposed theory.

Chapter 4 describes experimental details of measuring adsorption characteristics, such as isotherms and kinetics for adsorption of methane and H_2O onto different types of activated carbons, zeolites, metal-organic frameworks (MOFs). To conduct cryogenic adsorption experimentation, the design detail of a cryostat with working range 120 - 420 K is discussed. The Methods of describing experimental adsorption data with the theoretical models are also provided. Thermo properties of used adsorbent materials are extensively analyzed by X-ray diffraction (XRD), scanning electron microscope (SEM), N_2 ad-/desorption isotherms, as well as thermo gravimetric analysis (TGA).

Chapter 5 discusses the experimental results and justifies the proposed isotherm model from both experimental data and the literature. Grand Canonical Monte Carlo simulation is performed and verified with the experimental results, based on which the CH_4 adsorption within unit cell of MOFs is described.

Chapter 6 analyses the adsorptive cooling framework with silica gel + H_2O application, and verifies the proposed kinetics model with the experimentally measured kinetics data.

Chapter 7 summarises the major findings up to now along with further recommendations for future research directions.

Chapter 2

Literature Review

2.1 Introduction

The efficiency of an adsorbent + adsorbate system is determined by its adsorption isotherms, kinetics and isosteric heat of adsorption [79]. In order to gain a full view of adsorption mechanisms, the knowledge needed to be clarified include:

1. The essential driving factors of physisorption;
2. The process of the adsorption with respect to temperature T , pressure P ;
3. Adsorbent categories and their properties;
4. Thermodynamic properties of adsorbate+adsorbent framework;
5. Existing adsorption isotherm models and their corresponding limitations;
6. Adsorption kinetic models and diffusion mechanisms.

This chapter aims to give a literature justification of existing adsorption isotherm and kinetics theories, and leads to the necessary information for the development of adsorption thermodynamic frameworks for adsorption process applications.

Up to now, extensive works for adsorption isotherm modelling have already been done. Langmuir [62, 63] derived, for the first time, an adsorption isotherm equation for energetically homogeneous surface adsorption from the rigour of adsorption

kinetics. Later Brunauer, et al. [69] generalised Langmuir’s work for multilayer adsorption situation and proposed a universal theory of physical adsorption named BET isotherms. Polanyi [80] defined the adsorption potential from the differential molar work of adsorption, and employing this theory, isotherms of micro-pore filling mechanism were developed [66–68, 81–86], which are known as Dubinin Radushkievich (DR) and Dubinin Astakhov (DA) equations. Cerofolini and Re et al. [87, 88] studied the theoretical foundation of DR equation, and reviewed the mathematical theory of adsorption on heterogeneous adsorbent surface. In 2005, U. von Gemmingen [89] reviewed the integral isotherm equations for heterogeneous surfaces based on Fermi-Dirac function, which is applied as the occupation index for mono sites. From Gibbs approach, Guggenheim [90] proposed a general treatment to adsorption with heat and work exchange, and Myers [91–94] established the thermodynamic framework of adsorption by expressing adsorption thermodynamic properties including Gibbs free energy, enthalpy and entropy. Following these works, Chakraborty et al. [79, 95] developed thermodynamic property fields as a function of pressure, temperature and the amount of adsorbate uptake, and based on this work an estimation of isosteric heat of adsorption was proposed which is verified against all categories of adsorbent + adsorbate pairs [96].

2.2 Driving Force for Physisorption

The driving force for physical adsorption is the interaction fields between adsorbent-adsorbate pair, which include [64, 97]: dispersion-repulsion energy $\phi = \phi_D + \phi_R$, polarization energy ϕ_P , field dipole energy ϕ_μ , field gradient quadrupole energy ϕ_Q , sorbate-sorbate interaction energy ϕ_S .

The dispersion-repulsion energy is represented by the familiar Lennard-Jones potential function [98]

$$\phi = \phi_D + \phi_R = 4\epsilon \left[\left(\frac{\delta}{r} \right)^{12} - \left(\frac{\delta}{r} \right)^6 \right] \quad (2.1)$$

where the force constants ϵ and δ are characteristics of the particular molecular species, and r is the distance between centres of the interacting molecules, as shown at Figure 2.1 [99].

Figure 2.1: The dispersion-repulsion potential.

Interacting with ionic adsorbents such like zeolites which have a crystalline electric field, nonpolar molecules will be affected by electrostatic polarisation potential, which is expressed as

$$\phi_P = -\frac{1}{2}\alpha_P E^2 \quad (2.2)$$

where α_P is the polarisability, and E is the electric field.

In case of polar molecules interacting with ionic adsorbents, the field-dipole energy is given by

$$\phi_\mu = -\eta E \cos \varphi \quad (2.3)$$

where η is the permanent dipole moment of the adsorbed molecules, while φ is the angle between E and η .

The field gradient-quadrupole interaction potential is

$$\phi_Q = \frac{Q}{2} \frac{\partial E}{\partial r} \quad (2.4)$$

where Q is the quadrupole moment of the adsorbed molecules, defined by

$$Q = \frac{1}{2} \int q(\rho, \theta) (3 \cos^2 \theta - 1) \rho^2 dV \quad (2.5)$$

where $q(\rho, \theta)$ is the local charge density of point (ρ, θ) , and the origin located at the center of the molecule. The integration is processed over the entire volume of the molecule.

As a result, for any ionic adsorbent the overall potential could be written by summing the six energy terms as [22]

$$\phi = \phi_D + \phi_R + \phi_P + \phi_\mu + \phi_Q + \phi_S \quad (2.6)$$

2.3 Adsorption Process

Any unoccupied surface of solid is featured that not all van der Waals forces (dispersion-repulsion) field, electrostatic interactions and chemical bonds of the atoms that constitute this surface is saturated [80, 97]. This fact leads to the accumulation of molecules from the bulk onto the solid surface, and/or diffusion into macropores, mesopores, and micropores within the adsorbent solid, and then adhering onto the surface in the micropores, and/or fill up the volume within the micropores. The process is known as **adsorption**. Whenever the adsorbent solid is exposed to fluid of adsorbate composition, adsorption takes place, and the adsorbent + adsorbate equilibrium is reached with time [75, 79, 100, 101].

Although adsorption and desorption are conventionally considered reversible, recent research has found that this is not true, due to entropy generation [79, 95]. Figure 2.2 [95] shows how adsorbate molecules huddle in the porous surface of an

adsorbent during adsorption process.

Figure 2.2: Adsorbate behaviour in an adsorption process.

In practice, a heterogeneous adsorbent surface is characterised by adsorption sites with different energies distribution over the whole solid surface [87, 88]. The essence of adsorption process is the porous solid medium with high surface area and high micropore volume, for high adsorptive capacity. Adsorption equilibrium is reached over time and the uptake molecules on adsorbent do not vary, unless external condition changes. To understand an adsorption process, both equilibrium and kinetics need to be studied [22, 64, 65].

The characterisation of adsorbent + adsorbate systems is determined by its thermodynamic properties including [79, 95]: energy, enthalpy, entropy, specific heat, adsorbed phase volume and the isosteric heat of adsorption. The formulation of these properties are furnished in Table 2.1.

2.4 Adsorbent Material Properties

A highly capable and fast rate adsorption process requires the adsorbent have both high adsorptive capacity and kinetics performance simultaneously. Adsorptive

Table 2.1: Thermodynamic Properties of a Single Component Adsorbent + adsorbate System

Property	Formulation [79, 95]
entropy (s)	$ds = (c_{p,s}/T + c_{p,a}/T) dT - (\partial v_s/\partial T)_P dP - (\partial v_a/\partial T)_{P,x} dP + [s_g - (v_g - v_a)dP/dT] dx$
enthalpy (h)	$dh = (c_{p,s} + c_{p,a})dT + [v_a - T(\partial v_s/\partial T)_P] dP + [v_a - T(\partial v_a/\partial T)_{P,x}] dP + [h_g - Q_{st}] dx$
internal energy (u)	$du = (c_{p,s} + c_{p,a})dT + [v_s - T(\partial v_s/\partial T)_P] dP + [v_a - T(\partial v_a/\partial T)_{P,x}] dP + [h_g - Q_{st}] dx - (Pdv_s + v_s dP + Pdv_a + v_a dP)$
specific volume (v_a)	$v_a = v_g - [Q_{st}^{expt} - Tv_g(\partial P/\partial T)_g] / T(\partial P/\partial T)_x$
specific heat ($c_{p,a}$)	$c_{p,a} = c_{p,g} + Q_{st} [1/T - 1/v_g(\partial v_g/\partial T)_P] - \partial Q_{st}/\partial T _P$
isosteric heat of adsorption	$Q_{st} = Tv_g(\partial P/\partial m_g)_T(\partial m_g/\partial T)_P + Tv_g(\partial P/\partial m_g)_T(\partial m_g/\partial P)_T(dP/dT)_{gas} + Q_{st} _{C-C}$

* The meanings of all symbols are given in the nomenclature section.

capacity indicates more adsorbate uptakes, while the kinetics means less time it takes to reach equilibrium. To satisfy both requirements, the adsorbents must have: i) reasonably high effective surface area and micropore volume; ii) relatively large pore network for the molecules to transport to the interior of the adsorbent particle. Therefore, adsorbents are expected to combine two pore sizes: i) the micropore size for high adsorptive capacity and ii) the meso/macropore size for good kinetics.

Normally, as illustrated by Figure 2.3, different pore sizes (d) of adsorbent are classified according to scheme proposed by the **International Union of Applied Chemistry** (IUPAC), as [102]: **micropore** (< 2 nm), **mesopore** (< 50 nm & > 2 nm), **macropore** (> 50 nm).

Figure 2.3: Adsorbent structure.

General properties of some commonly used adsorbents, inclusive of zeolite [101] (Figure 2.4a), alumina [103], silica gel [43], activated carbon (Figure 2.4b [104]), carbon nanotubes [105, 106] (Figure 2.4c), graphite [107], Metal-organic Frameworks [3, 57] (Figure 2.4d), are listed in Table 2.2. The adsorption properties of various forms of activated carbon are found similar, including: powdered activated carbon (PAC), granular activated carbon (GAC), extruded activated carbon (EAC), bead activated carbon (BAC), and activated carbon fibre (ACF). The adsorbent surface characteristics of Maxsorb III [108] are also shown in Table 2.2.

Among various types of porous adsorbents, metal-organic frameworks (MOFs) [109, 110] have become one of the most actively studied candidates, for their high surface area, porosity and thermodynamic stability [111–114]. Synthesised in a self-assembly process in which metal vertices are connected by organic linkers, there are wide variety of possible linker and corner units for MOFs to choose from [48, 57, 110, 112, 113, 115–121], which results in a large number of metal-organic frameworks [114]. Among the many MOFs that are commercially available, the copper based MOF namely HKUST-1 is investigated in current work. As one of the first robust MOF following the topology of zeolite framework [32, 109], HKUST-1 can easily demonstrate the highest total uptakes of CH_4 of any MOFs that are reported, in terms

(a) Zeolite ACO.

(b) Activated Carbon.

SWNT

MWNT

(c) Carbon Nanotubes.

(d) MOF-5.

Figure 2.4: Adsorbent structure of (a) zeolite ACO, (b) activated carbon, (c) carbon nanotubes, and (d) MOF-5.

of the volumetric measurement [122]. Therefore, this research deems the study of HKUST-1 is indictable and predictable for majority of other MOFs. Insofar, extensive works have been done in the literature to determine the adsorption properties of CH_4 with HKUST-1 at room temperature [122–124] including: the adsorption isotherms, isosteric heat, adsorption selectivity with other guest gases, etc. These works provide solid reference and are applied to validate the result in current research.

Table 2.2: Adsorption Characterization of Adsorbents

Name of Adsorbent		Thermodynamic Properties	Suitable Adsorbate
Alumina		surface area: $>200 \text{ m}^2/\text{g}$ pore width: $15 - 60 \text{ \AA}$ macropore volume: $0.51 \text{ cm}^3/\text{g}$ micropore volume: $0.49 \text{ cm}^3/\text{g}$	F^- H_2O As S
Silica Gel (type RD)		surface area: $838 \pm 3.8 \text{ m}^2/\text{g}$ pore width: 2.2 nm porous volume: $1.00 \text{ cm}^3/\text{g}$ micropore volume: 49% mesopore volume: 51%	H_2O oil H_2S alcohols
A-C	PAC	surface area: $\sim 1200 \text{ m}^2/\text{g}$ pore width: 0.9 nm macropore volume: $0.47 \text{ cm}^3/\text{g}$ micropore volume: $0.44 \text{ cm}^3/\text{g}$	CO_2 CH_4 H_2 H_2O N_2
	GAC		
	EAC		
	BAC		
	ACF		
	Max-sorb III	surface area: $3140 \text{ m}^2/\text{g}$ pore width: 2.008 nm porous volume: $2.01 \text{ cm}^3/\text{g}$ micropore volume: $1.7 \text{ cm}^3/\text{g}$ mesopore volume: $0.3 \text{ cm}^3/\text{g}$	
Zeolite (type Y)		surface area: $900 \text{ m}^2/\text{g}$ macropore volume: $0.28 \text{ cm}^3/\text{g}$ micropore volume: $0.3 \text{ cm}^3/\text{g}$ macropore width: $30\text{-}1000 \text{ nm}$ micropore width: 0.5 nm	NH_3 H_2S CO
MOF		surface area: $1218 \sim 4930 \text{ m}^2/\text{g}$ pore volume: $0.14 \sim 2.13 \text{ cm}^3/\text{g}$	CH_4 CO_2 H_2 H_2O
CNT	SWCNT	surface area: $>500 \text{ m}^2/\text{g}$ pore volume: $\sim 1.4 \text{ cm}^3/\text{g}$	CH_4 CO_2
	MWCNT		

2.5 Adsorption Isotherms

2.5.1 Adsorption Equilibria and Isotherms

An adsorption isotherm is an adsorption equilibrium at constant temperature. It expresses the amount of adsorbed phase at constant temperature as a function of the equilibrium pressure. According to *Gibbs'* phase rule, the degree of freedom, F , of thermodynamic system for an adsorption framework in equilibrium can be expressed

as [97]

$$F = C - P_n + I + 2 \quad (2.7)$$

where C is the number of components, P_n is the number of phases in thermodynamic equilibrium, and I is the number of bi-dimensional or restricted phases. In the case of single component adsorbent-adsorbate system, where $C = 2$ (adsorbent and adsorbate), $P_n = 3$ (adsorbent, adsorbate, and adsorbed phase), and $I = 1$ (the adsorbed phase), it is obvious that

$$F = 2 - 3 + 1 + 2 = 2 \quad (2.8)$$

Therefore, it is possible to express the amount adsorbed, or the uptake of adsorbate, x_a , as a function of two intensive parameters: equilibrium pressure P of bulk phase adsorbate and temperature T . As to adsorption isotherm, which means temperature is constant, adsorption isotherms are expressed as

$$x_a = f(P)_T \quad (2.9)$$

2.5.2 Classification of Adsorption Isotherms

Adsorption on practical adsorbent solid exhibits diverse isotherm shapes. Established by Brunauer et al. [69], isotherms are identified by **IUPAC** into five classical **BET** types [22, 125–127], as shown in Figure 2.5.

The type I isotherm reaches a limitation capacity, and usually is applied to describe adsorption on microporous adsorbent. Type II describe adsorption on macroporous adsorbent with strong adsorbent + adsorbate interaction, while type III with the weak. Type IV and V represent mono- and multilayer adsorption plus capillary condensation [127].

Figure 2.5: IUPAC classification of five types of adsorption isotherm

2.5.3 Isosteric Heat of Adsorption

Isosteric heat of adsorption Q_{st} is a key thermodynamic variable to quantitatively express the heat involved during the adsorption process, which is determined by the adsorbed phase conditions, including temperature T , pressure P , and mass uptake x_a . With equilibrium of heat, mass and chemical potential, thermodynamic modelling that could reproduce all trends of Q_{st} have been reported in the literature, given as [79, 96]

$$\begin{aligned} Q_{st} &\cong T v_g \left(\frac{\partial P}{\partial x_a} \right)_T \frac{dx_a}{dT} + R T^2 \left(\frac{\partial \ln P}{\partial T} \right)_{x_a} \\ &= T v_g \left(\frac{\partial P}{\partial x_a} \right)_T \frac{dx_a}{dT} + Q_{st}|_{C-C} \end{aligned} \quad (2.10)$$

$Q_{st}|_{C-C}$ is the simplified isosteric heat of adsorption stemming from the Clausius-Clapeyron relation with the assumption of the ideal gas behaviour of adsorbate and the negligible volume effect of the adsorbed phase. With the use of Langmuir isotherm, $Q_{st}|_{C-C}$ can be expressed as [22]

$$\frac{Q_{st}|_{C-C}}{R_g T^2} = \frac{\partial \ln P}{\partial T} \bigg|_{x_a} \quad (2.11)$$

If it appears to be constant with increasing of adsorbate loading, Q_{st} indicates an energetically homogeneous adsorbent; If Q_{st} decreases with adsorbate uptake, there normally is a variability in the energetic heterogeneity of the adsorbent; Q_{st} may increase with adsorbate loading when strong lateral interactions occur between the adsorbed molecules at higher surface coverage. The relationships are listed below [96]

$$Q_{st} \begin{cases} \text{constant} & \text{energetically homogeneous adsorbent;} \\ \text{decrease} & \text{energetically heterogeneous adsorbent;} \\ \text{increase} & \text{lateral interactions between adsorbed molecules.} \end{cases}$$

2.5.4 Surface Adsorption Isotherm

From a generic *Gibbs* approach, several ideal isotherm equations can be derived, which are listed in Table 2.3 with their individual limitations [102, 125].

Table 2.3: Ideal Monolayer Surface Isotherm Equations

Isotherms	Isotherm Equation*	Limitations
Henry's Isotherm [102]	$\theta = K_h P$	Only valid within extremely low pressure or concentration range.
Langmuir Equation [102]	$\theta = \frac{b_\infty \exp(Q_{st}/R_g T) P}{1 + b_\infty \exp(Q_{st}/R_g T) P}$	Mobility & interaction between adsorbing molecules are NOT taken into account. Results are NOT accurate at high pressure range.
Volmer Isotherm [125]	$bP = \frac{\theta}{1 - \theta} \exp\left(\frac{\theta}{1 - \theta}\right)$	Interaction between adsorbing molecules are NOT taken into account.
Fowler-Guggenheim Equation [102, 125]	$bP = \frac{\theta}{1 - \theta} \exp\left(-\frac{z\phi_S \theta}{R_g T}\right)$	Mobility of adsorbing molecules are NOT taken into account.
Hill-de Boer Isotherm [102, 125]	$\frac{bP}{\theta} = \frac{\theta}{1 - \theta} \exp\left(\frac{\theta}{1 - \theta}\right) \exp\left(-\frac{z\phi_S \theta}{R_g T}\right)$	Invalid in the vicinity of the critical point.

* The meanings of all symbols are given in the nomenclature section.

Ideal isotherms as shown in Table 2.3 are developed based on assumptions that either the adsorbent surface is homogeneous or the adsorbate on surface is localized. However, these assumptions are rarely conformed in reality due to complex pore and surface structure of adsorbent [87]. As complements, many empirical or semi-empirical isotherms were proposed to overcome this limitation. These isotherms correlate experimental data with empirical parameters. Several commonly used empirical isotherm equations [61] are listed in Table 2.4, and with their individual limitations.

In general, the more parameters in the model, the better is the fit with experimental data. Nevertheless, the empirical isotherms are unrelated to physical factors, which means that they are invalid beyond the range of parameters where they have been determined, so that all of these empirical isotherms are qualified with no significant physical meaning [65].

2.5.5 Microporous Adsorption Isotherm

When micropore walls are in proximity of each other so that the size of micropores is comparable to the size of adsorbate molecule, theories from *Dubinin* [66–68, 81, 86] based on Polanyi potential theory [80] form the basis to model adsorption isotherm, which is particularly determined by the mechanism of volumetrically filling. Adsorption in pores smaller than 15 Å follows pore filling mechanism, and adsorption in pores larger than 15 Å while less than 1000 Å tends to follow a capillary condensation mechanism after the pressure reaches a threshold [22]. The distinction between adsorption by surface layering and by micropore filling is that in former case the chemical potential of the adsorbed is independent of the amount adsorbed, while in the latter it is function of uptake amount. The isotherms of Dubinin equations and their limitations are listed in Table 2.5.

2.5.6 Heterogeneous Adsorption Isotherm

The complexity of practical adsorption is associated with the heterogeneity of adsorbent + adsorbate pair [87, 88], which is contributed by the geometrical [128]

Table 2.4: Empirical Monolayer Surface Isotherm Equations

Isotherms	Isotherm Equation*	Limitations
Frendlich Equation	$\theta = K_h P^{1/n}$	Has no Henry law limit at low range and no saturation limit at high range, and mobility of adsorbing molecules are NOT taken into account.
Sips (LF) Equation	$\theta = \frac{(bP)^{1/n}}{1 + (bP)^{1/n}}$	Has no Henry law limit at low range, and interaction between adsorbing molecules are NOT taken into account.
Tóth Equation	$\theta = \frac{bP}{[1 + (bP)^t]^{1/t}}$	Temperature dependence of the parameter t has no theoretical footing.
Unilan Equation (Uniform + Langumir)	$\theta = \frac{1}{2s^*} \ln \left(\frac{1 + \bar{b}e^{s^*} P}{1 + \bar{b}e^{-s^*} P} \right)$	Mobility & interaction between adsorbing molecules are NOT taken into account, and surface energy distribution are assumed uniform.
Dubinin-Radushkevich Equation	$\theta = \exp \left[-\frac{1}{(\beta E_0)^2} \left(R_g T \ln \frac{P}{P_0} \right)^2 \right]$	Has no Henry law limit at low range.
Jovanovich Equation	$\theta = [1 - e^{-bP}]$	Applicable to mobile and localised adsorption, but not as popular.

* The meanings of all symbols are given in the nomenclature section.

** reference [61]

and energetical [78, 129, 130] characteristics of the adsorbent solid, as well as size, shape and conformation of adsorbate molecules.

To deal with these problems, several local isotherms, such that of Langmuir is often a popular choice, and will normally be chosen and then be averaged over distribution

Table 2.5: Ideal Microporous Isotherm Equations

Isotherms	Isotherm Equation*	Limitations
Dubinin-Radushkevich (DR) Equation [102]	$x_a = x_0 \exp \left[-\frac{1}{(\beta E_0)^2} \left(R_g T \ln \frac{P}{P_0} \right)^2 \right]$	Has no Henry law limit at low range as pressure approaching zero
Dubinin-Astakhov (DA) Equation [102]	$x_a = x_0 \exp \left[-\frac{1}{(\beta E_0)^n} \left(R_g T \ln \frac{P}{P_0} \right)^n \right]$	Has no Henry law limit at low range as pressure approaching zero

* The meanings of all symbols are given in the nomenclature section.

of some thermodynamic quantity, which could be one of the following: 1) interaction energy between adsorbent + adsorbate pair, 2) adsorbent solid micropore size, 3) Henry constant, and 4) free energy of adsorption. A number of commonly used local isotherms are furnished in Table 2.6. However, the heterogeneous isotherm equations inevitably inherit limitations of local isotherms [22].

Table 2.6: Heterogeneous Adsorption Isotherm Equations

Patch-wise Topography*	Random Topography*
$\theta^a = \left[1 + \frac{1}{bP} \exp \left(-\frac{Q_{st}}{R_g T} \right) \right]^{-1}$	
$\theta^b = \left[1 + \frac{1}{bP} \exp \left(\frac{\theta}{1-\theta} - \frac{Q_{st}}{R_g T} \right) \right]^{-1}$	
$\theta^c = \left[1 + \frac{1}{bP} \exp \left(-\frac{Q_{st} + \phi_S \theta}{R_g T} \right) \right]^{-1}$	$\theta^c = \left[1 + \frac{1}{bP} \exp \left(-\frac{Q_{st} + \phi_S \theta_{obs}}{R_g T} \right) \right]^{-1}$
$\theta^d = \left[1 + \frac{1}{bP} \exp \left(\frac{\theta}{1-\theta} - \frac{Q_{st} + \phi_S \theta}{R_g T} \right) \right]^{-1}$	$\theta^d = \left[1 + \frac{1}{bP} \exp \left(\frac{\theta}{1-\theta} - \frac{Q_{st} + \phi_S \theta_{obs}}{R_g T} \right) \right]^{-1}$

^a Local Langmuir isotherm.

^b Local Volmer isotherm.

^c Local Fowler-Guggenheim isotherm.

^d Local Hill-deBoer isotherm.

* The meanings of all symbols are given in the nomenclature section.

2.6 Adsorption Kinetics

The kinetics of adsorption is the study of the rate of adsorption to reach equilibrium [102]. Research of adsorption kinetics helps to monitor experimental conditions to have the adsorption process reach equilibrium in a designed time. When the adsorption rate and the dependent factors are known, the complicated adsorption dynamics can be understood and the adsorption frameworks can be developed for industrial applications.

Due to thermal energy, adsorbate molecules are always accompanied with a spontaneous tendency to occupy all accessible space through their random migration, to equalise their chemical potential within that space [77]. The basic mathematical model for diffusion phenomenon are Fick's first and second laws as shown in Equations (2.12) and (2.13):

$$J = -D(c) \frac{\partial c}{\partial x} \quad (2.12)$$

and

$$\frac{\partial c(x, t)}{\partial t} = D(c) \frac{d^2 c(x)}{dx^2} \quad (2.13)$$

The physical meaning of $D(c)$ depends on controlling mechanisms in specific diffusion situations, which are classified, according to pore size of adsorbent particle [75], into categories as shown in Figure 2.6:

The characteristics of different diffusion mechanisms of bulk gas phase are listed in Table 2.7 [64]. The effective diffusivity is actually a complex quantity consisting of more than one single mechanism. Though individual mechanisms are well understood, effective diffusivity is dependent on pore structure details of practical adsorbent, and therefore it proves difficult to make a precise priori prediction of any effective diffusivity.

It is well known that the adsorption chiller (ADC) utilises the adsorbent -

Table 2.7: Diffusivity of Different Diffusion Mechanisms

Mechanism	Diffusivity*	Valid Conditions
Molecular Diffusion	$D_m = \frac{0.00158T^{3/2}(1/M_1 + 1/M_2)^{1/2}}{P\sigma_{12}^2\Omega(\epsilon/kT)}$ (cm^2/s)	When pressure is larger than critical value, and mean free path of gas molecule is smaller than pore radius, therefore collisions between molecules are dominant
Knudsen Diffusion	$D_k = \frac{2}{3}\sqrt{\frac{8RT}{\pi M}}Rp$ $= 9700R_p(T/M)^{1/2}$ (cm^2/s)	When pressure is smaller than critical value, and mean free path of gas molecule is larger than pore radius, therefore collisions between molecules and pore wall are dominant
Intermediate Region	$1/D = 1/D_m + 1/D_K$	When pressure is about critical value, and mean free path of gas molecule is comparable to pore radius, therefore molecular diffusion and Knudsen diffusion coexist
Poiseuille Flow	$D = PR_p^2/8\mu_p$	when there is difference in total pressure across a particle, as in occurrence of uptake in a vacuum system
Hopping Model Surface Diffusion	$D_s = D_{s0} \frac{\theta_c}{\theta}$ $\cdot \frac{\exp(-\frac{E_{s0}}{RT}) - \exp(-\frac{Q_{st}}{RT})}{\left[1 - \exp(-\frac{Q_{st}}{RT})\right] \left[1 - \theta_c(1 - \frac{\tau_1}{\tau_0})\right]}$ $\frac{\tau_1}{\tau_0} = \frac{\left[\exp(-\frac{E_{s0}}{RT}) - \exp(-\frac{Q_{st}}{RT})\right]}{\left[\exp(-\frac{E_{s1}}{RT}) - \exp(-\frac{\lambda_{vap}}{RT})\right]}$ $\cdot \frac{\left[1 - \exp(-\frac{h_{fg}}{RT})\right]}{\left[1 - \exp(-\frac{Q_{st}}{RT})\right]}$	When heat of adsorption Q_{st} is larger than energy barrier E_s between adsorption site
Surface Flow Diffusion	$D_s = (qRT/SC_r)d \ln(p/d) \ln q$	When there is gradient of surface pressure
Micropore Diffusion	$D = D_{c0} \exp(-E_a/RT)$	When size of diffusion molecules is similar to that of pores

* The meanings of all symbols are given in the nomenclature section.

** reference [64]

Figure 2.6: Molecular diffusion controlling mechanisms

adsorbate characteristics to achieve useful cooling effect at the evaporator by the amalgamation of two processes namely ‘adsorption-triggered-evaporation’ and ‘desorption-activated-condensation’ [27]. The ADC works as a batch-wise process i.e. adsorption and desorption occur alternatively in the adsorption bed and is also time-dependent [23, 25, 38, 41]. Hence, the adsorption rate or kinetic equations are widely used to describe adsorption data at non-equilibrium conditions, and are of great significance to the basic understanding of the adsorption process that ranges from the transient to the cyclic steady state. The simplest kinetics or the Lagergren equation is commonly expressed by

$$\frac{d\theta_t}{dt} = \frac{1}{\gamma}(\theta - \theta_t) \quad (2.14)$$

where θ_t is the amount of adsorbate uptake fraction at time t , θ is its value at equilibrium, and γ is the time constant.

This rate equation indeed is in line with the concept of linear driving force (LDF) model or the first order kinetic equation [71]. The basic mathematical model for diffusion transport of adsorbates within a complex adsorbent structure is the Fick’s equation [38, 72, 74, 131–134], and is difficult to solve analytically under practical situation [75]. The linear Driving Force (LDF) model [31, 38, 50, 100, 131, 135–137] correlates experimental data in simple equation forms employing data fitting parameters. It assumes that the adsorbent particle temperature is uniform, and its

thermal conductivity is infinity, which means that the heat transfer effect is neglected. The LDF model also involves the intra-particle diffusion for mass transfer process. The physical evidence of the LDF coefficient is obtained thermodynamically from Langmuirian kinetics. LDF model gives excellent agreements with the experimental data [133]. More important, it has been proven that both the pseudo-first-order and pseudo-second-order models are special cases of Langmuir kinetics [138], the integrated form of which, described as Integrated Kinetics Langmuir equation (IKL), has also been generalised recently [70, 139]. Langmuir kinetics model is qualified with theoretical evidence, and, so are those parameters from the LDF model [137]. However, the Langmuir isotherm is limited to one site occupancy adsorption onto the homogeneous adsorbent surface. Moreover, the Langmuir isotherm gives inconsistent thermodynamic behaviour at the higher state range [89].

Bhatia et al. [75] gave an comprehensive theoretical perspective of molecular transport in nano-pores, with the proposed oscillator model and a distributed friction model. Sircar and Hufton [133] analysed the connection between the linear driving force (LDF) model and the Fickian Diffusion (FD) model, as the detailed characteristics of a local adsorption kinetic model are neglected during integrations. Based on the Langmuirian adsorption theory, Azizian [138] analyzed the general analytical solution of two extreme cases theoretically with high initial concentration of adsorbate, and lower initial concentration of solute, where the first one converts into a pseudo-first-order LDF model, while the latter follows a pseudo-second-order equation. Yu et al. [71] also gave a similar conclusion as Azizian. Based on Langmuir model, Marczewski [70] derived the integrated form of kinetics Langmuir equation (IKL), and compared it with the n th-order, mixed 1,2-order, and multi-exponential kinetic equations. Marczewski et al. [139] also proposed a generalised form of the Langmuir kinetics (gIKL), and Langmuir-Freundlich (LF) isotherm was applied to describe the non-ideal behaviour of adsorption phenomena. Later, Azizian and Bashiri [76] developed the adsorption kinetics with statistical rate theory (SRT) approach, and studied the solute adsorption at the solid/solution. The modified pseudo-first-order

(MPFO) kinetic equation, proposed by Yang et al. [74], was interpreted theoretically [76]. By applying different adsorptive site energy distribution, Rudzinski and Panczyk [130] derived the power form of Elovich equation from Langmuir-Freundlich and the Temkin isotherms. Corresponding to practical experimental conditions, Loh [140] and Chakraborty [100] proposed a theoretical framework to describe the adsorption kinetics for the non-isothermal system. Babrao and Jiang [111, 141] investigated the transport diffusivities of CO₂ and CH₄ in silicalite, C₁₆₈ schwarzite, and IRMOF-1 employing molecular dynamics simulation, and it was found that the computational results matched the Maxwell-stefan formulation for pure CO₂ and CH₄. To utilise the adsorption kinetics with adsorption chiller system, Aristov et al [26, 30, 34, 38, 42, 45, 142] studied the water adsorption kinetics on silica gel (type Fuji RD) under real operating conditions, and optimisation of various loose grains silica gel configuration.

The kinetics model of Langmuir [62, 63] is given by

$$\frac{d\theta_t}{dt} = k_{ads}P_t(1 - \theta_t) - k_{des}\theta_t \quad (2.15)$$

where θ_t is the fraction uptake as a function of time, $\theta_t = \frac{\bar{n}_t}{\bar{n}_{max}}$. $\bar{n}_{max}$ is the maximum amount of uptake. k_{ads} and k_{des} are adsorption and desorption rate coefficients. P_t is the real time equilibrium pressure of the adsorbed phase.

At equilibrium $\frac{d\theta_t}{dt} = 0$, and $\theta_t = \theta$, Equation (2.15) gives the Langmuir's isotherm as

$$\theta = \frac{K_h P}{1 + K_h P} \quad (2.16)$$

where $K_h = k_{ads}/k_{des}$. Under the situation where the initial pressure P_{ini} differs not much from the eventually equilibrium pressure P , that is $P \approx P_{ini}$, Equation (2.15) becomes to be the pseudo-first-order model [138], as given in (2.14), with $\frac{1}{\gamma} = k_{ads}P + k_{des}$. Both Equations (2.14) and (2.15) gives the same adsorption kinetics

expression as

$$\theta_t = \theta \left[1 - \exp\left(-\frac{t}{\gamma}\right) \right] + \exp\left(-\frac{t}{\gamma}\right) \theta_{ini} \quad (2.17)$$

with boundary conditions $\theta_t = \theta_{ini}$ at $t = 0$, and $\theta_t = \theta$ at $t \rightarrow \infty$.

Apart from analytical methods, numerical simulations sometimes provide a direct and intuitive result for adsorption kinetics problems. Within the microscopic scales, molecular dynamics describes the position and velocity of each particle with Hamiltons equation, taking into account the interaction potential between the particles [143]. However there are too much data to process the simulation of adsorption process into a macroscopic scale. Meanwhile, the macroscopic approaches including finite element method (FEM), finite volume method (FVM), finite difference method (FDM), etc., are also capable of adsorption simulations, only if the loading pressure is high enough so that the gaseous phase is reasonable to be treated as continuous medium.

The gap between micro-scale and macro-scale methods can be bridged with the lattice gas method (LG), stemming from cellular automata structure (CA) which allows high efficiency parallel computation [144]. Lattice Gas Cellular Automata (LGCA) with symmetry lattice configuration is capable of deriving the macroscopic Navier-Stokes equations [145–149], and therefore laid a foundation for computational fluid dynamics (CFD) methods including Lattice Boltzmann methods (LBM) [144, 150–156]. During 1973 to 1976, Hardy, Pomeau and de Pazzis proposed the first lattice gas model known as HPP model [157], where the lattice is square so that particles can move into 4 directions. However, as particles cannot move diagonally, the HPP model lacks rotation invariance and hence this model is anisotropic. Later in 1986, a hexagonal grid model was introduced by Frisch, Brosl Hasslacher and Yves Pomeau, namely FHP model [158]. This model overcomes the drawbacks of the anisotropic HPP model, and gives a symmetry performance. Therefore the FHP model is largely used today as the basis of CFD. In a 3-dimensional grid, the cube is the only regular polytope to fill the space, and hence there are up to 19 velocities. This configuration is labelled as D3Q19. 3D LGCA increases the number of dimensions, and therefore

requires more computational resources. However, the ability of parallel computation of LGCA sometimes overweighs the computational complexity introduced by dimension expansion.

Cellular automaton [143, 144, 149, 155, 157, 158] is a computation model consisting of an initial state space and those evolution rules that work on each element cell. The evolution rules of a cell depend only on a local neighborhood of cells around it. Thus, the state space is updated synchronously in parallel. Though the evolution rules are sufficient simple, cellular automaton is complex enough to demonstrate a variety of sophisticated phenomena.

2.7 Milestones of Adsorption Researches

The major theoretical work discussed in this chapter towards adsorption isotherms and kinetics, that has been done by other researchers from pioneering theoretical age to the up-date is covered in Table 2.8.

Table 2.8: Theoretical Work on Isotherm of Other Researchers

NO.	Authors & Reference	Contributions
1	Langmuir [62, 63]	From kinetic studies and for the first time, a clear concept of monolayer adsorption was derived formed on energetically homogeneous solid surfaces.
2	Polanyi [80]	Defined the differential molar work of adsorption as the adsorption potential, and assumed that it is independent of temperature. Laid a foundation for micropore isotherm from energy treatment.
3	BET [69]	Multilayer isotherm equation was proposed by Brunauer, Emmett and Teller, for the first time, from the kinetic consideration analogous to that by Langmuir. They applied Langmuir equation to every adsorption layer. BET isotherm represents a generalization of the Langmuir isotherm, and was the first attempt to create a universal theory of physical adsorption.
4	Freundlich [159, 160]	Great importance was assigned by Freundlich to the so-called Freundlich's equation as the first empirical adsorption isotherm.

NO.	Authors & Reference	Contributions
5	Hill [98, 132, 161–164]	The random model of adsorbent surfaces was introduced, in which the adsorption sites of equal adsorption energies are assumed to be distributed fully random over a heterogeneous surface.
6	Guggenheim [90]	A general approach was developed to adsorption with heat and work exchange. An interface is seen as a separate surface phase located between bulk phase and adsorbent. Proposed that the adsorption values are quantities as in the Gibbs theory.
7	Dubinin [66–68, 81, 86, 165] & Radushkevich [77, 129, 130, 166–168]	Based on Polanyi potential of adsorption, they introduced the adsorption potential as the negative work performed by the adsorption system. Isotherms suitable for volume filling micropores adsorption were developed from an energy treatment. Jovanovic isotherm was also reviewed from theoretical foundation for multilayer adsorption.
8	Everett [169, 170]	Proposed that the thermodynamics of physical adsorption is based on surface area and spreading pressure. Made an important explanation of the hysteresis feature from capillary mechanism from statistical thermodynamics approach.
9	Cerofolini [87, 88, 171, 172]	Studied the theoretical foundation of DR equation, and discussed multilayer adsorption on heterogeneous fractal surfaces. Mathematical theory of adsorption on heterogeneous surface was reviewed.
10	Binder [143]	Presented achievements of computer simulation methods in surface science, including both Monte Carlo (MC) and Molecular Dynamics (MD).
11	Myers [91, 93]	Based on isothermal condition, the thermodynamic function was developed including: Gibbs free energy, enthalpy and entropy. The heat capacity of adsorbate is equal to that in the perfect gas state.
12	Chakraborty et al. [79, 95, 96]	Based on the energy and entropy balances for adsorbent + adsorbate framework, thermodynamic property fields as a function of pressure, temperature and the amount of adsorbate uptake was developed. A theoretical framework for the estimation of isosteric heat of adsorption was proposed from view of thermodynamic requirements of chemical equilibrium, Maxwell relations, and the entropy of the adsorbed phase.
13	U. von Gemmingen [89]	Based on Fermi-Dirac function as occupation index for mono sites, the integral equation for isotherms is reviewed. He summarized that whether a surface is energetically heterogeneous or homogeneous is determined by the ratio of the energy level distribution to the thermal fluctuation.

NO.	Authors & Reference	Contributions
14	Anderson et al. [173]	Experiments and molecular simulations were combined for CO ₂ adsorption onto nano porous carbon membranes as function of temperature. CO ₂ is more readily adsorbed on nanoporous carbon than CH ₄ , and selectivity of CO ₂ from CH ₄ is increased.
15	Fernsle et al. [72]	A quasi-equilibrium model was developed to describe the adsorption and desorption of proteins to and from a surface film. A new framework is provided for analyzing interactions and adsorption of protein films, as an extension of the classical Smoluchowski analysis [62, 72].
16	Henninger et al. [28]	Thermophysical characterization of six activated carbons was reported for pore and surface analysis. The density and heat capacity of the adsorbent sample were determined.
17	Chilev et al. [174]	A new modelling type adsorption isotherm was proposed, describing the excess of adsorption of supercritical gases on microporous adsorbents. The phenomena of minimum of adsorption at very high pressure are described. A concept of inflection point and its thermodynamically treatments were developed.
18	Liu, Wilcox [175]	Carried out grand canonical Monte Carlo (GCMC) simulation of adsorption with different potential models for CO ₂ to calculate accurate fluid-wall interactions. The GCMC yields the adsorption isotherms for a given adsorbent-adsorbate interaction. Surface heterogeneity effects have also been investigated.
19	Mosquera [176]	Proposed the Hill model [161] fitting type I adsorption isotherm by dividing adsorbate phase into identical and non-interacting effective subsystems. Based on the grand canonical ensemble statistics as a ratio of two polynomial functions, a simple multi-parametric isotherm was developed. The parameters were interpreted as adsorption equilibrium constants. A simple recurrence relation was proposed for the equilibrium constants, which avoided over-parametrisation and improved fitting deviations.
20	Fan et al. [107]	Presented a experimental and simulation study of nitrogen adsorption on graphite at temperature ranging from below the triple point to above the boiling point. Both Bin-GCMC and Bin-CMC schemes were applied and showed "the heat spike and cusp phenomenon diminishes and eventually disappears as temperature increases".
21	Saha et al. [4–6]	Developed the S-B-K isotherms equations that can be used to silica gel water adsorption refrigeration cycles.

2.8 Summary

Physical adsorption phenomenon is mainly driven by Lennard-Jones potential stemming from van der Waals forces between adjacent molecules. The characteristics of adsorption behaviour are largely dependent on the properties of adsorbent materials, among which several most significant adsorbents are reviewed in this chapter. The adsorption isotherm is a functional relation between adsorption uptake and load at isothermal condition. As an exothermic process, the heat involved during adsorption is expressed by isosteric heat of adsorption. Thermodynamic properties of adsorption system is also demonstrated from literature. Several famous and recent adsorption isotherms are summarised, including ideal and empirical isotherms for adsorption on surface, micropore and heterogeneous adsorption media. Their individual limitations and the reasons giving rise to them are analysed and discussed. For isotherms that are valid at Henry's region, they would not be valid in the high pressure range. For those work in which the pressure approaches a saturated value, they would become fit experimental isotherms at low pressure range not well. Above all, most of existing isotherm models works well with only one or two of the five adsorption isotherm types at the same time, and those which are able to handle more isotherm types are manifestly difficult to deal with as there are numerous parameters. To overcome those limitations of existing adsorption isotherm models, a novel isotherm equation will be proposed in the next chapter. The adsorption kinetics explains the relationship between adsorption uptake and time constant, at different diffusion mechanisms within adsorbent structure. The major theoretical work done by other researchers on adsorption isotherm from pioneering theoretical age to the up-date is briefly covered in this chapter. On the basis of statistical thermodynamics partition function, the next chapter describes the general thermodynamic frameworks of adsorption isotherms and kinetics.

Chapter 3

Thermodynamic Formulation of Adsorption Isotherms and Kinetics

3.1 Introduction

3.1.1 Isotherms

Current adsorption isotherms that are valid at the Henry's region are seldom valid at the high pressure range, such as Henry, Tóth and Langmuir equations [61, 89, 177]. These isotherms perform nicely when the pressure reaches saturated value but failed to be consistent with experimental data at the low pressure range, such as the DA and DR equations [84, 85].

Many empirical or semi-empirical isotherms, including [61]: Tóth [178], Freundlich, Sips, Unilan, Fowler, and Jovanovich [179, 180] equations, etc., are correlated with experimental data with empirical parameters. These curve fitting parameters give little or no physical meanings. As a result, all of these empirical isotherms are qualified with insufficient physical meanings [65].

Adsorption on practical adsorbent solid exhibits diverse isotherm shapes. Brunauer et al. [125] derived the classical multi-layer isotherms, and they were identified by IUPAC into five classical types [127, 181]. Currently, almost all existing isotherms are able to simulate at most one or two types of adsorption isotherms.

Those isotherm models, which are capable to deal with multiple isotherm types, has been proven manifestly difficult to manipulate [87, 88].

This chapter aims to develop a formalism of adsorption isotherm from the rigour of partition distribution function of each adsorptive site and the isosteric heat of adsorption at zero surface coverage for the calculation of adsorbate uptakes on various adsorbent materials. The proposed thermodynamic framework ranges from Henry’s region to the saturated pressure. The proposed model is thermodynamically connected with the pore structures of adsorbent materials, and it is found that the adsorbate vapour uptake highly depends on the isosteric heat of adsorption at zero surface coverage and the adsorptive sites of the adsorbent materials.

3.1.2 Kinetics

Up to now, no attempts are yet reported to explain the theoretical origins of adsorption rate equations for a single component adsorbent + adsorbate system in detail, and the current understanding of adsorption kinetics not more established compared to the theoretical description of adsorption isotherm. The present study thus attempts to focus more on the theoretical origins of the adsorption rate equation from the thermodynamics foundation [40, 182] of adsorption uptakes that varies from the Henry’s region (pressure $\rightarrow 0$). To the saturated pressure (P_s) values. The proposed adsorption kinetics formulation (i) is connected with the pore structures or the heterogeneity factors of adsorbent materials and the isosteric heat of adsorption at zero surface coverage Q_{st}^* , and (ii) also calculates the adsorption and desorption rates of water vapour onto single and multi-layers of loose grain configures of silica gel [30, 34].

3.2 Thermodynamics of Adsorption Isotherms

3.2.1 Lattice Gas Statistics

It is assumed that n numbers of adsorbate molecules can be adsorbed on each adsorbent site of an adsorbent-adsorbate system, where n varies from 0 to its maximum value m . As the van der Waals force is short-range for physical adsorption, the lattice gas model lies within thermodynamic limit, where the system volume grows in proportion with the number of molecules [87]. Therefore the partition function of each isothermal site $\varpi(n)$ is

$$\varpi(n) = \varpi^n(1) \quad (3.1)$$

for $n > 0$. The absolute activity is $\lambda = \exp(\mu/kT)$, where μ is the chemical potential of the adsorbed molecules and comprises the bulk chemical potential μ_{gas} , and the external adsorbent wall potential μ_{ext} , as [183]

$$\mu = \mu_{gas} - \mu_{ext} \quad (3.2)$$

The grand partition function of each single adsorptive site is [184]

$$\begin{aligned} \xi_m &= \varpi(0) + \varpi(1)\lambda + \cdots + \varpi(m)\lambda^m \\ &= \sum_{n=0}^m \varpi(n)\lambda^n \end{aligned} \quad (3.3)$$

where $\varpi(0) = 1$. The average number of molecules within each individual site is [184]

$$\bar{n} = \lambda \left(\frac{\partial \ln \xi_m}{\partial \lambda} \right)_T = \frac{\sum_{n=0}^m n \varpi(n) \lambda^n}{\sum_{n=0}^m \varpi(n) \lambda^n} \quad (3.4)$$

Substituting $\varpi(1)$ of Equation (3.1) into Equation (3.4), the result becomes

$$\begin{aligned}\bar{n} &= \frac{\sum_{n=0}^m n [\varpi(1)\lambda]^n}{\sum_{n=0}^m [\varpi(1)\lambda]^n} \\ &= \begin{cases} m + \frac{1}{1 - \varpi(1)\lambda} + \frac{1+m}{[\varpi(1)\lambda]^{1+m} - 1} & \varpi(1)\lambda \neq 1 \\ \frac{m}{2} & \varpi(1)\lambda = 1 \end{cases}\end{aligned}\quad (3.5)$$

From the Gibbs factor, A [185], we have

$$A(N, V, T) = -kT \ln \varpi(N, V, T) \quad (3.6)$$

where V is the volume of N molecules, and k is the Boltzmann constant. The Grand potential (or Landau free energy, Landau potential) of one particle is [186, 187]

$$\phi_G = -kT \ln \varpi(1)\lambda = A(1, v_1, T) - \mu_{gas} + \mu_{ext} \quad (3.7)$$

Here, 1 is for one molecule, and v_1 is the volume occupied by unit particle. Therefore,

$$\begin{aligned}\varpi(1)\lambda &= \exp\left(-\frac{A}{kT}\lambda\right) \\ &= \exp\left(-\frac{A - \mu_{gas} + \mu_{ext}}{kT}\right) \\ &= \exp\left(-\frac{\phi_G}{kT}\right)\end{aligned}\quad (3.8)$$

Substituting the expression of $\varpi(1)\lambda$ into Equation (3.5), a general adsorption isotherm model with respect to grand potential can be expressed as

$$\bar{n} = \frac{\sum_{n=0}^m n [\exp(-\frac{\phi_G}{kT})]^n}{\sum_{n=0}^m [\exp(-\frac{\phi_G}{kT})]^n} \quad (3.9)$$

The adsorbed phase is eventually in equilibrium with the gaseous phase at pressure P , we have

$$\mu_{gas} = \mu^\Theta + kT \ln \frac{P}{P^\Theta} \quad (3.10)$$

where μ^Θ indicates the reference chemical potential of gas at reference pressure P^Θ . From Equation (3.8), we have

$$\begin{aligned} \varpi(1)\lambda &= \exp\left(-\frac{A - \mu^\Theta + \mu_{ext}}{kT}\right) \frac{P}{P^\Theta} \\ &= \exp\left(-\frac{A - \mu^\Theta + \mu_{ext} + h_{fg}}{kT}\right) \frac{P}{P_s} \\ &= \exp\left(-\frac{-kT + \mu_{ext} + h_{fg}}{kT}\right) \frac{P}{P_s} \end{aligned} \quad (3.11)$$

Here, $h_{fg} = -kT \ln P_s/P^\Theta$ is the latent heat of evaporation during adsorption, and $A - \mu^\Theta = -kT$ indicates the work done of the system. The isosteric heat of adsorption at zero surface coverage is written by [9, 183]

$$\begin{aligned} Q_{st}^* &= kT - \mu_{ext} \\ &= kT - \frac{\int_0^{H_c} \mu_{ext}(j) \exp[-\mu_{ext}(j)/kT] dj}{\int_0^{H_c} \exp[-\mu_{ext}(j)/kT] dj} \end{aligned} \quad (3.12)$$

where H_c is the pore width of solid adsorbents [9]. The adsorbent wall potential is described by $\mu_{ext}(j) = U_{sf}(j) + U_{sf}(t-j)$, where U_{sf} defines the adsorbent-adsorbate interaction potential, t is the distance between the nuclei of the outer adsorbent atoms on opposite walls. The adsorption interaction potential of adsorbate along the pore width direction j is written as

$$U_{sf} = 2\pi\varepsilon_{sf}\rho_s\sigma_{sf}^2\Delta \left[\frac{2}{5} \left(\frac{\sigma_{sf}}{j} \right)^{10} - \left(\frac{\sigma_{sf}}{j} \right)^4 - \frac{\sigma_{sf}^4}{3\Delta(0.61\Delta + j)^3} \right] \quad (3.13)$$

where σ_{sf} and ε_{sf} are the solid-fluid collision diameter and the solid-fluid well depth potential, respectively. Δ defines the separation between the adsorbent planes and ρ_s

is the density of solid adsorbent [9]. Equation (3.11) can be further expressed as

$$\begin{aligned}\varpi(1)\lambda &= \exp\left(-\frac{\phi_G^*}{kT}\right) \frac{P}{P_s} \\ &= \exp\left(\frac{Q_{st}^* - h_{fg}}{kT}\right) \frac{P}{P_s}\end{aligned}\tag{3.14}$$

where $\phi_G^* = h_{fg} - Q_{st}^*$ is the extreme constant of grand potential, and it corresponds to the adsorption characteristics energy [9], and it is a function of pressure, temperature, and pore width distribution of solid adsorbent. Therefore, Equation (3.14) is related to the porous structure of adsorbent materials according to the parallel slit model. Substituting the expression of $\varpi(1)\lambda$ into Equation (3.5), a general adsorption isotherm is obtained and can be expressed as

$$\bar{n} = \frac{\sum_{n=0}^m n \exp\left(-n \frac{\phi_G^*}{kT}\right) \left(\frac{P}{P_s}\right)^n}{\sum_{n=0}^m \exp\left(-n \frac{\phi_G^*}{kT}\right) \left(\frac{P}{P_s}\right)^n}\tag{3.15}$$

where $\frac{P}{P_s} \in [0, 1]$. For adsorption below critical point, the boundary condition of adsorption isotherm is followed by $\theta \rightarrow 1$ when $P \rightarrow P_s$, where $\theta = \frac{\bar{n}}{\bar{n}_{max}}$ is the surface coverage of adsorbent-adsorbate system about its limiting isotherm capacity

$$\bar{n}_{max} = \frac{\sum_{n=0}^m n \exp\left(-n \frac{\phi_G^*}{kT}\right)}{\sum_{n=0}^m \exp\left(-n \frac{\phi_G^*}{kT}\right)}\tag{3.16}$$

The gravimetric expression of the maximum uptake can be estimated as $\bar{n}_{max} = \rho_l \cdot v_p$, where ρ_l is the condensed liquid phase density and v_p is the specific pore volume of

adsorbent. The surface coverage can be written as

$$\begin{aligned}\theta &= \frac{\bar{n}}{\bar{n}_{max}} \\ &= \frac{1}{\bar{n}_{max}} \cdot \frac{\sum_{n=0}^m n \exp\left(n \frac{Q_{st}^* - h_{fg}}{kT}\right) \left(\frac{P}{P_s}\right)^n}{\sum_{n=0}^m \exp\left(n \frac{Q_{st}^* - h_{fg}}{kT}\right) \left(\frac{P}{P_s}\right)^n}\end{aligned}\quad (3.17)$$

The numerator of Equation (3.17) can be regarded as a high order curve of $\frac{P}{P_s}$ with coefficient $\frac{n}{\bar{n}_{max}} \exp(-n \frac{\phi_G^*}{kT})$, which intersects the denominator of Equation (3.17) when $\frac{P}{P_s} \rightarrow 1$, that is another curve of $\frac{P}{P_s}$ with coefficient $\exp(-n \frac{\phi_G^*}{kT})$. The numerator curve of Equation (3.17) can be expressed by a power function

$$\frac{1}{\bar{n}_{max}} \sum_{n=0}^m n \exp\left(n \frac{Q_{st}^* - h_{fg}}{kT}\right) \left(\frac{P}{P_s}\right)^n \cong \beta \exp\left(m \frac{Q_{st}^* - h_{fg}}{kT}\right) \left(\frac{P}{P_s}\right)^m \quad (3.18)$$

where the pre-exponential coefficient β is determined by $\exp(\frac{Q_{st}^* - h_{fg}}{kT})$ and m , such that,

$$\beta \exp\left(m \frac{Q_{st}^* - h_{fg}}{kT}\right) = \frac{1}{\bar{n}_{max}} \sum_{n=0}^m n \exp\left(n \frac{Q_{st}^* - h_{fg}}{kT}\right) \quad (3.19)$$

Similarly, the denominator of Equation (3.17) can be represented by another power function with intercept 1, i.e.:

$$\sum_{n=0}^m \exp\left(n \frac{Q_{st}^* - h_{fg}}{kT}\right) \left(\frac{P}{P_s}\right)^n \cong 1 + \left[\beta \exp\left(m \frac{Q_{st}^* - h_{fg}}{kT}\right) - 1 \right] \left(\frac{P}{P_s}\right)^m \quad (3.20)$$

The numerator, the denominator of Equation (3.17), and their specific simplified versions as presented in Equations (3.18) and (3.20), are plotted in Figure 3.1.

Substituting $K_h = \beta \exp(-m \frac{\phi_G^*}{kT}) = \beta \exp(-m \frac{N_A \phi_G^*}{R_g T})$, where N_A is the

Figure 3.1: The high order curves from numerator and denominator of equation (3.17) and their corresponding shortcuts.

Avogadro's number and R_g is the gas constant, we have

$$\theta = \frac{\bar{n}}{\bar{n}_{max}} = \frac{K_h \left(\frac{P}{P_s}\right)^m}{1 + (K_h - 1) \left(\frac{P}{P_s}\right)^m} \quad (3.21)$$

Equation (3.21) is the simplified version of Equation (3.17). After the simplification, m is not obliged to be only an integer but any positive real number. The Henry's coefficient K_h as a function of temperature and adsorbent pore width can be expressed as $K_h = \beta \exp(m \frac{Q_{st}^* - h_{fg}}{R_g T})$. It should be noted here that β and m are calculated from experimental observations.

3.2.2 Heterogeneity Factor

The basic thermodynamic equation for the adsorbed phase is [22]

$$du = Tds - \varphi d\zeta + \mu dN \quad (3.22)$$

where u is the internal energy, s is the entropy, N is the number of adsorbed molecules, and φ is the spreading pressure of the adsorbed phase, which is related to the grand partition function ξ_m as [184]

$$\varphi = kT \ln \xi_m \quad (3.23)$$

Therefore φ is a function of ϕ_G and m , and any two of them determine the rest. For $\phi_G = 0$, that is $\varpi(1)\lambda = 1$, Equation (3.3) becomes $\xi_m = m + 1$, and Equation (3.5) turns to be $\frac{m}{2}$. As a result, $\phi_G = 0$ gives the symmetry point of adsorption isotherm [89], which yields

$$\varphi|_{\phi_G=0} = kT \ln(m + 1) \quad (3.24)$$

or

$$m = \exp\left(\frac{\varphi|_{\phi_G=0}}{kT}\right) - 1 \quad (3.25)$$

This provide necessary information to correct the limitation of B.E.T isotherm theory. When $\varpi(1)\lambda = 1$ it leads to $\varphi \rightarrow \infty$, which is thermodynamically inconsistent [184].

m can be named as the heterogeneity factor. If the adsorbent surface is heterogeneous, each adsorptive site can hold much different number of molecules depending on either the geometry or the energetic heterogeneity. The Boltzmann ratio of the population of state with grand energy $m\phi_G$ to the ground state is $\exp(-m\frac{\phi_G}{kT})$. The higher is the capacity m of each site, the smaller is the Boltzmann ratio, which means more energy levels are presented, and then, the larger is the heterogeneity. Equation (3.25) could be used to calculate m at the symmetry point of adsorption isotherm, which depends on the experimental observations of spreading pressure φ of the adsorbed phase.

The distributions of grand potential $\gamma'\phi_G$ on a surface with 20×20 lattice adsorptive sites, where integer γ' varying from 0 to m , are presented in Figure 3.2a

(a) $m = 1$ for 2 Boltzmann levels, and the distribution is relatively homogeneous.

(b) $m = 3$ for 4 Boltzmann levels, and the distribution is relatively heterogeneous.

(c) $m = 10$ for 11 Boltzmann levels, and the distribution is much heterogeneous.

Figure 3.2: The population distribution of adsorption uptakes with different Boltzmann levels.

($m = 1$), 3.2b ($m = 3$), and 3.2c ($m = 10$). The population ratio of adsorptive sites with grand potential $\gamma\phi_G$ to sites at ground state follows $\exp(-m\frac{\phi_G}{kT})$. In Figure 3.2a, the population is parted into two Boltzmann levels, and it presents the homogeneity ($m = 1$); In Figure 3.2b, the population is partitioned into four Boltzmann levels when $m = 3$, and the relative heterogeneity is found with respect to Figure 3.2a; When $m = 10$, the population is partitioned into eleven Boltzmann levels, and more heterogeneity is obtained. These are shown in Figure 3.2c. The larger is m , the more partitions will be, and therefore the much heterogeneity will be presented. In other words, the average uptake capacity of each site is the measurement of adsorption heterogeneity, and m can be expressed as a function of spreading pressure $\varphi|_{\phi_G=0}$ employing Equation (3.24) or (3.25).

3.2.3 Isosteric Heat of Adsorption

When $m = 1$, Equations (3.5), (3.9) and (3.15) change into the Langmuir's isotherm, as

$$\theta = \frac{\exp(-\frac{\phi_G^*}{kT})\frac{P}{P_s}}{1 + \exp(-\frac{\phi_G^*}{kT})\frac{P}{P_s}} \quad (3.26)$$

Equation (3.26) follows the *Fermi-Dirac* distribution as

$$\theta = \frac{1}{\exp(\frac{\Phi_G^*}{RT}) + 1} \quad (3.27)$$

where $\Phi_G^* = N_A\phi_G^*$. Employing Equation (3.27), a plot of θ against Φ_G^* is shown in Figure 3.3. As can be seen from Figure 3.3, unless with an infinite value of Φ_G^* , which rarely occurs in practical, the Langmuir isotherm is not satisfied with the boundary condition as $\theta \rightarrow 1$ when $P \rightarrow P_s$. In other words, the Langmuir isotherm is a mid-load isotherm [89], and, it overestimates the limiting uptake capacity $\bar{n}_{max}$.

Figure 3.3: Langmuir adsorption coverage θ for temperature 10K, 80K, 150K, 220K, 290K, and 360K, with Φ_G^* ranging from -10 to 10 kJ/mol.

The isosteric heat of adsorption from equation (3.26) is

$$Q_{st} = \Phi_G^* \quad (3.28)$$

This means that the isosteric heat of adsorption is constant.

The isosteric heat of adsorption Q_{st} is obtained from Equation (3.21) in the form of Clausius-Clapeyron coordinate equation and is expressed by

$$\begin{aligned} Q_{st} &= \frac{RT^2}{P} \frac{\partial P}{\partial T} \\ &= h_{fg} + \left[\left(\frac{P}{P_s} \right)^m - 1 \right] \Phi_G^* \\ &= h_{fg} - \frac{K_h(1-\theta)}{K_h(1-\theta) + \theta} \Phi_G^* \end{aligned} \quad (3.29)$$

At the Henry's range, where $P \rightarrow 0$, Equation (3.29) becomes $Q_{st} \rightarrow h_{fg} - \Phi_G^* = Q_{st}^*$, and when $P \rightarrow P_s$, it leads to $Q_{st} \rightarrow h_{fg}$ according to micro-pore filling theory [3, 44, 50, 61, 135, 175, 179, 183, 188–194]. Therefore, the isotherm given in Equation (3.21) is considered thermodynamically consistent.

3.2.4 Adsorption Isotherm Classifications

The proposed isotherm equation shows various shapes according to various adsorbent structures and the nature of adsorbent + adsorbate interactions. With the manipulation of two parameters namely (i) K_h , stemming from the grand potential Φ_G^* , and (ii) the heterogeneity factor m , Equation (3.21) presents various adsorption isotherm curves corresponding to IUPAC categories, as shown in Figures 3.4a, 3.4b and 3.4c.

Table 3.1: Adsorption Isotherm Classification with Parameters K_h and m

Type	K_h	m
Henry	1	1
Type I ^a	>1	≤ 1
Type II ^b	<1	<1
Type III ^c	<1	≥ 1
Type V ^d	>1	>1

^a Adsorption on microporous adsorbent.

^b Adsorption on macro porous adsorbent with strong adsorbent + adsorbate interactions.

^c Adsorption on macro porous adsorbent with weak adsorbent + adsorbate interactions.

^d Multilayer adsorption with microporous filling mechanism.

From Figure 3.4a, it is found that Type I isotherm is obtained with $m = 1$ and $K_h > 1$, due to stronger influence of $(Q_{st}^* - h_{fg})$. They are generally found in micro-pores of the adsorbent materials. When $K_h < 1$, weak adsorptive interaction occurs and Type III is resulted. When $K_h = 1$ and $m = 1$, Equation (3.21) presents the explicit Henry's isotherm as $\theta = K_h P$. As can be seen from Figure 3.4b that type II isotherm are observed for $m < 1$ and $K_h < 1$. As for a micropore filling mechanism, which obligates high heterogeneity factor m , and strong interaction given by large value of grand potential Φ_G^* ($m > 1$ and $K_h > 1$), Type V is presented. These are illustrated in Figure 3.4c. Therefore, the proposed isotherm given by Equation (3.21) is capable to deal with multi-type isotherms. However, it is found that equation (3.21) fails to explain layer by layer adsorptions (Type IV) and isotherms with hysteresis behaviours. The

(a) With increase of K_h from a number smaller than unity to large, the isotherm spans over Type III, Henry's isotherm, to Type I for the value of $m = 1$.

(b) When $m < 1$ and $K_h < 1$, the isotherm gives type II.

(c) When K_h is larger than unity, with increasing of m from unity to large, the isotherm spans over Type I to V.

Figure 3.4: Isotherm behaviours of Equation (3.21).

relation between adsorption classifications and parameters space of K_h and m are furnished in Table 3.1 as the universal results.

3.3 Kinetics with Lattice Statistics

The adsorbent-adsorbate system consists of equivalent and distinguishable adsorptive sites, where any number, n , from 0 to maximum m , of molecules can be adsorbed [184]. Considering van der Waals force as short-range for physical adsorption, the partition function of each isothermal site is $\varpi(n) = \varpi^n(1)$. The absolute activity is given by $\lambda = \exp(\mu/kT)$, where μ is the chemical potential of the adsorbed molecules and it comprises the bulk chemical potential μ_{gas} , and the external adsorbent wall potential μ_{ext} , or $\mu = \mu_{gas} - \mu_{ext}$ [183]. The grand partition function of each single adsorptive site is [184]:

$$\begin{aligned}\xi_m &= \varpi(0) + \varpi(1)\lambda + \cdots + \varpi(m)\lambda^m \\ &= \sum_{n=0}^m \varpi(n)\lambda^n\end{aligned}\tag{3.30}$$

where $\varpi(0) = 1$. The average number of molecules within each individual site is [184]

$$\bar{n} = \lambda \left(\frac{\partial \ln \xi_m}{\partial \lambda} \right)_T = \frac{\sum_{n=0}^m n \varpi(n) \lambda^n}{\sum_{n=0}^m \varpi(n) \lambda^n} = \frac{\sum_{n=0}^m n \{\varpi(1)\lambda\}^n}{\sum_{n=0}^m \{\varpi(1)\lambda\}^n}\tag{3.31}$$

From Equations (3.8) to (3.13), it can be derived that the surface coverage θ of

adsorbent-adsorbate system is

$$\begin{aligned}\theta &= \frac{\bar{n}}{\bar{n}_{max}} \\ &= \frac{1}{\bar{n}_{max}} \cdot \frac{\sum_{n=0}^m n \exp\left(n \frac{Q_{st}^* - h_{fg}}{kT}\right) \left(\frac{P}{P_s}\right)^n}{\sum_{n=0}^m \exp\left(n \frac{Q_{st}^* - h_{fg}}{kT}\right) \left(\frac{P}{P_s}\right)^n}\end{aligned}\quad (3.32)$$

Here, $\bar{n}_{max} = \rho_l \cdot v_p$ and ρ_l is the liquid density and v_p is the pore volume. To simplify Equation (3.32), the numerator curve is defined by a power function as

$$\frac{1}{\bar{n}_{max}} \sum_{n=0}^m n \exp\left(s \frac{Q_{st}^* - h_{fg}}{kT}\right) \left(\frac{P}{P_s}\right)^n \cong \beta \exp\left(m \frac{Q_{st}^* - h_{fg}}{kT}\right) \left(\frac{P}{P_s}\right)^m \quad (3.33)$$

where the pre-exponential coefficient β is determined by $\exp\left(\frac{Q_{st}^* - h_{fg}}{kT}\right)$ and m . Similarly, the denominator of Equation (3.32) can be replaced by another power function with intercept 1, i.e.:

$$\sum_{n=0}^m \exp\left(s \frac{Q_{st}^* - h_{fg}}{kT}\right) \left(\frac{P}{P_s}\right)^n \cong 1 + \left[\beta \exp\left(m \frac{Q_{st}^* - h_{fg}}{kT}\right) - 1 \right] \left(\frac{P}{P_s}\right)^m \quad (3.34)$$

Equation (3.32) can be presented by

$$\theta + \left[\beta \exp\left(m \frac{Q_{st}^* - h_{fg}}{kT}\right) - 1 \right] \theta \left(\frac{P}{P_s}\right)^m = \beta \exp\left(m \frac{Q_{st}^* - h_{fg}}{kT}\right) \left(\frac{P}{P_s}\right)^m \quad (3.35)$$

$$\theta + (K_h - 1) \theta \left(\frac{P}{P_s}\right)^m = K_h \left(\frac{P}{P_s}\right)^m \quad (3.36)$$

where $K_h = \beta \exp\left(m \frac{Q_{st}^* - h_{fg}}{kT}\right)$. According to Langmuirian analogy, the adsorption equilibrium constant K_h is expressed in terms of adsorption and desorption rate coefficient k_{ads} and k_{des} , respectively i.e. $K_h = k_{ads}/k_{des}$ for simplification. Employing Equation (3.36), the adsorption surface coverage θ under equilibrium condition turns

out to be:

$$k_{des}\theta\left\{1 - \left(\frac{P}{P_s}\right)^m\right\} = k_{ads}(1 - \theta)\left(\frac{P}{P_s}\right)^m \quad (3.37)$$

According to Langmuir, adsorption can be regarded as a reversible process between the adsorbents and adsorbate molecules. Therefore, under non-equilibrium condition, the amount of adsorbate surface coverage as a function of time (θ_t) can be written as

$$\frac{d\theta_t}{dt} = k_{ads}(1 - \theta)\left(\frac{P}{P_s}\right)^m - k_{des}\theta\left[1 - \left(\frac{P}{P_s}\right)^m\right] \quad (3.38)$$

Here, k_{ads} is related to the gas molecular collision frequency and is represented by $k_{ads} = \frac{\beta_o}{\sqrt{2\pi MRT}} \exp(-E_a/RT)$, where $\beta_o \exp(-E_a/RT)$ is the sticking coefficient that ranges from 0 to 1, which depends on the practical packing configuration of adsorbent materials. M defines the molecular weight of molecules, and A_s defines the Brunauer-Emmett-Teller (BET) surface area of adsorbents. E_a is related to the activation energy.

Writing $\frac{1}{\gamma} = k_{ads}\left(\frac{P}{P_s}\right)^m + k_{des}\left[1 - \left(\frac{P}{P_s}\right)^m\right]$, the analytical solution of Equation (3.38) becomes

$$\theta_t = C' \exp\left(-\frac{t}{\gamma}\right) + \gamma k_{ads} \left(\frac{P}{P_s}\right)^m = C' \exp\left(-\frac{t}{\gamma}\right) + \theta \quad (3.39)$$

Employing the initial condition $\theta_t = \theta_{ini}$ at $t = 0$ of the adsorption process, It can be derived that $C' = \theta_{ini} - \theta$, and the solution becomes

$$\theta_t = \theta \left[1 - \exp\left(-\frac{t}{\gamma}\right)\right] + \exp\left(-\frac{t}{\gamma}\right)\theta_{ini} \quad (3.40)$$

which is identical to Equation (2.17) in the Langmuir's theory [138], or

$$\frac{\Delta\theta_t}{\Delta\theta} = \frac{\theta_t - \theta_{ini}}{\theta - \theta_{ini}} = 1 - \exp\left(-\frac{t}{\gamma}\right) \quad (3.41)$$

Note,

$$\frac{1}{\gamma} = k_{ads} \left(\frac{P}{P_s} \right)^m + k_{des} \left[1 - \left(\frac{P}{P_s} \right)^m \right] \quad (3.42)$$

3.4 Lattice Gas Cellular Automata

In one of current studies [195], the lattice gas cellular automata are constructed as particle dynamics with discretised space and time steps. All same species particles have the same mass M and are indistinguishable. In FHP LGCA, the state of each node of lattice can be described by its six neighborhoods in 6 bits and 6-ary, as:

$$\psi_{ip}(time) = \sum_{v=1}^6 6^{v-1} e_v \quad (3.43)$$

where i and p are the coordinates of the cell, $time$ is the time step, and e_v is the number on each bit varying from 0 to 5, which means:

$e_v = 0$ no particles and surface on site v at $time$

$e_v = 1$ a particle is moving to site v at $time$

$e_v = 2$ a surface is present on site v

$e_v = 3$ a particle is moving to a surface on site v at $time$

$e_v = 4$ a particle is adsorbed by a surface on site v , and

$e_v = 5$ a particle is moving to an adsorbed particle on a surface at site v at $time$

Also a default rule exists as no more than one particle is able to sit on the same site, and this exclusion principle leads to Fermi-Dirac type equilibrium distribution of the mean occupation numbers.

As shown in Figure 3.5, for the central cell, $e_1 = 5$ as one particle is moving to an adsorbed particle on a surface at site 1, $e_2 = 0$ as no particles is moving to site 2 and no surface is located at site 2, $e_3 = 1$ as one particle is moving to site 3, $e_4 = 0$

is same as e_2 . $e_5 = 4$ as a surface with an adsorbed particle is present at site 5, and $e_6 = 0$ same as e_2 and e_4 . Therefore the state of the node can be described as

$$\psi(time) = (e_6 e_5 e_4 e_3 e_2 e_1)_6 = (040105)_6 \quad (3.44)$$

Figure 3.5: The hexagonal lattice of the FHP model. Lattice particles are represented by arrows, and surface with adsorption force field is represented by dashed line. The adsorbed particles are represented by point at the centre.

After being converted to 10-ary number, $\psi(time)$ as shown in Figure 3.5 is 5225. The complete grid of LG could be given as a matrix of number $\psi_{ip}(time)$, and these are shown in Figure 3.6 [157].

3.4.1 Rule Space and Boundary Condition

A single step evaluation of LGCA consists of two stages: movement and interaction. Firstly, the movement part of the rule collects the digit corresponding to particles moving to one cell from its six possible neighbourhoods; then, the interaction part of the rule handles particles colliding with each other and with the possible adsorbent surfaces. The LGCA rules of collision among particles obey the conservation laws of mass, energy and momentum, which are implemented by the specification of collision rules. The rules of adsorption and desorption onto and from the surfaces follow phase

Figure 3.6: The FHP lattice with hexagonal symmetry. The lattice particles movements are represented by arrows

transition potential theory [76], as shown in Equations (3.45) and (3.46).

$$k_{ads} = \exp\left(\frac{\mu_{gas} - \mu}{kT}\right) \quad (3.45)$$

and

$$k_{des} = \exp\left(\frac{\mu - \mu_{gas}}{kT}\right) \quad (3.46)$$

As a whole, the LGCA evaluation rule turns the digit corresponding to the incoming particles into another digit representing the outgoing state.

As can be seen from Figure 3.7, the lattice on the left has a state digit of Figure 3.5 and the digit is collected during the movement stage. For head-on collision, the two particles move directly towards the inverse direction or through each other while for other collision angles, the movement locus is restrained by the six possible directions. With the consideration of conversation laws and adsorption potential theory, the incoming state is evaluated at interaction stage into a result digit 5225. As the 6 bit digit is in 6-ary, the rule space would be as large as $6^6 = 46656$. However, for

constrains as no particle could come across a surface, there are in total 1848 rules.

Figure 3.7: The evaluation rule of FHP model for 2 incoming particles onto 2 surfaces with 1 adsorbed particle. Lattice on the left with incoming state as 5225, will evaluate into lattice on the right as digit 5440.

At the edge of LGCA, the boundary conditions are applied. Methods include, for instance, mirror/random reflection, non-slip/slip conditions, etc. In this emulation, however, the periodic boundary conditions are utilised, which means the top row is connected with the bottom row, while the left column is wrapped around with the right column. In this way, particles moving acrossing upwards arrive on the bottom, while particles crossing the left boundary appear from the right, and vice versa.

3.4.2 Porous Network

To emulate the characteristics of adsorbent material, the porous network should be built within hexagonal lattice configuration. This is realised by producing random surfaces on each cell. As a result, the microporous structure is emulated, and these are shown in Figure 3.8.

Figure 3.8: Porous network within hexagonal lattice space by random surface of each cell.

3.4.3 Virtualisation

Initializing a LGCA in 25×25 space size, lattice gas in 5×5 , and porous surface in 15×15 , the result is illustrated by Figure 3.9a, and the code¹ is programmed with Mathematica 9.0[®]. From Figures 3.9b, 3.9c and 3.9d, it is found that the adsorbate molecules diffuse into the inner side of the porous structure for various long steps, and from Figures 3.9c and 3.9d it is also found that the amount of adsorbate molecules uptakes reach equilibrium eventually. The uptake is related with pressures and random movement of adsorbate particles. At higher pressure, more uptakes of molecules occur. In the present LGCA method, the emulation was run for 20 times with 1,500 steps each. A plot of uptake (the number of adsorbed molecules) against the number of steps is shown in Figures 3.10 for various adsorption and desorption rates. The number of steps depends on pressure and time. Figure 3.10 indicates the basic concept of adsorption kinetics.

¹This work was supported by the Wolfram Research Corporate Summer School 2013, <https://www.wolframscience.com/summerschool/2013/alumni/sun.html>. The author is grateful for all helps received from Dr. Stephen Wolfram, Dr. Todd Rowland, Dr. Carlo Barbleri.

(a) LGCA initialized with 25×25 lattices, 5×5 particles, and 15×15 porous surfaces.

(b) LGCA evaluation after 200 steps.

(c) LGCA evaluation after 1,000 steps.

(d) LGCA evaluation after 1,500 steps.

Figure 3.9: LGCA evaluation for adsorption kinetics emulation.

Figure 3.10: LGCA adsorption kinetics with various emulation steps. The experimental data of silica gel + water are added herein for qualitative comparison purpose [195].

3.5 Summary

Based on the statistical foundation of physical adsorption with lattice gas and parallel slit models of adsorbent structures, a general adsorption isotherm thermodynamics framework is established, which is related to the grand potential of adsorbent + adsorbate system. The heterogeneity factor is qualified with physical evidence to the spreading pressure. The Henry's coefficient K_h is expressed by heterogeneity factor m and the isosteric heat of adsorption at zero uptake or $P \rightarrow 0$ is derived as a function of temperature and pore width of adsorbent materials. To overcome the mid-load limitation of Langmuir's isotherm, the proposed isotherm is qualified with satisfied boundary condition ranging from Henry's to the saturated region. From a perspective of theoretical justification based on partition distribution function of adsorptive site on adsorbent, it is found that the proposed isotherm framework is thermodynamically consistent, and is also capable to describe multi-type isotherms according to IUPAC categories. The proposed adsorption isotherm theory captures the relationship between the pore sizes of adsorbents with the enthalpy of adsorption. This work could laid a fundamental contribution towards the applications of adsorption based cooling and gas storage.

By analysing the physical foundation of adsorption kinetics from the viewpoint of statistical thermodynamics, it is found that the Langmuir kinetics equation over-estimates the desorption rate. To overcome the limitations of the general LDF kinetics equation, an adsorption kinetics framework is developed. The proposed equation includes the knowledge of (i) adsorption isotherm coefficient K_h , and (ii) activation energy E_a . Employing the experimentally verified values of K_h and E_a , one can predict the amount of adsorbate uptake as a function of time. This study offers new insights into the adsorption kinetics and also provides an explanation for calculating the rate of adsorbate uptakes on various adsorbent configurations. The following chapter deals with an experimental investigation for the calculation of various parameters used in adsorption isotherms and kinetics. It should be noted here that the proposed kinetics model is derived analogous to the Langmuirian kinetics,

under assumption that the initial concentration of adsorption is extremely high.

Lattice Gas Cellular Automata (LGCA), as a fluid dynamic simulation method, is conceptually simple and can be applied to deal with thermal interface effects to a wide array of boundary conditions. Based on LGCA, lattice Boltzmann Method (LBM) has been successfully used to model a number of typical continuous fluid dynamic problems. In this research, however, general FHP method is extended from LGCA into microscopic scale to emulate surface adsorption process. Specifically, hexagonal grids topology and geometry are applied in two-dimension (2D) with 6 bits digit to represent different states of each grid node. The rule space is then determined as 6^6 . 2D porous network is constructed for simulating practical adsorbent material structure. The lattice gas collision and movement are implemented within periodic space boundary conditions. Local rules of lattice gas interaction with network surface are defined and examined. The adsorption probabilities on each adsorptive site, corresponding to adsorption potential with relationship to temperature, are taken into account. As a result, an intuitive visualization of physical surface adsorption kinetics is achieved. Lattice Gas Cellular Automata (LGCA) has been successfully applied to deal with problems of continuous fluid dynamics in macroscopic. However, this chapter illustrates that LGCA would also be helpful to handle rarefied gas dynamics problems, such as nano-scale pore diffusion of physical adsorption at low pressure conditions.

Chapter 4

Characterisation of Adsorbent Structures and Measurements of Adsorption Isotherms

4.1 Introduction

In order to verify their thermo physical properties of adsorbent materials that are supplied, synthesised, and used in this experimental study, this chapter begins with the measurement of adsorbent materials properties employing the X-ray deflection method, scanning electron micrography, N₂-adsorption thermogravimetric analyzer (TGA) and Fourier transform infrared (FTIR) spectra. This chapter also presents the experimental volumetric methods for the measurement of (1) water vapour adsorption onto silica gel, zeolite type ZQSOA-Z01 and ZQSOA-Z02 for the designed development of an adsorption chiller, (2) methane adsorption on various mental-organic frameworks for temperatures both in sub-/supercritical states of methane (ranging from 125 K to 303 K) for CH₄ storage. The volumetric technique is employed to measure the cryogenic adsorption uptake data for temperatures ranging from 120 K to 220 K and pressures up to 1 MPa. The experimental environment at the cryogenic temperature is maintained with a purpose-built cryostat. These experimental results are significant in

the study of (1) adsorption chiller development, and (2) adsorbed natural gas (ANG) storage system under ANG-CNG (Compressed Natural Gas) coupling conditions, which is one of the motivation of the present work.

4.2 Characteristics of Adsorbent Materials

In this thesis, it is of interest to measure the adsorbent characteristics of zeolite (type AQSOA-Z01 and AQSOA-02), Maxsorb III activated carbon, HKUST-1 and MIL-101(Cr) metal-organic frameworks to fulfill the motivation of this thesis from the application view point.

4.2.1 Zeolites

The solid adsorbent, AQSOA-Z01 is an one-dimensional structure and its framework consists of AlO_4 , PO_4 and FeO_4 tetrahedrons, where Al and P atoms are partially substituted by Fe atoms. AQSOA-Z01 was synthesised in the presence of organic amines under the hydrothermal condition. AQSOA-Z02 is a CHA type molecular sieve having three-dimensional structure with large ellipsoidal cages. AQSOA-Z02 framework consists of AlO_4 , PO_4 and SiO_4 tetrahedrons, where Al and P atoms are partially substituted by Si atoms. The phase structure and crystallinities of AQSOA-Z01 and AQSOA-Z02 were carried out by X-ray diffraction (XRD) measurements (Shimadzu XRD-6000) with a step size of 0.02° using monochromatic CuK_α radiation (wavelength = 0.154 nm) at 40 kV and 40 mA. The microstructure, morphologies and particle size of AQSOA01 and AQSOA02 were determined using JEOL Field Emission Scanning Electron Microscopy (FESEM) operating at 5 kV. The specific surface area, pore volume and pore radius of these adsorbents were measured using a Sorptomatic 1990 (Thermo Electron Corporation) instrument by obtaining the N_2 adsorption/desorption isotherms at 77 K. Prior to adsorption measurements, samples were degassed at 160°C for 8 h. The isotherm data were used to determine the surface areas with Brunauer-Emmett-Teller (BET) equation. The

Barret-Joyner-Halenda method was employed to calculate the porosity parameters. Thermal decomposition of AQSOA-Z01 and AQSOA-Z02 was performed using a thermo gravimetric analyzer (TGA Q500 instrument). Powder sample was heated to 500 °C at a ramp rate of 10 °C/min under oxygen flow and the weight loss of powder was measured as a function of temperature.

The powder X-ray diffraction patterns of AQSOA-Z01 and AQSOA-Z02 samples are presented in Figure 4.1. All the peaks corresponding to the reflection planes are indexed. AQSOA-Z01 has the iron aluminophosphate phase with chemical formula $\text{FeAl}_2(\text{PO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (Figure 4.1a) and AQSOA-Z02 has the silico aluminophosphate phase with chemical formula $\text{Al}_{0.56}\text{Si}_{0.02}\text{P}_{0.42}\text{O}_2$ (Figure 4.1b).

Figure 4.1: X-ray diffraction (XRD) patterns of AQSOA-Z01 and AQSOA-Z02 adsorbents, peaks corresponding to reflection planes are indexed.

The morphology and topological features of AQSOA-Z01 and AQSOA-Z02 were studied by Field Emission Scanning Electron Microscopic (FESEM), and these are shown in Figure 4.2. Figure 4.2 (a) shows the SEM micrograph of AQSOA-Z01 zeolite powder. It is clearly seen that AQSOA-Z01 has an elongated plate like

structure. Some partial destruction of the plate structure is observed which indicates that AQSOA-Z01 is brittle in nature. The particle size of AQSOA-Z01 ranges from 3 to 5 μm . The SEM micrograph of AQSOA-Z02 zeolite powder is shown in Figure 4.2 (b). Interestingly, AQSOA-Z02 has solid regular cubic or brick-like shape with a uniform particle size of 5 μm .

Figure 4.2: SEM micrographs of (a) AQSOA-Z01, and (b) AQSOA-Z02 zeolite powders.

The specific surface area and the pore volume of AQSOA-Z01 and AQSOA-Z02 zeolite powders were determined from nitrogen adsorption/desorption isotherms at 77 K. The BET surface area and micro pore volume of AQSOA-Z01 were found to be 132 m^2/g and 0.087 cm^3/g , respectively for the relative pressure of $P/P_s = 0.97$. In case of AQSOA-Z02, the BET surface area and micro-pore volume were calculated as 590 m^2/g and 0.2769 cm^3/g . This large difference of specific surface area and pore volume of AQSOA-Z01 and AQSOA-Z02 is attributed to the fact that the difference of ionic radii of Fe^{3+} and Si^{4+} in the lattice structure of AQSOA-Z01 and AQSOA-Z02, respectively.

Thermo-stability analyses of AQSOA-Z01 and AQSOA-Z02 were carried out employing a Thermo Gravimetric Analyser (TGA). The thermogravimetric curves of both adsorbents are shown in Figure 4.3 with prominent weight-loss steps when heated up to 250 $^{\circ}\text{C}$ in air. For AQSOA-Z01 as shown in curve (a) of Figure 4.3, the weight loss (~ 7 wt%) occurs at 100 $^{\circ}\text{C}$ due to the desorption of guest water molecules from the large cages (internal diameter 7.4 Å. In case of AQSOA-Z02, two stage

Figure 4.3: Weight loss versus temperature TGA curves of (a) AQSOA-Z01, and (b) AQSOA-Z02 zeolite powders heated up to 500 °C in air.

weight losses are observed (curve (b) of Figure 4.3). In the first stage, a rapid weight loss (~ 12 wt%) up to 100 °C is due to the desorption of physisorbed water bound to AQSOA-Z02 structure (internal diameter of 3.7 Å) and in the second stage, the weight loss (~ 2 wt%) ranging from 100 to 250 °C takes place for the loss of water from the inner cages.

4.2.2 Carbonaceous adsorbents

Carbonaceous adsorbent materials being non-polar have preferential adsorption to similar gases such as carbon dioxide and methane. It is commercially available in multiple forms from nanotubes, granules, beads to fibers, and is suitable candidate for use in CO₂ separation processes involving adsorption.

Up to now, It has been studied that the pitch based activated carbon type Maxsorb III (N₂ treated). It is experimentally found that carbonaceous materials with low impurities increase adsorption capacity by more than 50% [196]. The activated

carbon (type Maxsorb III) possesses high and low temperature stability with high microporosity and surface areas up to 3200 m²/g, which makes it favourable for CO₂ capture in harsh conditions and CH₄ storage at relatively lower temperatures. The scanning electron microscopy (SEM) pictures of NO₂ treated Maxsorb III, and its pore width distribution is shown in Figure 4.4.

The thermo-physical properties of Maxsorb III and other adsorbents are measured by an adsorbent analyzer. It provides evaluation of a materials adsorption surface area, pore volume and other adsorption properties quickly. It operates on the principles of nitrogen adsorption method, where capillary condensation and adsorption of nitrogen occurs on the adsorbent surface at 77.3 K, resulting in maximum penetration of pores. Table 4.1 tabulates the porous properties of Maxsorb III.

Table 4.1: Porous Properties of Maxsorb III

BET Surface Area (m ² /g)	3140
Micropore Volume (mL/g)	1.70
Total Pore Volume (mL/g)	2.01
Apparent Density (g/mL)	0.31
Skeleton Density (g/mL)	2.2
Particle Porosity	0.81
Residual Heat (%)	0.1
pH(-)	4.1
Mass Reduction during Preparation from Carbon	0.8
Average Particle Diameter (μm)	72
Mean Pore Diameter (nm)	2.008

4.2.3 Metal-organic Frameworks

In the present work, the characteristics of HKUST-1 and MIL-101 (Cr) were investigated experimentally.

(a) SEM photograph of Maxsorb III sample at magnifications 2,000.

(b) SEM photograph of Maxsorb III sample at magnifications 3,700.

(c) Pore size distribution of Maxsorb III.

Figure 4.4: SEM Photographs and Pore Size Distribution of Maxsorb III.

HKUST-1

HKUST-1 MOF (Basolite C 300, Copper benzene-1,3,5-tricarboxylate, Cu-BTC MOF) was supplied by Sigma-Aldrich®. Field Emission Scanning Electron Microscopy (FESEM) was used to study the microstructure, morphologies and particle

size of this HKUST-1. The structure of the solid phase and crystallinities were analysed from X-ray diffraction (XRD) measurements (Shimadzu XRD-6000) with a step size of 0.02° using monochromatic $\text{CuK}\alpha$ radiation (wavelength = 0.154 nm) at 40 kV and 40 mA. The Rietveld refinement of the XRD pattern was conducted using TOPAS[®] software. The XRD pattern is useful to construct the unit cell of HKUST-1 for GCMC simulation purposes. Thermal decomposition of HKUST-1 MOF was performed using a thermo gravimetric analyzer (TGA Q500 instrument).

The FESEM photomicrograph was used to study the morphology and particle size of HKUST-1 MOF. Figure 4.5 shows that most particles are octahedral in shape with average size of 5 μm . Some particles appeared elongated toward a hexagonal symmetry.

Figure 4.5: SEM micrograph of HKUST-1 MOF showing particles having octahedral shape with average diameter of 5 μm .

Powder X-ray diffraction (PXRD) analysis was performed to study the crystal structure of HKUST-1 MOF material. The diffraction pattern of HKUST-1 MOF was presented in Figure 4.6. HKUST-1 MOF possesses cubic crystal structure with space group $\text{Fm}\bar{3}\text{m}$ [123]. All the peaks corresponding to reflection planes were indexed. The intensive peaks of Figure 4.6 appearing at small angles $2\alpha_B$ are

characteristics of microporous material which possesses tiny pores or cavities. The mean crystallite size was calculated using Scherrers formula $\tau_{cry}0.9\lambda_{ray}/\beta_{int} \cos \alpha_B$; where τ_{cry} = mean crystallite size, β_{int} = the line broadening at half the maximum intensity, λ_{ray} = X-ray wavelength and α_B = Braggs angle. Rietveld refinement of the XRD pattern of HKUST-1 MOF using TOPAS[®] software was shown in the inset of Figure 4.6. The lattice parameter of HKUST-1 was calculated by Rietveld refinement and this value is found 26.4 Å. From the PXRD result, the unit cell framework of HKUST-1 is constructed, as shown in Figure 4.7. The framework consists of copper and Benzene-1,3,5-tricarboxylic acid (BTC) linker, and forms into a cuboid with dimensions of $26.34 \times 26.34 \times 26.34 \text{ Å}^3$.

Figure 4.6: X-ray diffraction pattern of HKUST-1 MOF showing peaks corresponding to reflection planes are indexed. The inset shows the Rietveld refinement of this XRD pattern.

The thermo-gravimetric analysis of HKUST-1 MOF is shown in Figure 4.8 with prominent weight-loss steps when the adsorbent sample is heated up to 550 °C in air. The initial weight loss (12 wt%) up to 150 °C is due to desorption of physically adsorbed water or guest molecules. It was observed that the sample was not shown any significant weight change up to 330 °C and then started to lose the weight. This result

Figure 4.7: Unit cell crystallization structure of the HKUST-1 viewed from the [100] direction. (C, gray; H, white; O, red; Cu, pink)

confirmed the stability of the HKUST-1 MOF at higher temperature and there are almost no impurities in the structure. A sudden weight loss (51 wt%) was observed at 330 °C due to the total degradation of Benzene-1,3,5-tricarboxylic acid (BTC) linker. The remaining residue was CuO. The stability analysis of HKUST-1 at higher temperature is essential as the regeneration temperature of HKUST-1 is nearly 160 °C to remove moisture from the HKUST-1 MOF surface. It should be noted here that before adsorption, the regeneration phase is a part of CH₄ storage on porous adsorbents.

MIL-101

Chromium (III) terephthalate [MIL-101(Cr)] (MIL stands for Materials of Institut Lavoisier) possesses numerous unprecedented features such as zeotype architecture including mesoporous cages and microporous windows, huge cell volume, large surface area, and many unsaturated chromium sites. The MIL-101(Cr) framework is constructed from a hybrid solid superterahedral building unit, which is formed by

Figure 4.8: Weight loss vs. temperature TGA curves of HKUST-1 MOF heated up to 550 °C in air. The initial weight loss (12 wt%) up to 150 °C due to desorption of physically adsorbed moisture and the sudden weight loss (51 wt%) at 330 °C due to the total degradation of BTC linker are observed.

the linkage of 1,4-benzenedicarboxylate (BDC) ligands and trimeric chromium(III) octahedral clusters. MIL-101(Cr) was synthesised by the hydrothermal reaction method using a modified fluorine free synthesis route. The synthesised materials were characterised by various experimental techniques including X-ray diffraction (XRD), scanning electron microscope (SEM), N₂ adsorption/desorption isotherms, thermo gravimetric analysis (TGA) and Fourier transform infrared (FTIR) spectroscopy. All the chemicals used for the synthesis of MIL-101(Cr) in this study were of analytical grade and used without further purification. Chromic nitrate [Cr(NO)₃ · 9 H₂O], terephthalic acid [HOOC–C₆H₄–COOH], hydrochloric acid (HCl) were purchased from Sigma-Aldrich®. Deionised water was used as a solvent during chemical synthesis. The MIL-101(Cr) was prepared using a modified fluorine-free synthesis route via the hydrothermal reaction without using HF. The description of

MIL-101(Cr) synthesis is as follows: chromic nitrate (4 g), terephthalic acid (1.66 g), concentrated hydrochloric acid (1 mL), and deionized water (50 mL) were mixed together in a teflon-lined stainless steel autoclave reactor and kept at 200 °C for 12 h. Next, the autoclave reactor was slowly cooled down to room temperature. After cooling, dimethylformamide (DMF) was added to this reaction mixture which was then heated at 80 °C to eliminate any unreacted free terephthalic acid. The green crystals of MIL-101(Cr) were recovered by centrifugation. Further, the solvothermal treatment of synthesised MIL-101(Cr) was carried out by using anhydrous ethanol in an autoclave at 80 °C for 12 h to remove the DMF or any free terephthalic acid resided in the MIL-101(Cr) pores. The final product was cooled down, centrifuged and dried overnight at 80 °C.

X-ray diffraction (XRD) measurements (Shimadzu XRD-6000 diffractometer) were conducted with a step size of 0.02° using a monochromatic CuK α radiation (wavelength = 0.154 nm) operated at 40 kV and 40 mA. The microstructure, morphologies and particle size of MIL-101(Cr) MOF were determined using a JEOL Field Emission Scanning Electron Microscopy (FESEM) operated at 5 kV. The pore volume, pore radius and specific surface area of MIL-101(Cr) MOF were measured using a Sorptomatic1990 (Thermo Electron Corporation) instrument from the N₂ adsorption/desorption isotherms at 77 K. The samples were degassed at 160 °C for 8 h before the adsorption measurements. The isotherm data were used to calculate the surface area with Brunauer-Emmet-Teller (BET) equation. The Barret-Joyner-Halenda method was used to determine the porosity parameters. The thermal stability of MIL-101(Cr) MOF was assessed using a thermo gravimetric analyzer (TGA Q500 instrument). The powder sample was heated up to 550 °C at a ramp rate of 10 °C/min under oxygen flow and the weight loss of powder was measured as a function of temperature. FTIR of MIL-101(Cr) MOF samples were conducted on KBr/sample pellets using a Nicolet 6700 Thermal Scientific spectrometer. The X-ray diffraction (XRD) pattern of synthesised MIL-101(Cr) is presented in Figure 4.9. The diffraction peaks corresponding to reflection planes are indexed, which are consistent

with the peak positions as reported for standard MIL-101(Cr) structure, indicating that the synthesised material has good crystallinity. The intensive peaks appearing at small angles (2θ) in the XRD pattern indicate that this porous material possesses abundant pores in the structure. In fact, MIL-101(Cr) possesses two types of inner cages with internal diameters of 29 and 34 Å³, respectively.

Figure 4.9: X-ray diffraction pattern of MIL-101 (Cr) MOF, peaks corresponding to reflection planes are indexed.

The specific surface area and the pore volume of synthesized MIL-101(Cr) were calculated from N₂ adsorption/desorption isotherms at 77 K. The specific surface area of MIL-101(Cr) is calculated as 3302 m²/g (BET method) and 4688 m²/g (Langmuir method), respectively. The total pore volume of MIL-101(Cr) is 1.54 cm³/g at the relative pressure of 0.98. The pore size distribution of MIL-101(Cr) confirms the presence of two types of pore sizes (18 and 12 Å), which is the same as those estimated from the lattice structure.

The FESEM micrograph is presented in Figure 4.10 to show the morphology

Figure 4.10: SEM micrograph of MIL-101(Cr) (a) before and (b) after purification, showing particles having octahedral shape with average size of 1 μm .

and particle size of synthesised particles of MIL-101(Cr) before purification (Figure 4.10a) and after purification (Figure 4.10b). The particles are octahedral in shape with double-side pyramid type geometry. The particles have uniform size of 1 μm . Figure 4.10a shows some unreacted terephthalic acid (highlighted), whereas Figure 4.10b shows that particles are free from terephthalic acid which was removed during the purification process. Wang et al. [197] synthesized MIL-101 (Cr) in alkaline solution of tetramethylammonium hydroxide (TMAOH) under hydrothermal condition (210 °C, 24 h) and reported MIL-101 (Cr) particles having regular shapes with size ranging from 200-500 nm. Lebedev et al. [116] reported MIL-101 crystals ranging from 0.1 to 0.4 μm synthesised by hydrothermal method using HF as mineralizing agent at 220 °C for 8 h. Jhung et al. [198] synthesised MIL-101 (Cr) using microwave irradiation method at 210 °C for various crystallization times with particles smaller than 100 nm.

The thermogravimetric curve of MIL-101(Cr) is presented in Figure 4.11 with prominent weight-loss stages when heated up to 550 °C in air. The first stage weight loss ($\sim 45\%$) up to 125 °C is mainly due to the desorption of physically adsorbed water molecules from the large cages ($\sim 34 \text{ \AA}$). The second step weight loss at temperature 300 °C corresponds to the loss of water molecules from middle-sized cages ($\sim 29 \text{ \AA}$). The third stage weight loss ($\sim 25\%$) at 350 °C corresponds to the decomposition

of benzenedicarboxylate (BDC) linker of MIL-101(Cr) MOF structure, resulting in Cr_2O_3 as residue. This analysis shows the thermal stability of MIL-101(Cr) MOF structure, as the sample has to be heated to 160°C during the regeneration process. The thermal stability of other reported MOFs with their corresponding decomposition temperature obtained from the TGA is as follows: HKUST-1 (290°C), PCN-14 (310°C), UTSA-20 (280°C), NU-111 (325°C), Ni-MOF-74 (400°C), Al-MOF-519 (500°C).

Figure 4.11: Weight loss vs. temperature TGA curve of MIL-101(Cr) heated up to 550°C in air. The initial weight loss (45 wt%) up to 125°C due to desorption of physically adsorbed water and the sudden weight loss (25 wt%) at 350°C due to the total degradation of BDC linker of MOF are observed.

FTIR analysis was conducted to identify the functional groups present in MIL-101(Cr) MOF and their status when exposed to CH_4 adsorption. FTIR patterns of MIL-101(Cr) before and after CH_4 adsorption runs are presented in Figure 4.12 and salient features are discussed here. The broad band at 3394 cm^{-1} corresponding to

Figure 4.12: Fourier transform infrared (FTIR) spectra of MIL-101 (Cr) (a) before and (b) after CH_4 adsorption runs.

stretching vibrations and the band at 1620 cm^{-1} corresponding to bending vibrations are due to the adsorbed water on the surface of MIL-101(Cr) particles. The band observed at 1402 cm^{-1} is assigned to symmetric (O-C-O) vibrations of dicarboxylate, thus confirming the presence of benzenedicarboxylate (BDC) linker within the MIL-101(Cr) framework structure. The bands observed between 600 and 1600 cm^{-1} are due to benzene ring, including stretching vibrations (C=C) at 1508 cm^{-1} and deformation vibrations (C-H) at 1160 , 1015 , 880 , and 750 cm^{-1} . The positions of all bands remain the same (no peak shift) in the FTIR spectrum of MIL-101(Cr) after exposure to CH_4 (Figure 4.12b) confirming that the MIL-101(Cr) framework does not change after CH_4 adsorption runs. The comparison of the two spectra (Figures 4.12a and 4.12b) indicates the chemical stability of MIL-101(Cr) towards CH_4 , showing a potentially good adsorbent for CH_4 . The unit cell crystallisation structure of the

MIL-101 (Cr), as well as its comparison with HKUST-1, is shown in Figure 4.13.

Figure 4.13: Unit cell crystallisation structure of the MIL101(Cr) viewed from the [100] direction, and its geometry size comparison with HKUST-1. (C, gray; H, white; O, red; Cu, pink; Cr, blue-gray)

4.3 Experimental Investigation for Adsorbate Uptakes

The experimental apparatus is described in two sections: (i) the volumetric apparatus to measure the adsorption uptake for an adsorbate-adsorbent pair at ambient isothermal conditions, and (ii) the cryostat to maintain the adsorption cell at constant temperature in cryogenic states (varied from 120 K to 220 K).

4.3.1 Volumetric Apparatus

The experimental apparatus consists of a stainless steel adsorption cylinder and a charging cylinder with internal volumes of 183.842 ± 0.159 mL and 323.347

± 0.273 mL. The schematic for the adsorption and charging chambers where the adsorption occurs are shown in Figure 4.14. Two pressure transducers (Kyowa-PGS-200KA) are mounted on the stainless steel adsorption and charging chambers by 6.35×10^{-3} m stainless steel tube. The uncertainty of the pressure transducers are of 0.2 % in measurement. The temperature of the adsorption and charging chambers were recorded using class-A Pt 100 Ω RTDs with estimated uncertainty of $\pm 0.15^\circ\text{C}$. The RTD in the adsorption cell is in contact with the adsorbent materials to enable direct temperature measurement, by wrapping the adsorbents with metal mesh onto the RTD probes. All temperature and pressure data are logged into the Agilent 34972A LXI data acquisition every 1 s to enable real time monitoring of the adsorption uptake. A set of compression fittings to withstand pressure of larger than 40 MPa are used.

Figure 4.14: Schematic of experimental apparatus.

The adsorption and charging chambers were immersed in a bulk of circulated water at a controlled constant temperature until they were thermally stabilised before the experiments are conducted. The specification accuracy of the heating/refrigeration circulator is $\pm 0.01^\circ\text{C}$ to maintain the preset temperature. With this design and mechanism, it was assumed that the experiments were performed under isotherm

conditions with no significant temperature fluctuation.

Helium gas with purity of 99.999 %, supplied in small cylinder from SOXAL, was used to remove residual gases on the surfaces of adsorption chamber before the experiments.

Procedures

Step 1: Preparation of the Adsorbent Before the adsorbent samples were loaded into the adsorption cell, they were first weighed in the A&D MX-50 moisture analyzer, which has an accuracy of 0.10 % over 1 g. The samples were heated at 140 °C until the analyser beeped, and the dry weights of the samples were recorded from the analyser display. Each time about 1000.0 mg samples were weighed and in total about 5000.0 mg wrapped by metal mesh against the RTD probe. Following that, a RTD probe with adsorbent packing was inserted into the adsorption chamber.

Step 2: Regeneration Before the adsorption experiment, the entire assembly was evacuated for 24 h to a vacuum level of 0.5 mbar and degassed at 140 - 160 °C for 4 h. The regeneration temperature was preset for the optimum degassing of the specific adsorbent loaded in the adsorption cell, and was determined by specific adsorbent characteristics. During the degassing, helium was purged into the chambers intermittently during regeneration to remove the residue gas.

Step 3: Temperature Control After the evacuation, the adsorption cell was isolated from the charging chamber, by switching off all needle valves. The adsorbent sample was cooled down to the required adsorption temperature, by that both adsorption and charging cells were immersed in the water bath, which is connected to the refrigerating/heating circulators.

Step 4: Pressure Control When the system is thermally stabilised, the charging cylinder was pressurised with the adsorbate from its source. After sufficient time, the charging cell reached the thermally stable temperature, and the needle valve between

the charging and adsorption cells was opened gently. The adsorbate was released into the adsorption cell. The changes of both temperature and pressure were recorded at 1 s intervals over the entire experiment. These two readings play a central role to calculate the amount of bulk phase uptake during the adsorption, which took no less than half an hour to reach the equilibrium state.

Step 5: Isothermal Cycle After each adsorption process, the needle valve between charging and adsorption cells was closed to isolate the adsorption cell from charging chamber. The charging cylinder was then again pressurized to different value with adsorbate. The increasing step size of the pressure was about 1 bar, and the pressure range covered up to 35 bar. The same procedures were repeated for different temperatures ranging from 5 - 55 °C. The experiment range of pressure and temperature were determined upon characteristics of adsorbate gas, and pressure ranges should always be below the saturation pressure value for respective temperatures, in case of condensation of gas molecules inside the adsorbent capillary, and associated errors in estimating of adsorbate uptake.

Step 6: Gaseous Compressibility In addition, to understand the gaseous transport mechanism in the adsorbent particles, transport parameters from the experimental uptake results must be extracted. Hence, it is necessary quantify the effect of temperature changes due to the sudden compression of adsorbate into the adsorption cell without adsorbent from charging chamber. The effect is measured by performing blank adsorbate charging into adsorption cells without adsorbent samples loaded at respective conditions similar to the actual adsorption experiments. As a result, the temperature effects due to adsorption, which is heat of adsorption, could to be determined by offsetting the temperatures increase from the adsorption experiment by the temperature increasing during the blank charging.

4.3.2 Cryostat Setup

In order to conduct adsorption isotherm experiments at the cryogenic temperature range 120 - 220 K, a cryogenic adsorption setup was designed, developed and fabricated, as shown in Figures 4.15 and 4.16. This setup is necessary for understanding the adsorption of CH_4 under ANG-LNG coupling conditions.

Figure 4.15: Schematic diagram of cryogenic adsorption setup.

The setup consists of an adsorption reactor chamber, made up with oxygen-free high thermal conductivity (OFHC) copper, which has been electrolytically refined to reduce the level of oxygen to 0.001% or below, for optimum isothermal operation by

Figure 4.16: Pictorial view of cryogenic adsorption setup.

its high thermal conductivity. The internal volume of the chamber is 100 ± 0.5 mL and indium wire seal is used to prevent leakage of adsorbate gas. Liquid nitrogen was introduced from the 50 L aluminium dewar by cryogen entry and flow through the convey hose, which is isolated from the ambient by an evacuated sleeve outside. Following that, liquid nitrogen flows out from the cryogen venting port, and heat was drawn out from the reacting chamber by the copper stick which led to the liquid nitrogen flow cycle. The copper stick was isolated from the ambient by a vacuum shroud. The temperature inside the chamber was expected to be cooled down to 77 K. Two cartridge heaters are mounted into the lower wall of the reactor at 180° from each other to increase the temperature of the reactor from 77 K to 420 K depending

on experimental requirements. The heaters are manipulated by Model 22C cryogenic temperature controller with enhanced PID (proportional-integral-derivative) adjustor. An internal spring and pressure plate are applied to hold adsorbent materials and push them up against the DT-670B-CU-HT silicon diode thermometers (uncertainty $\pm 0.5^{\circ}\text{C}$), so that the temperature of the adsorbent could be measured directly. The working pressure range of this setup is 0 - 15 bar, which is controlled by the gas source regulator. The pressure changes were recorded by GS4200-USB digital pressure transducer with an error of $\pm 0.1\%$. The adsorption isotherm of methane were experimentally studied here for temperatures varying from 125 K to 303 K, and pressures up to 10 bar.

4.4 Calculations of Adsorbate Uptakes

The data collected from the volumetric adsorption experiment are pressure and temperature readings of the charging and the adsorption cells as shown in Figures 4.14 and 4.15. These readings need to be reduced into uptake data and be fitted into isotherm and kinetics equations. In order to calculate the uptake, additional information such as the volume of the charging and the adsorption cells, and the density of the gas as a function of temperature and pressure, are required.

To determine the volume of the charging and the adsorption cells, both liquid volume calibration and gas volume calibration were conducted. In the liquid calibration method, two sub-methods were applied, (i) volume of water filled into the cells measurement, and (ii) liquid within the cells gravimetric measurement. In this research, both methods were performed to evaluate the suitability and accuracy of each chamber. The liquid calibration was conducted on the charging cell, and the adsorption cell was calibrated by gas calibration. Therefore, the charging cell had to be calibrated very precisely, as it would affect the measurements of the subsequent gas calibration. As the adsorbents were later placed inside the adsorption cell, the volume taken by the adsorbent samples V_{solid} need to be deducted. Firstly, liquid

water was injected into the charging cell with a syringe, and amounts of injected by syringe and drained from the measuring cylinder are recorded. Secondly, dry cells under vacuum were weighed and then water was charged into the cell, and be weighed again together. The weight of water occupying all space inside the cell can be measured. Finally, after volume of charging cell V_{char} was determined by liquid calibration, high purity carbon dioxide gas was filled into the charging cell and the equilibrium temperature and pressure were recorded. By allowing He gas to travel to the adsorption cell, the values of T and P were recorded again. With the density of He gas as function of temperature and pressure based on real gas model, the volume of the adsorption cell, V_{react} , was determined by the difference between the total volume of charging and adsorption cells, i.e. $V_{char} + V_{react}$ and V_{char} . All calibration steps were repeated for five times to maintain precision and accuracy.

The density of gas, with respect to temperature and pressure, $\rho(T_{read}, P_{read})$, was obtained from *NIST Standard Reference Database* of Version 8.0 at specified state points.

At the first step, there is remaining gas inside the adsorption cell, and was calculated by:

$$x_{remain} = \rho_{react}(T_{read}, P_{read}) \cdot V_{react} \quad (4.1)$$

The amount of adsorbate gas in the charging cell is given by

$$x_{char} = \rho_{char}(T_{read}, P_{read}) \cdot V_{char} \quad (4.2)$$

After the adsorption reaction, the residual mass is left in the apparatus as

$$x_{res} = \rho_{res}(T_{read}, P_{read}) \cdot (V_{char} + V_{react}) \quad (4.3)$$

Therefore, the subsequent adsorbed mass is calculated from

$$x_a = x_{remain} + x_{char} - x_{res} \quad (4.4)$$

The mass adsorbed at equilibrium after each charging pressure will be accumulated to obtain the uptake of adsorption under each equilibrium pressure. This cumulative adsorbed uptake are plotted with the absolute equilibrium pressure or the relative pressure to saturated value, to obtain the experimental adsorption isotherm chart.

4.5 Summary

In this section, physical properties of experiment materials applied are analysed, and experimental setups working within ambient and cryogenic temperature range are also introduced. In this study, the volumetric measurement method was applied. To minimise the system error, the volumes of charging and reaction cells were calibrated with different methods, and pressure transducers were also calibrated over entire experimental pressure range. The experimental procedures were designed to minimise the operation error. A cryostat device was also designed in order to examine adsorption performance of adsorbent + adsorbate framework under cryogenic conditions, and provide reference for the novel adsorption isotherm proposal. Measurement to reduce adsorption uptake data from the experimental readings is demonstrated at the last part. The following chapter discusses various adsorption isotherms and kinetics results for the validation of the proposed isotherm and kinetics model. The experimental data of AQSOA-zeolite + H₂O indicate a new generation of adsorption cooling. The experimental realisation of various MOFs - CH₄ systems explains and describes the coupling of LNG and ANG for CH₄ storage purposes, as an urgent agenda according to US Government Department of Energy (DOE).

Chapter 5

Results and Discussion: Adsorption Isotherms

The derived adsorption isotherm model is verified with the experimental data of AQSOA-Z02 zeolite + water, silica gel + water, MIL-100 MOF + water systems. The amount of CH₄ uptakes on HKUST-1 and MIL-101(Cr) were measured for the temperature range of 130 K to 303 K, and pressures up to 10 bar. These experimental data were analysed by the grand canonical Monte Carlo method, based on which the distribution of guest molecules within unit cell of MOFs is understood. The experimental data are fitted with the proposed isotherm model within the acceptable error ranges.

5.1 Various Adsorbents and Water Isotherms

The proposed adsorption uptake formulations as shown in Equation (3.21) in chapter 3 were verified with experimentally measured isotherm data of various adsorbents such as silica gel, zeolites type AQSOA-Z02, MOFs type MIL-100 and activated carbon, and these are shown in Figure 5.1.

One can use Equation (3.21) to calculate the amount of water vapour uptakes for type I and V adsorption isotherms. From the experimental data of water adsorption, the value β is predicted as 9×10^{-7} for all adsorbents. So, one has to predict m to

Figure 5.1: Adsorption characteristics of various hydrophilic and hydrophobic porous adsorbents with adsorption cooling operation ranges. Here, the red dotted lines indicate the DA isotherm model, the blue lines define the isotherms models of BET theory, and the black dotted lines refer to Langmuir isotherm model. The proposed adsorption uptake model agrees well with experimental data within $\pm 5\%$ error. The Langmuir equation fails to fit with the experimental data of S-shape isotherms.

calculate the amount of water vapour uptake. Q_{st}^* is calculated from Equation (3.12) as a function of pore width. For silica gel + water system, $Q_{st}^* = 4000$ kJ/kg as silica gel is mainly the combination of micro and meso-porous structures, Q_{st}^* is estimated as 3600 kJ/kg for AQSOA-Z02 and 2960 kJ/kg for MIL-100(Cu) MOF. This means that AQSOA-Z02 is microporous based and MIL-100 MOF is mainly mesoporous according to Equation (3.12). AQSOA-Z02 is a chabazite (CHA) type molecular sieve with three-dimensional structure, where small guest molecules, such as water, can enter the cages through 0.38 nm windows. For comparison purposes, the Langmuir, Brunauer-Emmett-Teller (BET), and DA isotherm models are included in Figure 5.1. It is found that the amount of water vapour uptake increases from Henry's region to the saturated pressure for silica gel and AQSOA-Z02 zeolites. However, MIL-100 shows the S-shaped isotherm with hydrophobic behaviours for the relative pressure P/P_s varying from 0 to 0.15.

Figure 5.2 shows the uptakes of water vapour against P/P_s on two types of zeolites, namely, AQSOA-Z01 and AQSOA-Z05. The S-shaped isotherms are found, and it should be noted that AQSOA-Z05 structure consists of AlO_4 , PO_4 tetrahedrons with 0.73 nm pores and it shows hydrophobic nature when P/P_s varies from 0 to 0.2. On the other hand, the structural framework of AQSOA-Z01 comprises AlO_4 , PO_4 , and FeO_4 tetrahedrons, where Al and P atoms are partially substituted by Fe atoms. From Figure 5.2, it is found that AQSOA-Z01 is hydrophobic from Henry region to $P/P_s = 0.1$ and this is suitable for adsorption chiller design. Employing the present thermodynamics formulation, it is observed that for AQSOA-Z05 + water system, $Q_{st}^* = 2790$ kJ/kg with the heterogeneity factor m of 13. This means that the adsorbent structure is mesoporous, i.e., little or no adsorption occurs at low pressure side. For AQSOA-Z01 zeolite + water systems, Q_{st}^* and m are calculated as 2910 kJ/kg and 9.4, respectively. Here, the surface structure of AQSOA-Z05 is modified by the addition of Fe atoms to form zeolite AQSOA-Z01. Due to the addition of Fe , the pore size is decreased and therefore, Q_{st}^* increases. From the proposed thermodynamics modeling of Equation (3.21), it is established that the pore-surface

structure of AQSOA-Z01 can be further modified by increasing its pore volume and BET surface area.

Figure 5.2: Water vapour uptakes on AQSOA-Z01 and AQSOA-Z05. The experimental data are fitted with the proposed adsorption isotherm equation and the DA isotherm model (red dotted lines).

The adsorption-desorption cycles for silica gel + water ($A'B'CD$) and AQSOA-Z01 + water ($ABCD$) are illustrated in Figure 5.3. Here, the amount of water vapour uptakes are calculated by the proposed thermodynamic formulation and is found that the S-shaped isotherms are suitable for adsorption chiller design due to the fact that the cycled mass of water vapour for AQSOA-Z01 + water system is higher than that of silica gel + water system. Employing the S-shaped isotherm based adsorbent + water system, the size of adsorption/desorption reactor is minimised for the same cooling capacity and coefficient of performance of the conventional adsorption chiller, which indicates a significant breakthrough in cooling science and technology. All fitting parameters with the proposed isotherm Equation (3.21) are listed in Table 5.1,

Figure 5.3: Adsorption-desorption cycle of silica gel + water ($A'B'CD$) and AQSOA-Z01 + water ($ABCD$), where the evaporator pressure is 1 kPa and the condenser pressure is 5 kPa. The SEM picture of silica gel and AQSOA-Z01 are shown here.

resulted from the least squares fitting.

Table 5.1: Fitting parameters with least squares from the proposed isotherm Equation (3.21) for cooling applications.

Adsorbent	β	Q_{st}^* (kJ/kg)	m	$\bar{n}_{max}$ (kg/kg)
AQSOA Z01	9×10^{-7}	2910	9.4	0.189
AQSOA Z02	9×10^{-7}	3600	3.08	0.3
AQSOA Z05	9×10^{-7}	2790	13	0.187
Silica Gel RD	9×10^{-7}	4000	1.46	0.28
MIL-100	9×10^{-7}	2960	5.32	0.32

$$K_h = \beta \exp\left(m \frac{Q_{st}^* - h_{fg}}{R_g T}\right)$$

$$\bar{n}/\bar{n}_{max} = K_h (P/P_s)^m / (1 + (K_h - 1) (P/P_s)^m)$$

5.2 Isotherm of MOFs + Methane Systems

The amount of CH_4 uptakes on HKUST-1 MOF (in terms of gravimetric and volumetric basis) against pressures for the temperatures of 130 K, 140 K and 200 K are shown in Figure 5.4. The experimentally measured CH_4 uptakes on HKUST-1 data (at 125 K) [32] are added for comparison purposes. Methane uptakes at 298 K are also included in Figure 5.4. For the temperatures ranging from 125 K to 140 K, it can be seen that the adsorption uptake increases significantly with the loading pressure, and after around 1 bar, this increase of uptake trend is gradually slowed down. On the other hand, the bulk phase condensation is observed at the ambient of the saturated pressure, which leads to a sharp increase of adsorption uptake. At 200 K (above the critical point temperature) CH_4 uptake increases significantly up to 10 bar. At 35 bar and 298 K, HKUST-1 exhibits a total CH_4 uptake of $227 \text{ cm}^3/\text{cm}^3$, a value lower than the new DOE targets of $350 \text{ cm}^3/\text{cm}^3$. At 298 K and 35 bar, the gravimetric uptake is 0.2 g/g, which is notably lower than the DOE target (0.5 g/g) [56]. However, at 100 bar and 298 K, the volumetric uptake is found below $300 \text{ cm}^3/\text{cm}^3$. So methane gas storage at low temperature improves both the gravimetric and volumetric uptake capacities. The fitting results from the proposed isotherm are shown in red line by Figure 5.4, and parameters are tabulated in Table 5.2. For this application, the reference pressure $P^\ominus$ in Equation (3.21) can be set to 1 bar instead of the saturated pressure P_s .

The HKUST-1 + CH_4 isosteric heat of adsorption Q_{st} is plot in Figure 5.5, calculated with Equation (3.29). It can be found that (1) with increasing of CH_4 uptakes, Q_{st} decreases from its maximum value towards the latent heat of evaporation h_{fg} , and (2) the isosteric heat of adsorption at the Henry's region Q_{st}^* decreases with temperature increasing, which is thermodynamic consistent as adsorption would be favoured at lower temperature.

The cryogenic experimental results are also normalised with respect to P/P_s and $\bar{n}/\bar{n}_{max}$. The limiting uptake is estimated as $\bar{n}_{max} = \rho_l V_{pore}$, where ρ_l is the adsorbed phase density. The pressure is also normalised by the saturated pressure P_s . The

Figure 5.4: Gravimetric and volumetric adsorption isotherms of CH_4 on HKUST-1 MOF at 125 K, 130 K, 140 K, 200 K and 298 K. The logarithmic pressure scale is employed. The red lines show the fitting results with the proposed isotherm Equation (3.21). The fitting parameters are: $K_h = 3433.15, 205.35, 262.85, 1.79, 1.05$, $m = 2.26, 1.52, 2.19, 1.33, 1.07$, and $\bar{n}$ at 1 bar is estimated to be 0.32, 0.31, 0.29, 0.14, 0.014. The Langmuir (blue line) and DA (green line) isotherms are also applied for comparison.

normalised experimentally measured CH_4 uptakes (for the temperatures ranging from 120 K to 180 K) on HKUST-1 are compared with others MOFs + CH_4 adsorption data at 125 K [32]. The adsorption isotherms of HKUST-1 and CH_4 obtained from GCMC simulation are also added for comparison, the details of which is discussed in the following section. All these results are shown in Figure 5.6. At the relative pressure of 0.4, almost all isotherms reach their limiting uptake capacity, and there is no significant uptake increasing. It is also found that Maxsorb III [199] is better in terms of gravimetric uptakes of methane as it meets the targets of DOE. A comparison of volumetric uptakes of CH_4 on various MOFs (HKUST-1, Ni-MOF74, NU-125 and Fe-BTC) and activated carbon (type Maxsorb III) is presented in Figure 5.7. It is

Table 5.2: Fitting parameters from the proposed isotherm Equation (3.21) for CH₄ adsorption with HKUST-1.

Temperature (K)	K_h	m	$\bar{n}_{1bar}$ (g/g)
125	3433.15	2.26	0.32
130	205.35	1.52	0.31
140	262.85	2.19	0.29
200	1.79	1.33	0.14
298	1.05	1.07	0.014

$$\bar{n}/\bar{n}_{1bar} = K_h P^m / (1 + (K_h - 1)P^m)$$

Figure 5.5: Isosteric heat of adsorption for HKUST-1 + CH₄ against uptakes for 125 K and 140 K.

found that HKUST-1 is comparable with other adsorbents for methane uptakes in terms of cm³ per cm³. However, the volumetric methane uptakes on Maxsorb III do not meet the targets of DOE.

To understand LNG gasification and its adsorption on MOFs as an objective of the proposed study, an experimental investigation of CH₄ uptakes on MIL-101 (Cr) was performed for the temperatures ranging from 125 K to 298 K over a broad range

Figure 5.6: A comparison of various MOFs and Maxsorb III for gravimetric CH_4 uptakes at 130 K. The fitting results with the proposed isotherm Equation (3.21) are plotted. The fitting parameters are tabulated in Table 5.4.

of pressures. The gravimetric and volumetric adsorption of CH_4 on MIL-101(Cr) are illustrated in Figure 5.8. The isotherms at 125 K, 130 K and 140 K were recorded up to the saturation pressure of CH_4 . The bulk phase condensation is observed at the beginning of the saturated pressure which leads to a sharp increase of adsorption uptake (3.5 bar at 130 K). The maximum possible gravimetric and volumetric uptakes of CH_4 on MIL-101 (Cr) are found to be 0.42 kg/kg and $370 \text{ cm}^3/\text{cm}^3$, respectively. These are very close to the materials level target of natural gas storage according to US Department of Energy (DOE) [122] for vehicular applications [$350 \text{ (STP)cm}^3/\text{cm}^3$ and 0.5 (STP)g/g]. The fitting results from the proposed isotherm Equation (3.21) are illustrated in red lines, and fitting parameters are furnished in Table 5.3. The HKUST-1 + CH_4 isosteric heat of adsorption Q_{st} is plot in Figure 5.9, calculated with Equation (3.29).

Figure 5.7: A comparison of various MOFs and Maxsorb III for volumetric CH_4 uptakes at 130 K.

Table 5.3: Fitting parameters from the proposed isotherm Equation (3.21) for CH_4 adsorption with MIL-101(Cr).

Temperature (K)	K_h	m	$\bar{n}_{1bar}$ (g/g)
125	3.75	0.63	0.38
130	3.95	0.69	0.36
140	2.78	0.71	0.30
160	1.52	0.63	0.17
200	1.25	0.55	0.098
298	1.03	1.3	0.008

$$\bar{n}/\bar{n}_{1bar} = K_h P^m / (1 + (K_h - 1)P^m)$$

The adsorption phenomenon strongly depends on temperature. As the temperature of the adsorbent is lowered, a lower gas pressure is needed to accomplish the

Figure 5.8: Gravimetric and volumetric uptake isotherms of CH_4 onto MIL-101(Cr) for the temperatures ranging from 130 K to 298 K. The fitting results from the proposed isotherm Equation (3.21) are shown in red lines. The fitting parameters are listed in Table 5.3. The Langmuir (blue line) and DA (green line) isotherms are also applied for comparison.

Figure 5.9: Isothermic heat of adsorption for MIL-101(Cr) + CH_4 against uptakes for 125 K, 130 K and 140 K.

same uptake. When the temperature of the adsorbent is significantly reduced relative to the environment temperature, the required pressure can fall from ~ 10 to a few bar. Employing this technique, more adsorption can be achieved without the requirement of a gas compressor. The desorption process takes place due to heat transfer from the environment after the completion of filling process of CH_4 on MOF. Eventually the pressure inside the tank rises to ~ 10 bar level. So the knowledge of CH_4 adsorption at very low pressures and temperatures (below critical) is necessary. Figure 5.10 shows the pressure benefits of CH_4 adsorption on MIL-101 (Cr) at 160 K and discharge of CH_4 at 298 K and 5 bar (ANG-LNG coupling). The adsorption uptake of CH_4 at 160 K and 1.5 bar is equivalent to CH_4 uptake at 298 K and 35 bar. In this case, the net delivery/working capacity of CH_4 is calculated as $140 \text{ cm}^3/\text{cm}^3$. Similarly, the net delivery/working capacity of CH_4 is $245 \text{ cm}^3/\text{cm}^3$ for the operating parameters ranging from 6 bar at 160 K to 5 bar at 298 K. Thus the delivery/working capacity of CH_4 in ANG-LNG coupling is better than that of the filling and discharge of CH_4 at 298 K only.

Figure 5.10: Pressure benefits of CH_4 adsorption on MIL-101(Cr) MOF at 160 K. The discharge of CH_4 is shown at 298 K and 5 bar with net working or delivery capacity.

From Figure 5.11 (a), it is also found that the volumetric CH_4 uptake characteristic of MIL-101(Cr) is well comparable with the benchmarking adsorbents such as HKUST-1, Ni-MOF-74, PCN-14, UTSA-20. In the case of gravimetric uptake characteristics as shown in Figure 5.11 (b), NU-111 and activated carbon (Maxsorb III) are the top two materials; however, the volumetric CH_4 uptake of Maxsorb III is the lowest. Significantly, the gravimetric CH_4 uptake characteristic of NU-111 and USTA-20 are better than the other reported benchmarking adsorbents such as HKUST-1, Ni-MOF-74, PCN-14 and MIL-101(Cr). Details of grand canonical Monte Carlo (GCMC) simulation are discussed in the following section. All the fitting parameters with the proposed isotherm Equation (3.21) are presented in Table 5.4.

Figure 5.11: Comparison of excess volumetric and gravimetric uptakes of CH_4 at 130 K onto eight adsorbent materials: MIL-101(Cr), HKUST-1, Ni-MOF-74, PCN-14, UTSA-20, NU-125, NU-111 and activated carbon (Maxsorb III). The results are fitted with the proposed isotherm Equation (3.21).

Table 5.4: Fitting parameters from the proposed isotherm Equation (3.21) for eight adsorbent materials at cryogenic 130 K.

MOFs	K_h	m	$\bar{n}_{max}$	
			Gravimetric	Volumetric
MIL-101(Cr)				
(this work)	0.956	0.19	0.44	373.91
Fe-BTC				
(this work)	679.52	1.68	0.12	151.1
HKUST-1[200]	3.11	0.33	0.32	344.389
Ni-MOF-74[200]	24.3	0.63	0.22	375.06
PCN-14 [201]	15.09	0.57	0.29	366.94
UTSA-20 [109]	197299	3.6	0.27	334.97
NU-111 [202]	3.11	0.38	0.84	485.46
NU-125 [203]	0.62	0.15	0.52	410.62
Maxsorb III [79]	2.33	0.352	0.67	288.66

Observation of Methane Adsorption in MOFs Employing GCMC

To obtain theoretical insight of CH_4 adsorption on the unit cell of HKUST-1 and MIL-101(Cr) MOF, the grand canonical Monte Carlo (GCMC) simulation technique [204] is applied for understanding the density distribution of CH_4 mass center in HKUST-1 and MIL-101(Cr). It is well known that the gas adsorption isotherms can be calculated employing GCMC simulation the detail of which are well described by Frenkel and Smit [185]. Getman et al. [205] reviewed and analysed CH_4 storage in MOFs with GCMC methods, and concluded that the simulations were significant for understanding the molecular-level adsorption phenomena, and provide guidelines for the design of various MOFs. Getzschmann et al. [124] studied CH_4 storage mechanism at 77 K using GCMC. Four main adsorption sites were identified inside the small and larger pores of the metal organic frameworks. Karra and Walton [118, 119] investigated the influence of open metal sites in HKUST-1 on the selectivity between CO and CH_4 , and found that the main pore size was large enough to hold both molecules. Zeitler et al. [206] conducted a GCMC simulation of nano-porous

frameworks including HKUST-1, at low pressure CH₄ adsorption, and justified the usage of pure methane GCMC simulations for large scale screening of nanoporous framework materials.

Within a grand canonical ensemble, the chemical potential, the system volume, and the temperature are maintained constant. The GCMC simulation is run with MuSic¹ code [207]. 12-6 Lennard-Jones (LJ) potential in Equation (2.1) is used for the van der Waals interactions between CH₄ and HKUST-1 adsorbent framework. Lorentz-Berthelot mixing rules are utilised to calculate the cross interaction parameters between different atoms, as given by the following equations [208]:

$$\phi_{12} = 4\epsilon_{12} \left[\left(\frac{\delta_{12}}{r_{12}} \right)^{12} - \left(\frac{\delta_{12}}{r_{12}} \right)^6 \right] \quad (5.1a)$$

$$\delta_{12} = \frac{1}{2}(\delta_1 + \delta_2) \quad (5.1b)$$

$$\epsilon_{12} = \sqrt{\epsilon_1 \epsilon_2} \quad (5.1c)$$

where ϕ indicates the adsorbent-adsorbate interaction potential, ϵ defines the solid-fluid well depth potential, r is the distance between a site of molecule 1 and another site of molecule 2 or the framework atom, and δ defines the solid-fluid collision diameter. Employing the PXRD result, the unit cell framework of HKUST-1 constructed at Figure 4.7. The framework consists of copper and Benzene-1,3,5-tricarboxylic acid (BTC) linker, and forms into a cuboid with dimensions of $26.34 \times 26.34 \times 26.34 \text{ \AA}^3$. The potential parameters of HKUST-1 framework are calculated from the Universal Force Field [209] (UFF), while the potential for CH₄ is computed with TraPPE Force Field model [210], in which the actual CH₄ molecule is regarded as one pseudo atom. All parameters are listed in Table 5.5.

As CH₄ is a non-polar molecule, the electrostatic interactions are not taken into

¹MuSic is a general purpose molecular simulation code package designed, developed and maintained by research team led by Professor Randall Q. Snurr at Northwestern University. <http://zeolites.cqe.northwestern.edu/software.php>

Table 5.5: Lennard-Jones (LJ) Potential Parameters for CH₄ with HKUST-1 and MIL-101(Cr)

	Atom types	δ (Å)	ϵ/k (K)
Adorbate	CH ₄	3.73	148
HKUST-1	C	3.43	52.84
	H	2.57	22.14
	O	3.12	30.19
	Cu	3.11	2.516
MIL-101(Cr)	Cr	2.69	7.55

account in this work. For computation efficiency, the potential energies of HKUST-1 framework are pre-tabulated into a potential map with nodes spaced of 0.2 Å, and the potential energies at other nodes are calculated by interpolation techniques. $2 \times 2 \times 2$ unit cells of frameworks are used, and the periodic boundary condition is applied in all three different directions. The cutoff radius between CH₄ and HKUST-1 is set to be half of MOF lattice box length, which is 13.17 Å. To each equilibrium state, 20 million steps are trailed including random translation, random insertion, and random deletion. The last 40 % steps are adopted for ensemble average calculation. All three types of moves are given equal weight.

The absolute uptake from GCMC is converted into excess uptake, as represented by $x_{ex} = x_{abs} - \rho V_{pore}$, where, x_{abs} is the absolute uptake, whereas x_{ex} is the excess uptake. V_{pore} is the helium accessible pore volume of HKUST-1, and ρ is the density of CH₄ at the bulk phase with given temperature and pressure. ρ is computed by Peng-Robinson equation of state, and V_{pore} is estimated employing the method as proposed by Talu and Myers [94], which is also demonstrated by Guo et al [211]. By assuming that Helium is a non-adsorbing gas, the amount of helium molecules x_{He} contained in a unit mass of HKUST-1 framework, at Henrys region ($P \rightarrow 0$) and ambient temperature T , can be used to calculate V_{pore} as

$$V_{pore} = \frac{kT}{P} x_{He} \quad (5.2)$$

The estimated result of pore volume is $0.775 \pm 0.00064 \text{ cm}^3/\text{g}$, which is consistent with the reported value [122] of $0.75 \sim 0.78 \text{ cm}^3/\text{g}$. As to the CH_4 accessible specific surface area S_{surface} of the adsorbent framework, it can be estimated with one CH_4 probe molecule and roll it over the framework from Monte Carlo technique [212]. In current work, S_{surface} is calculated to be $2176.96 \text{ m}^2/\text{g}$. The isosteric heat of adsorption Q_{st} can be calculated as [211, 213]:

$$Q_{st} = R_g T - \left. \frac{\partial \langle v \rangle}{\partial \langle x \rangle} \right|_T \quad (5.3)$$

where $\langle v \rangle$ is the potential average of the adsorbed phase, and $\langle x \rangle$ is the uptake amount average at temperature T . Equation (5.3) is used to estimate the isosteric heat of adsorption at the Henry's region. For HKUST-1 + CH_4 system, the Q_{st}^* at Henry's region is calculated as 16.22 kJ/mol .

The present GCMC simulation setup is used for excess adsorption isotherm between CH_4 and HKUST-1 at 298 K, and compared with that of the reference result [118] as shown in Figure 5.12. As good agreement is indicated by the comparison, the present force field setup is verified to study the subcritical area in current work.

The simulation snapshots of CH_4 at 140 K for 1 kPa, 5 kPa and 600 kPa are shown in Figure 5.13. It can be seen that CH_4 molecules will first occupy the tetrahedron-shaped pockets near the copper sites (Figure 5.13 left); when the pockets are saturated, they start to capture the larger diamond-shaped channels in the centre of the framework (Figure 5.13 middle); with further increase of loading pressure, all pockets, channels, and cavities are eventually occupied (Figure 5.13 right). This sequence indicates that CH_4 adsorption onto HKUST-1 at cryogenic temperatures is heterogeneous, as two types of pore structures and sizes are presented. Figure 5.14a illustrates the contour plot of density distribution of CH_4 adsorption on HKUST-1 at 140K and 5 kPa from the viewpoints of [100] directions. Figure 5.14b shows the density distribution from direction [111]. Both Figures 5.14a and 5.14b indicate that the favourite uptake sites of CH_4 in HKUST-1 framework to be the tetrahedron-shaped pockets near the copper atoms, located around the 8 corners and 4 diagonals of the

Figure 5.12: Verification of the GCMC simulated excess isotherm of CH_4 on HKUST-1 with the reference results at ambient temperature 298 K.

framework.

Figure 5.13: Snapshots of CH_4 (green spheres) in HKUST-1 MOF at 140 K for 1 kPa (Left), 5 kPa (Center), and 600 kPa (Right). Here C-gray, H-white, O-red, Cu-pink.

Similarly, the simulation snapshots of CH_4 onto MIL-101(Cr) structure at 130 K in the pressure range from 1 kPa to 100 kPa are shown in Figure 5.15. It is observed that CH_4 molecules will first occupy the tetrahedron-shaped pockets near the Cr sites (Figure 5.15, Top); when the pockets are saturated, CH_4 molecules start

(a) Contour plot of the density distribution of CH₄ mass centre in HKUST-1 at 5 kPa and 140 K, from [100] direction.

(b) Density distribution of CH₄ in HKUST-1 at 5 kPa and 140 K viewed from the [111] direction.

Figure 5.14: Density distribution of CH₄ in HKUST-1 at 5 kPa and 140 K.

to capture the larger diamond-shaped channels near centre of the framework (Figure 5.15, Middle). Finally, all pockets, channels and cavities are eventually occupied with further increase of loading pressure (Figure 5.15, Bottom). This sequence indicates

that CH_4 adsorption onto MIL-101(Cr) is heterogeneous, as two types of inner cages are present in MIL-101(Cr) structure.

5.3 Summary

Employing the proposed model, the thermodynamic trends of water vapour uptakes on various adsorbents were estimated by calculating the amount of water vapour uptakes on various adsorbents including zeolites, metal organic frameworks (MOFs) and silica gel for the development of an advanced adsorption chiller. The crystal structure of HKUST-1 and MIL-101(Cr) MOFs employing PXRD is examined. A general volumetric apparatus is successfully incorporated with a cryostat where the uptakes of pure methane on MOFs type HKUST-1 and MIL-101(Cr) are measured for temperatures ranging from (120 to 200) K and pressure up to 1 MPa. The amount of methane uptakes are computed in the unit cell of HKUST-1 and MIL-101(Cr) employing GCMC simulation and these results agree well with the experimental data. The isotherm results and the density distribution of CH_4 in the adsorbent structures provide the necessary information about the charging pressure for ANG storage systems, especially when the natural gas is charged from the LNG terminal at near cryogenic temperatures. The calculated heat of adsorption is useful to predict the final temperature of the storage chamber.

Figure 5.15: Snapshots view from $[110]$ direction of CH_4 (green sphere) in MIL-101(Cr) at 130 K for 1 kPa (Top), 5 kPa (Middle) and 100 kPa (Bottom).

Chapter 6

Results and Discussion:

Adsorption Kinetics

The performance of an adsorption chiller depends mainly on the nature of adsorption isotherms, kinetics and the isosteric heat of adsorption of adsorbent + adsorbate pairs. Up to now, numerous investigations are reported on various adsorption system configurations, experimental investigations and mathematical modelling of adsorption cycles [7–10]. From the literature review [214–220] it is understood that (i) the Freundlich, Toth and Dubinine-Astakhov equations are mainly used for describing the amount of adsorbate uptakes for various pressures and temperatures, (ii) the enthalpy of adsorption derived from the isosteric chart of adsorbent + adsorbate pair in the Clausius-Clapeyron coordinates is used to calculate the theoretical maximum COP (coefficient of performance) and (iii) adsorption kinetics approximated by the LDF (linear driving force) model are used to calculate the dynamic behaviour of adsorption chiller [221, 222]. All these information are needed to model and simulate an adsorption chiller. Silica gels and zeolites are commonly used as adsorbents for adsorption chiller purposes.

It is found experimentally that very simple monolayer configuration of loose adsorbent grains results in rather fast adsorption dynamics [223–225]. Its experimental desorption rate is also found to be faster than appropriate adsorption

rate by a factor of 2.2-3.5 [223, 226]. The size of silica gel grains was found to be a powerful tool to manage the dynamics of isobaric water ad-/desorption. For large grains (>0.5 mm), the characteristic time for adsorption and desorption is strongly dependent on the adsorbent grain size and was found to be proportional to the size of silica gel that is in accordance with the LDF model [223, 226]. For smaller silica grains, the maximum specific cooling power can exceed 5 kW/kg [223, 226], which is very attractive for designing compact adsorption chiller as a monolayer configuration of loose silica gel grains provides quite fast adsorption dynamics. However, it is expected that employing the present configuration of adsorption chiller, the COP (coefficient of performance) is not optimal as the mass of adsorbent housed in the monolayer is small as compared with the inert masses of adsorption bed unit. Because of this, the design with more than one layer is more realistic. So, the investigation of adsorption dynamics in a thin bed containing a small number of loose grain layers (1 to 10) is of high practical interest [223–226]. The various configurations of adsorbent particles that are housed in the beds of a typical adsorption chiller are shown in Figure 6.1 [227].

Figure 6.1: Schematic layout of a two-bed adsorption chiller with various configurations of adsorbent layer in the sorption beds.

This chapter mainly focuses on the validation of the proposed kinetics model as described in Chapter 3, for the understanding of adsorption kinetics under various site-layer configurations of adsorbent surface. Due to the availability of experimental data during adsorption-desorption periods of a cooling cycle, the silica gel + water system is chosen to verify the proposed kinetics model.

6.1 Silica gel and Water Adsorption Kinetics

Employing Equation (3.12) of Chapter 3, Q_{st}^* can be plotted as a function of pore width, and a plot of Q_{st}^* against pore widths of silica gel for H₂O adsorption is shown in Figure 6.2. The model parameters [9, 228] are given in Table 6.1. It is observed that a rapid change in Q_{st}^* occurs for pore sizes ranging from 3 Å to 7 Å. The pore size distribution of type RD silica gel employing N₂ adsorption data and density function theory (DFT) is shown in Figure 6.3, where the plots of incremental pore volume against pore widths are shown.

Table 6.1: Model parameters of H₂O for slit-shaped nanopores theory

Adsorbate	ε_{sf} (J/mol)	σ_{sf} (Å)	Δ (Å)	ρ_s (g/cm ³)
H ₂ O	8.119×10^{-21}	3.43	3.35	0.055

¹ $Q_{st}^* = kT - \int_0^{H_c} \mu_{ext}(j) \exp[-\mu_{ext}(j)/kT] dj / \int_0^{H_c} \exp[-\mu_{ext}(j)/kT] dj$

² $\mu_{ext}(j) = U_{sf}(j) + U_{sf}(t - j)$

³ $U_{sf} = 2\pi\varepsilon_{sf}\rho_s\sigma_{sf}^2\Delta \left[2/5 (\sigma_{sf}/j)^{10} - (\sigma_{sf}/j)^4 - \sigma_{sf}^4/(3\Delta(0.61\Delta + j)^3) \right]$

The local maxima of type RD are observed at 12.2 Å with minimum pore width of around 4.7 Å. The Q_{st}^* at 4.7 Å is calculated as 72 kJ/mol (≈ 4000 kJ/kg). As can be seen from the top end of Figure 6.2, the variation of Q_{st}^* for various temperatures are not significant.

Figure 6.4 shows the amount of water uptakes on silica gel for the temperatures ranging from 15 °C to 75 °C and pressures up to 7 kPa. The experimental data are fitted with the newly developed adsorption isotherm formulation [40] [Equation (3.21)]

Figure 6.2: Isosteric heat of adsorption for silica gel water system at zero surface coverage against pore widths of silica gels. Here Q_{st}^* for type RD silica gel and water is shown. Here, blue: 303.15 K, green: 308.15 K, red: 328.15 K, and black: 358.15 K.

Figure 6.3: The pore size distribution of type RD silica gel for its local maxima and minimum pore width information.

within the acceptable error ranges ($\pm 5\%$). The adsorption-desorption cycle (ABCD) is plotted in Figure 6.4. The experimental data are also fitted with the Langmuir isotherm equation, given in Equation (2.16). The adsorption kinetics are analysed here for the temperatures ranging (i) from 50°C to 30°C during adsorption phase (D $\rightarrow$ A of Figure 6.4) and (ii) from 55°C to 75°C during desorption phase (B $\rightarrow$ C of Figure 6.4) of the adsorption chiller (ADC).

Figure 6.4: Isotherms of silica gel and water vapour for temperatures of 15°C , 25°C , 35°C , 45°C , 55°C and 75°C . The experimental results are fitted with Equation (3.21), where $\beta = 9 \times 10^{-7}$, $Q_{st}^* = 4000 \text{ kJ/kg} \cdot \text{K}$, and $m = 1.46$. ABCD indicates here the ideal adsorption-desorption cycle. Langmuir isotherms, denoted by the dotted lines, are also presented for comparison, where $\beta = 9 \times 10^{-7}$, and $Q_{st}^* = 4678 \text{ kJ/kg} \cdot \text{K}$.

Figure 6.5 shows water vapour uptakes on silica gel against time in a normalised form (Equation (3.41) in Chapter 3) for the adsorption periods of an ADC [26, 30, 38, 42, 45, 142]. During adsorption and desorption phase of ADC, the dynamic behaviours of water vapour on various layers and sizes silica gels are calculated employing the Langmuiran analogy and the proposed model. The results are also compared with the experimentally measured kinetics data. All parameters used in the present model

Figure 6.5: Dimensionless average adsorption kinetics behaviours of silica gel + water system from pre-cooling to adsorption stage ($50^{\circ}\text{C} \rightarrow 30^{\circ}\text{C}$) for experimentally measured 1 $\square$, 4 $\blacksquare$ and 8 $\circ$ layers configuration with grain sizes of 0.2-0.25 mm. The bulk thick lines indicate the present model. The conventional LDF model (red dotted line) of adsorption chiller during adsorption phase is included here for comparison. The normalized uptake of LDF model is given by $\Delta\theta_t/\Delta\theta = 1 - \exp(-t/\gamma)$, where $1/\gamma = 15D_{so}/R_p^2 \exp(-E_a/RT)$ with $D_{so} = 2.54 \times 10^{-4} \text{ m}^2/\text{s}$, $E_a = 42 \text{ kJ/mol}$ and $R_p = 0.17 \times 10^{-3} \text{ m}$.

are furnished in Table 6.2. The kinetics curves for the smallest layer reveal the least sensitivity to the layer thickness. This means that the water vapour transfer in single layer silica gel configuration is very fast.

Figure 6.6 gives the Langmuir kinetics model behaviour. Figure 6.7 also shows the normalised water vapour uptakes on silica gel as a function of time for desorption periods of ADC with experimental verifications. For comparison purposes, the results obtained from the general LDF model for silica gel + water systems are also included. It is found from Figures 6.5 and 6.7 that the adsorption/desorption kinetics of various silica gel layers sizes configurations depend on β_o . The ideal adsorption/desorption rates are found at $\beta_o = 1$ for thin film silica gel layers. The values of β_o decreases

Figure 6.6: The dimensionless average adsorption kinetics behaviours with Langmuir Equation (2.17).

when the number of silica gel layers in the sorption bed increases. The desorption rate is found to be faster than the adsorption rate (Figure 6.7) due to higher temperatures and vapour pressures. So, the tangible difference in adsorption and desorption times allows an optimisation of overall performance factors of the ADC in terms of cooling capacity and coefficient of performance (COP) by the prolongation of the adsorption stage at the expense of shortening desorption phase. The Langmuir desorption behaviour is shown in Figure 6.8.

From Figures 6.4, 6.6 and 6.8, it can be found that even though Langmuir theory gives satisfactory performance with isotherm, it does so by over-estimating the desorption rate. On the other hand, Langmuirian theory, as a special case whose heterogeneity parameter equals one, loses one degree of freedom and can hardly fit with the experimental desorption kinetics data. This problem, as shown in Figure 6.8, turns obvious with increasing of adsorbent layers, which indicates an enhancement of heterogeneity. On the contrary, the proposed kinetics model overcomes these

Table 6.2: Parameters for adsorption isotherms and kinetics (303 K and 880 Pa) of type RD silica gel + water system

Isotherm	β	$\bar{n}_{max}$ kg/kg	m	Q_{st}^* (kJ/kg)
Equation (3.21)	9×10^{-7}	0.28	1.46	4000
Langmuir	9×10^{-7}	0.43	1	4678

Kinetics	Layer	E_a kJ/mol	β_o	k_{ads}	k_{des}	k_{des}^*
	Thin	42	1	0.077591	0.01758	0.052
	Single	42	0.7	0.054314	0.01231	0.036
	Four	42	0.38	0.029485	0.00668	0.0197
	Eight	42	0.22	0.017070	0.00387	0.011
	>Eight	42	0.1	0.007759	0.00176	0.0052

* Langmuirian kinetics desorption coefficient
 $K_h = k_{ads}/k_{des} = \beta \exp[m(Q_{st}^* - h_{fg})/(R_g T)]$
 $k_{ads} = 12061.8 \exp(-5051.42/T) \beta_o P$

limitations.

Compared to the LDF kinetics model, the proposed adsorption kinetics Equation (3.41) is flexible to simulate different adsorption kinetics behaviours for multilayer adsorbent configurations, under the same temperature and pressure conditions. Equation (3.41) also takes into account the heterogeneity factor m and influence from pressure while considering the desorption kinetics rate. This feature is a significant improvement to the Langmuirian kinetics theory.

From Table 6.2, it is found that (1) regardless the layer configurations, the H₂O + silica gel pair demonstrates consistent equilibrium parameters for isotherm, that are coefficient β , heterogeneity factor m , isosteric heat of adsorption at Henry's region Q_{st}^* , and limiting uptakes $\bar{n}_{max}$. (2) With increasing of layer number, both adsorption rate coefficient k_{ads} and desorption rate coefficient k_{des} decrease. This is consistent with the physical fact that H₂O becomes harder to penetrate the adsorbent layers in/out. (3) Langmuirian theory largely over-estimates the desorption rate coefficient,

Figure 6.7: Dimensionless desorption kinetics behaviours of silica gel + water system ranging from pre-heating to desorption mode ($58^{\circ}\text{C} \rightarrow 80^{\circ}\text{C}$) of adsorption cooling cycle for experimentally measured 1 $\square$, 4 $\blacksquare$ and 8 $\circ$ layers configuration with grain sizes of 0.2-0.25 mm. The bulk thick lines indicate the present model. The conventional LDF model (red dotted line) of adsorption chiller during adsorption phase is included here for comparison.

as well as the limiting uptakes $\bar{n}_{max}$.

6.2 Summary

Employing the proposed adsorption kinetics model, the adsorption rate of H_2O on silica gel type RD is estimated, with perspectives to different grain size and layer numbers. It is found that the performances of adsorption chiller incorporating adsorbents with smaller grain size and layers, in terms of cooling capacity, coefficient of performance and average chilled water temperature, are better than those of larger grain size and layer based silica gel + H_2O adsorption chiller. The results might

Figure 6.8: The dimensionless average desorption kinetics behaviours with Langmuir Equation (2.17).

provide important clue in developing highly efficient solar and/or thermally powered adsorption chillers. Nevertheless, reducing the grain size and number of layer reduces the amount of silica gel that can be used per unit volume of the adsorber bed and hence, increase the overall size of the system leading to the increase in the capital cost. The design of adsorption bed with higher effective thermal conductivity, high packing density of adsorbents in the adsorbent beds, and the multiple channels in the adsorption bed could solve these issues and may favour the commercialisation of the chiller.

Chapter 7

Conclusions and Recommendations

From the perspective of overcoming limitations of the existing adsorption uptake models, an adsorption isotherm equation is proposed [40] in Chapter 3 from the rigour of partition distribution function of each adsorptive site, and the isosteric heat of adsorption Q_{st}^* at zero surface coverage. The analytic model developed calculates adsorbate uptakes on various adsorbent materials, and the isotherm model (a) includes thermodynamically consistent boundary conditions that range from the Henry's region to the saturated pressure, (b) is connected with the porous structures of adsorbent materials, and (c) can be applied to type I, II, III, and V isotherms according to the International Union of Pure and Applied Chemistry (IUPAC). The proposed isotherm equation is validated (Chapter 5) with the experimentally measured data, and it simulates the S-shaped isotherms within acceptable error ($\pm 5\%$) ranges. Based on the novel isotherm model, it is also found that the maximum isosteric heat of adsorption at the Henry's region Q_{st}^* depends on various pore widths, and heterogeneity factor m defines the shape of the adsorption isotherm. So the knowledge of Q_{st}^* and m helps to design new adsorbent materials [40] for adsorption cooling and natural gas storage systems.

On the other hand, an adsorption kinetics equation [182] is presented in Chapter 3, by analysing the grand partition function within the statistics lattice gas model. It takes into account the heterogeneity factor m and influence from pressure while

considering the desorption kinetics rate. The kinetics data of silica gel + water adsorption cooling system are used. It is found the proposed kinetics model fits with experimental data under wide temperature and pressure ranges with accuracy, by taking into account the heterogeneity factor m and influence from pressure while considering the desorption kinetics rate. This feature is a fundamental revision to the Langmuirian kinetics theory, which neglects the pressure influence while considering the desorption rate [182].

A cryostat assisted volumetric apparatus was designed, developed, and fabricated [204], as discussed in Chapter 4, which has been proven to be accurate, robust, and economic compared to the commercially available cryo-adsorption instruments. The proposed setup was utilised to measure the adsorbate uptakes onto various adsorbents, for temperature ranging from 120 K to 303 K and pressure up to 10 bar. It can be seen that utilising the LNG-ANG coupling techniques, the working capacity of natural gas storage would be largely enhanced by 25 %, with respect to both volumetric and gravimetric uptake requirements [204]. The cryogenic adsorption experiment provides necessary information to understand the LNG-ANG coupling techniques.

Besides the analytical and experimental studies, grand canonical Monte Carlo simulation is performed and verified with the experimental isotherm results [204] in Chapter 5, based on which the adsorption of CH_4 molecules within unit cell of MOFs is snapshot. From the simulation studies, it is found that the guest CH_4 molecules favour the metal atom sites at relatively lower pressure range, and with increasing of the loading pressure, they start to capture the larger porous channels of the MOFs cell [204]. Therefore, the adsorption of CH_4 within MOFs is concluded to be a heterogenous process.

The present chapter provides concluding remarks of the thesis, and based on current research works, the improvements of this research topic could be:

1. Establish the adsorption thermodynamics from the view point of grand canonical ensemble to develop analytical solutions of internal energy, enthalpy, Helmholtz free energy, and specific heat capacities.

2. Correlate the heterogeneity factor m in the proposed isotherm equation with physical properties of adsorbate + adsorbent frameworks, by studying the lattice gas model and conducting nano-scale experiments.
3. High-throughput GCMC simulation screening of adsorbent properties, to provide guidance and reference for novel adsorbent material development and synthesis.
4. Employing the concept of the proposed isotherm and kinetics model, as well as the GCMC results, develop novel MOFs for the adsorption of H_2O for cooling applications.

References

- [1] K. C. Ng, K. Thu, Y. Kim, A. Chakraborty, and G. Amy, “Adsorption desalination: An emerging low-cost thermal desalination method,” *Desalination*, vol. 308, pp. 161–179, aug 2013.
- [2] K. C. Ng, K. Thu, B. B. Saha, and A. Chakraborty, “Study on a waste heat-driven adsorption cooling cum desalination cycle,” *International Journal of Refrigeration*, vol. 35, pp. 685–693, may 2012.
- [3] J.-R. Li, Y. Ma, M. C. McCarthy, J. Sculley, J. Yu, H.-K. Jeong, P. B. Balbuena, and H.-C. Zhou, “Carbon dioxide capture-related gas adsorption and separation in metal-organic frameworks,” *Coordination Chemistry Reviews*, vol. 255, pp. 1791–1823, aug 2011.
- [4] B. B. Saha, E. C. Boelman, and T. Kashiwagi, “Computer simulation of a silica gel-water adsorption refrigeration cycle – the influence of operating conditions on cooling output and cop,” *ASHRAE Transactions*, vol. 101, pp. 348–357, 1995.
- [5] B. B. Saha and T. Kashiwagi, “Experimental investigation of an advanced adsorption refrigeration cycle,” *ASHRAE Transactions*, vol. 103, pp. 50–58, 1997.
- [6] E. C. Boelman, B. B. Saha, and T. Kashiwagi, “Parametric study of a silica gel-water adsorption refrigeration cycle – the influence of thermal capacitance and heat exchanger ua-values on cooling capacity, power density, and cop,” *ASHRAE Transactions*, vol. 103, pp. 139–148, 1997.

- [7] K. C. Ng, M. A. Sai, A. Chakraborty, B. B. Saha, and S. Koyama, "The electro-adsorption chiller: Performance rating of a novel miniaturized cooling cycle for electronics cooling," *Journal of Heat Transfer*, vol. 128, no. 9, pp. 889–896, 2006.
- [8] A. Chakraborty, B. B. Saha, S. Koyama, and K. C. Ng, "Thermodynamic modelling of a solid state thermoelectric cooling device: Temperature-entropy analysis," *International Journal of Heat and Mass Transfer*, vol. 49, pp. 3547–3554, sep 2006.
- [9] A. Chakraborty, K. C. Leong, K. Thu, B. B. Saha, and K. C. Ng, "Theoretical insight of adsorption cooling," *Applied Physics Letters*, vol. 98, no. 22, p. 221910, 2011.
- [10] K. Habib, B. B. Saha, A. Chakraborty, S. Koyama, and K. Srinivasan, "Performance evaluation of combined adsorption refrigeration cycles," *International Journal of Refrigeration*, vol. 34, pp. 129–137, jan 2011.
- [11] K. Hirose, "Hydrogen as a fuel for today and tomorrow: expectations for advanced hydrogen storage materials/systems research," *Faraday Discussions*, vol. 151, pp. 11–8, 2011.
- [12] W. I. F. David, "Effective hydrogen storage: a strategic chemistry challenge," 2011.
- [13] R. Ahluwalia and J. Peng, "Automotive hydrogen storage system using cryo-adsorption on activated carbon," *International Journal of Hydrogen Energy*, vol. 34, pp. 5476–5487, jul 2009.
- [14] D. Mori and K. Hirose, "Recent challenges of hydrogen storage technologies for fuel cell vehicles," *International Journal of Hydrogen Energy*, vol. 34, pp. 4569–4574, may 2009.
- [15] J. Wegrzyn and M. Gurevich, "Adsorbent storage of natural gas," *Applied Energy*, vol. 55, pp. 71–83, oct 1996.

- [16] K. Inomata, K. Kanazawa, Y. Urabe, H. Hosono, and T. Araki, "Natural gas storage in activated carbon pellets without a binder," *Carbon*, vol. 40, no. March 2001, pp. 87–93, 2002.
- [17] D. Quinn and J. MacDonald, "Natural gas storage," *Carbon*, vol. 30, pp. 1097–1103, jan 1992.
- [18] J. Sun, T. A. Brady, M. J. Rood, C. M. Lehmann, M. Rostam-Abadi, and A. A. Lizzio, "Adsorbed Natural Gas Storage with Activated Carbons Made from Illinois Coals and Scrap Tires," *Energy & Fuels*, vol. 11, pp. 316–322, mar 1997.
- [19] H. Najibi, A. Chapoy, and B. Tohidi, "Methane/natural gas storage and delivered capacity for activated carbons in dry and wet conditions," *Fuel*, vol. 87, pp. 7–13, jan 2008.
- [20] L. Vasiliev, L. Kanonchik, D. Mishkinis, and M. Rabetsky, "Adsorbed natural gas storage and transportation vessels," oct 2000.
- [21] V. C. Menon and S. Komarneni, "Porous adsorbents for vehicular natural gas storage : A review," *Journal of Porous Materials*, vol. 58, pp. 43–58, 1998.
- [22] D. D. Do, *Adsorption Analysis: Equilibria and Kinetics*, vol. 2 of *Series on Chemical Engineering*. Imperial College Press, 1998.
- [23] C. Chen, R. Wang, Z. Xia, and J. Kiplagat, "Study on a silica gel water adsorption chiller integrated with a closed wet cooling tower," *International Journal of Thermal Sciences*, vol. 49, pp. 611–620, mar 2010.
- [24] H. T. Chua, A. Chakraborty, and X. Wang, "An adsorption chiller driven by thermoelectricity," in *Refrigeration And Air Conditioning*, pp. 1–8, 2004.
- [25] Y. Liu and K. Leong, "Numerical study of an internal-reforming solid oxide fuel cell and adsorption chiller co-generation system," *Journal of Power Sources*, vol. 159, pp. 501–508, sep 2006.

- [26] I. Glaznev and Y. Aristov, “The effect of cycle boundary conditions and adsorbent grain size on the water sorption dynamics in adsorption chillers,” *International Journal of Heat and Mass Transfer*, vol. 53, pp. 1893–1898, apr 2010.
- [27] T. Núñez, W. Mittelbach, and H.-M. Henning, “Development of an adsorption chiller and heat pump for domestic heating and air-conditioning applications,” *Applied Thermal Engineering*, vol. 27, pp. 2205–2212, sep 2007.
- [28] S. Henninger, M. Schicktanz, P. Hügenell, H. Sievers, and H.-M. Henning, “Evaluation of methanol adsorption on activated carbons for thermally driven chillers part I: Thermophysical characterisation,” *International Journal of Refrigeration*, vol. 35, pp. 543–553, may 2012.
- [29] S. Qian, K. Gluesenkamp, Y. Hwang, R. Radermacher, and H.-H. Chun, “Cyclic steady state performance of adsorption chiller with low regeneration temperature zeolite,” *Energy*, vol. 60, pp. 517–526, oct 2013.
- [30] Y. I. Aristov, I. S. Glaznev, and I. S. Girnik, “Optimization of adsorption dynamics in adsorptive chillers: Loose grains configuration,” *Energy*, vol. 46, pp. 484–492, oct 2012.
- [31] J. W. Wu, M. J. Biggs, and E. J. Hu, “Dynamic model for the optimisation of adsorption-based desalination processes,” *Applied Thermal Engineering*, vol. 66, pp. 464–473, may 2014.
- [32] A. Rezk, R. Al-Dadah, S. Mahmoud, and A. Elsayed, “Characterisation of metal organic frameworks for adsorption cooling,” *International Journal of Heat and Mass Transfer*, vol. 55, pp. 7366–7374, dec 2012.
- [33] A. Khutia, H. U. Rammelberg, T. Schmidt, S. Henninger, and C. Janiak, “Water Sorption Cycle Measurements on Functionalized MIL-101Cr for Heat Transformation Application,” *Chemistry of Materials*, vol. 25, pp. 790–798, mar 2013.

- [34] Y. I. Aristov, “Challenging offers of material science for adsorption heat transformation: A review,” *Applied Thermal Engineering*, vol. 50, pp. 1610–1618, feb 2013.
- [35] A. Rezk, R. Al-Dadah, S. Mahmoud, and A. Elsayed, “Characterisation of metal organic frameworks for adsorption cooling,” *International Journal of Heat and Mass Transfer*, vol. 55, pp. 7366–7374, dec 2012.
- [36] H. Demir, M. Mobedi, and S. Ülkü, “A review on adsorption heat pump: Problems and solutions,” *Renewable and Sustainable Energy Reviews*, vol. 12, pp. 2381–2403, dec 2008.
- [37] Y.-D. Kim, K. Thu, and K. C. Ng, “Adsorption characteristics of water vapor on ferroaluminophosphate for desalination cycle,” *Desalination*, vol. 344, pp. 350–356, jul 2014.
- [38] B. B. Saha, A. Chakraborty, S. Koyama, and Y. I. Aristov, “A new generation cooling device employing CaCl_2 -in-silica gel water system,” *International Journal of Heat and Mass Transfer*, vol. 52, pp. 516–524, jan 2009.
- [39] A. A. Askalany, B. B. Saha, K. Kariya, I. M. Ismail, M. Salem, A. H. Ali, and M. G. Morsy, “Hybrid adsorption cooling systems An overview,” *Renewable and Sustainable Energy Reviews*, vol. 16, pp. 5787–5801, oct 2012.
- [40] B. Sun and A. Chakraborty, “Thermodynamic formalism of water uptakes on solid porous adsorbents for adsorption cooling applications,” *Applied Physics Letters*, vol. 104, p. 201901, may 2014.
- [41] S. K. Henninger, H. a. Habib, and C. Janiak, “MOFs as adsorbents for low temperature heating and cooling applications,” *Journal of the American Chemical Society*, vol. 131, pp. 2776–7, mar 2009.
- [42] Y. I. Aristov, M. M. Tokarev, A. Freni, I. S. Glaznev, and G. Restuccia, “Kinetics of water adsorption on silica Fuji Davison RD,” *Microporous and Mesoporous Materials*, vol. 96, pp. 65–71, nov 2006.

- [43] H. T. Chua, K. C. Ng, A. Chakraborty, N. M. Oo, and M. A. Othman, “Adsorption Characteristics of Silica Gel + Water Systems,” *Journal of Chemical & Engineering Data*, vol. 47, pp. 1177–1181, sep 2002.
- [44] M. Goldsworthy, “Measurements of water vapour sorption isotherms for RD silica gel, AQSOA-Z01, AQSOA-Z02, AQSOA-Z05 and CECA zeolite 3A,” *Microporous and Mesoporous Materials*, vol. 196, pp. 59–67, sep 2014.
- [45] Y. I. Aristov, B. Dawoud, I. S. Glaznev, and A. Elyas, “A new methodology of studying the dynamics of water sorption/desorption under real operating conditions of adsorption heat pumps: Experiment,” *International Journal of Heat and Mass Transfer*, vol. 51, pp. 4966–4972, sep 2008.
- [46] R. Wang, “Performance improvement of adsorption cooling by heat and mass recovery operation,” *International Journal of Refrigeration*, vol. 24, pp. 602–611, 2001.
- [47] J. Cai, J. Qi, C. Yang, and X. Zhao, “Poly(vinylidene chloride)-based carbon with ultrahigh microporosity and outstanding performance for CH₄ and H₂ storage and CO₂ capture,” *ACS Applied Materials and Interfaces*, vol. 6, pp. 3703–11, mar 2014.
- [48] K. Sumida, S. Horike, S. S. Kaye, Z. R. Herm, W. L. Queen, C. M. Brown, F. Grandjean, G. J. Long, A. Dailly, and J. R. Long, “Hydrogen storage and carbon dioxide capture in an iron-based sodalite-type metal organic framework (Fe-BTT) discovered via high-throughput methods,” *Chemical Science*, vol. 1, no. 2, p. 184, 2010.
- [49] Q. Liu, L. Ning, S. Zheng, M. Tao, Y. Shi, and Y. He, “Adsorption of carbon dioxide by MIL-101(Cr): regeneration conditions and influence of flue gas contaminants,” *Scientific reports*, vol. 3, p. 2916, jan 2013.
- [50] J.-R. Li, Y. Ma, M. C. McCarthy, J. Sculley, J. Yu, H.-K. Jeong, P. B. Balbuena, and H.-C. Zhou, “Carbon dioxide capture-related gas adsorption

- and separation in metal-organic frameworks,” *Coordination Chemistry Reviews*, vol. 255, pp. 1791–1823, aug 2011.
- [51] W. Morris, B. Leung, H. Furukawa, O. K. Yaghi, N. He, H. Hayashi, Y. Houndonougbo, M. Asta, B. B. Laird, and O. M. Yaghi, “A combined experimental-computational investigation of carbon dioxide capture in a series of isorecticular zeolitic imidazolate frameworks,” *Journal of the American Chemical Society*, vol. 132, pp. 11006–8, aug 2010.
- [52] M. Plaza, S. García, F. Rubiera, J. Pis, and C. Pevida, “Post-combustion CO₂ capture with a commercial activated carbon: Comparison of different regeneration strategies,” *Chemical Engineering Journal*, vol. 163, pp. 41–47, sep 2010.
- [53] Z. Yang, X. Peng, and D. Cao, “Carbon dioxide capture by pafcs and an efficient strategy to fast screen porous materials for gas separation,” *The Journal of Physical Chemistry C*, vol. 117, pp. 8353–8364, apr 2013.
- [54] S. M. Lucena, V. A. Gomes, D. V. Gonçalves, P. G. Mileo, and P. F. Silvino, “Molecular simulation of the accumulation of alkanes from natural gas in carbonaceous materials,” *Carbon*, vol. 61, pp. 624–632, sep 2013.
- [55] F. Gándara, H. Furukawa, S. Lee, and O. M. Yaghi, “High methane storage capacity in aluminum metal-organic frameworks,” *Journal of the American Chemical Society*, vol. 136, pp. 5271–4, apr 2014.
- [56] E. Roszak and M. Chorowski, “Exergy analysis of combined simultaneous liquid natural gas vaporization and adsorbed natural gas cooling,” *Fuel*, vol. 111, pp. 755–762, sep 2013.
- [57] J. A. Mason, M. Veenstra, and J. R. Long, “Evaluating metal organic frameworks for natural gas storage,” *Chemical Science*, vol. 5, no. 1, p. 32, 2014.

- [58] Y. Zhou and L. Zhou, “Fundamentals of High Pressure Adsorption,” *Langmuir*, vol. 25, pp. 13461–13466, dec 2009.
- [59] F. Rodríguez-Reinoso, Y. Nakagawa, J. Silvestre-Albero, J. Juárez-Galán, and M. Molina-Sabio, “Correlation of methane uptake with microporosity and surface area of chemically activated carbons,” *Microporous and Mesoporous Materials*, vol. 115, pp. 603–608, nov 2008.
- [60] <http://www.slng.com.sg/website/content.aspx?wpi=Importance+of+LNG+to+Singapore&mmi=27&smi=117>. accessed date 20-October-2012.
- [61] K. Foo and B. Hameed, “Insights into the modeling of adsorption isotherm systems,” *Chemical Engineering Journal*, vol. 156, pp. 2–10, jan 2010.
- [62] I. Langmuir, “The evaporation, condensation and reflection of molecules and the mechanism of adsorption,” *Physical Review*, vol. 8, pp. 149–176, aug 1916.
- [63] I. Langmuir, “The adsorption of gases on plane surfaces of glass, mica and platinum.,” *Journal of the American Chemical Society*, vol. 40, pp. 1361–1403, sep 1918.
- [64] D. M. Ruthvan, *Principles of Adsorption and Adsorption Processes*. Singapore: Wiley-Interscience Publication, 1984.
- [65] M. Suzuki, *Adsorption Engineering*. Oxford: Elsevier Science, 1990.
- [66] M. M. Dubinin, “Theory of the physical adsorption of gases and vapors and adsorption properties of adsorbents of various natures and porous structures,” *Bulletin of the Academy of Sciences of the USSR Division of Chemical Science*, vol. 9, pp. 1072–1078, jul 1960.
- [67] M. M. Dubinin, “The potential theory of adsorption of gases and vapors for adsorbents with energetically nonuniform surfaces,” *Chemical Reviews*, vol. 60, pp. 235–241, apr 1960.

- [68] M. Dubinin, “Adsorption in micropores,” *Journal of Colloid and Interface Science*, vol. 23, pp. 487–499, apr 1967.
- [69] S. Brunauer, L. S. Deming, W. E. Deming, and E. Teller, “On a Theory of the van der Waals Adsorption of Gases,” *Journal of the American Chemical Society*, vol. 62, pp. 1723–1732, jul 1940.
- [70] A. W. Marczewski, “Analysis of kinetic langmuir model. part I: Integrated kinetic langmuir equation (ikl): A new complete analytical solution of the langmuir rate equation,” *Langmuir*, vol. 26, pp. 15229–15238, oct 2010.
- [71] Y. Liu and L. Shen, “From langmuir kinetics to first- and second-order rate equations for adsorption,” *Langmuir*, vol. 24, pp. 11625–11630, oct 2008.
- [72] J. Fernsler, “A quasi-equilibrium theory of protein adsorption,” *Langmuir*, vol. 27, pp. 148–157, jan 2011.
- [73] R. Bird, *Transport phenomena*. John Wiley & Sons, Inc., 2002.
- [74] X. Yang and B. Al-Duri, “Kinetic modeling of liquid-phase adsorption of reactive dyes on activated carbon,” *Journal of colloid and interface science*, vol. 287, pp. 25–34, jul 2005.
- [75] S. K. Bhatia, M. R. Bonilla, and D. Nicholson, “Molecular transport in nanopores: a theoretical perspective,” *Physical Chemistry Chemical Physics*, vol. 13, p. 15350, sep 2011.
- [76] S. Azizian and H. Bashiri, “Adsorption kinetics at the solid/solution interface: statistical rate theory at initial times of adsorption and close to equilibrium,” *Langmuir*, no. 18, pp. 11669–11676, 2008.
- [77] W. Rudzinski and T. Panczyk, “The langmuirian adsorption kinetics revised: A farewell to the xxth century theories?,” *Adsorption*, pp. 23–34, 2002.

- [78] T. Panczyk and W. Rudzinski, “On the ways of generalization of adsorption kinetic equations for the case of energetically heterogeneous surfaces,” *Applied Surface Science*, vol. 252, pp. 678–686, oct 2005.
- [79] A. Chakraborty, B. B. Saha, K. C. Ng, S. Koyama, and K. Srinivasan, “Theoretical insight of physical adsorption for a single-component adsorbent + adsorbate system: I. thermodynamic property surfaces,” *Langmuir*, vol. 25, pp. 2204–2211, feb 2009.
- [80] M. Polanyi, “Section III. Theories of the adsorption of gases. A general survey and some additional remarks. Introductory paper to section III,” *Transactions of the Faraday Society*, vol. 28, p. 316, 1932.
- [81] B. Bering, M. Dubinin, and V. Serpinsky, “Theory of volume filling for vapor adsorption,” *Journal of Colloid and Interface Science*, vol. 21, pp. 378–393, apr 1966.
- [82] V. A. Astakhov and M. M. Dubinin, “Development of the concept of volume filling of micropores in the adsorption of gases and vapors by microporous adsorbents,” *Bulletin of the Academy of Sciences of the USSR Division of Chemical Science*, vol. 20, pp. 13–16, jan 1971.
- [83] B. P. Bering, V. A. Gordeeva, M. M. Dubinin, L. I. Efimova, and V. V. Serpinskii, “Development of concepts of the volume filling of micropores in the adsorption of gases and vapors by microporous adsorbents,” *Bulletin of the Academy of Sciences of the USSR Division of Chemical Science*, vol. 20, pp. 17–22, jan 1971.
- [84] M. M. Dubinin and V. A. Astakhov, “Development of the concepts of volume filling of micropores in the adsorption of gases and vapors by microporous adsorbents,” *Bulletin of the Academy of Sciences of the USSR Division of Chemical Science*, vol. 20, pp. 3–7, jan 1971.

- [85] M. M. Dubinin and V. A. Astakhov, “Development of the concepts of volume filling of micropores in the adsorption of gases and vapors by microporous adsorbents,” *Bulletin of the Academy of Sciences of the USSR Division of Chemical Science*, vol. 20, pp. 8–12, jan 1971.
- [86] B. Bering, M. Dubinin, and V. Serpinsky, “On thermodynamics of adsorption in micropores,” *Journal of Colloid and Interface Science*, vol. 38, pp. 185–194, jan 1972.
- [87] G. F. Cerofolini and N. Re, “The mathematical theory of adsorption on non-ideal surfaces,” *La Rivista Del Nuovo Cimento Series 3*, vol. 16, pp. 1–63, jul 1993.
- [88] G. Cerofolini, L. Meda, and T. Bandoz, “Adsorption with soft adsorbents or adsorbates. Theory and practice,” *Studies in Surface Science and Catalysis*, vol. 120, pp. 227–272, 1999.
- [89] U. von Gemmingen, “The Fermi Dirac concept for isotherms of adsorbents with heterogeneous surfaces,” *Chemical Engineering Science*, vol. 60, pp. 5198–5205, sep 2005.
- [90] E. A. Guggenheim, “The thermodynamics of interfaces in systems of several components,” *Transactions of the Faraday Society*, vol. 35, p. 397, 1940.
- [91] A. L. Myers, “Thermodynamics of adsorption in porous materials,” *AIChE Journal*, vol. 48, pp. 145–160, jan 2002.
- [92] K. R. Matranga, A. L. Myers, and E. D. Glandt, “Storage of natural gas by adsorption on activated carbon,” *Chemical Engineering Science*, vol. 47, pp. 1569–1579, may 1992.
- [93] A. L. Myers and P. A. Monson, “Adsorption in porous materials at high pressure: Theory and experiment,” *Langmuir*, vol. 18, pp. 10261–10273, dec 2002.

- [94] O. Talu and A. L. Myers, “Molecular simulation of adsorption: Gibbs dividing surface and comparison with experiment,” *AIChE Journal*, vol. 47, pp. 1160–1168, may 2001.
- [95] A. Chakraborty, B. B. Saha, K. C. Ng, S. Koyama, and K. Srinivasan, “Theoretical insight of physical adsorption for a single component adsorbent + adsorbate system: II. the henry region,” *Langmuir*, vol. 25, pp. 7359–7367, jul 2009.
- [96] A. Chakraborty, B. B. Saha, S. Koyama, and K. C. Ng, “On the thermodynamic modeling of the isosteric heat of adsorption and comparison with experiments,” *Applied Physics Letters*, vol. 89, no. 17, p. 171901, 2006.
- [97] R. Roque-Malherbe, *Adsorption and Diffusion in Nanoporous Materials*. CRC Press, 2007.
- [98] T. L. Hill, “Theory of physical adsorption,” *Adv. Catal*, vol. 4, p. 1, 1952.
- [99] http://www.sv.vt.edu/classes/MSE2094_NoteBook/MolecDyn/lj.html. accessed date 19-July-2012.
- [100] W. Loh and A. Chakraborty, “Experimental and theoretical insight of nonisothermal adsorption kinetics for a single component adsorbent adsorbate system,” *Journal of Chemical & Engineering Data*, 2012.
- [101] S. Sen Gupta and K. G. Bhattacharyya, “Kinetics of adsorption of metal ions on inorganic materials: A review,” *Advances in Colloid and Interface Science*, vol. 162, pp. 39–58, feb 2011.
- [102] Duong D. Do, *Adsorption Analysis: Equilibria and Kinetics*, vol. 2 of *Series on Chemical Engineering*. London: Imperial College Press, 1998.
- [103] A. Serbezov, J. D. Moore, and Y. Wu, “Adsorption equilibrium of water vapor on selexsorb-cdx commercial activated alumina adsorbent,” *Journal of Chemical & Engineering Data*, vol. 56, pp. 1762–1769, may 2011.

- [104] E. Di Biase and L. Sarkisov, “Systematic development of predictive molecular models of high surface area activated carbons for adsorption applications,” *Carbon*, vol. 64, pp. 262–280, nov 2013.
- [105] V. N. Popov, “Carbon nanotubes: Properties and application,” jan 2004.
- [106] C. Zanzottera, M. Armandi, S. Esposito, E. Garrone, and B. Bonelli, “CO₂ adsorption on aluminosilicate single-walled nanotubes of imogolite type,” *The Journal of Physical Chemistry C*, vol. 116, pp. 20417–20425, sep 2012.
- [107] C. Fan, D. D. Do, D. Nicholson, J. Jagiello, J. Kenvin, and M. Puzan, “Monte Carlo simulation and experimental studies on the low temperature characterization of nitrogen adsorption on graphite,” *Carbon*, vol. 52, pp. 158–170, feb 2013.
- [108] B. Saha Bidyut, S. Kandadai, A. Chakraborty, K. Habib, I. El Sharkawy Ibrahim, and S. Koyama, “Adsorption characteristics of maxsorb-iii + methane systems by desorption experiments,” *ASME International Mechanical Engineering Congress and Exposition, Proceedings*, vol. 6, pp. 415–419, 2008.
- [109] S. S. Chui, “A chemically functionalizable nanoporous material [Cu₃(TMA)₂(H₂O)₃]_n,” *Science*, vol. 283, pp. 1148–1150, feb 1999.
- [110] H. Li, M. Eddaoudi, M. O’Keeffe, and O. Yaghi, “Design and synthesis of an exceptionally stable and highly porous metal-organic framework,” *Nature*, vol. 402, no. November, pp. 276–279, 1999.
- [111] R. Babarao, Z. Hu, J. Jiang, S. Chempath, and S. I. Sandler, “Storage and separation of CO₂ and CH₄ in silicalite, C₁₆₈ schwarzite, and irmo-1: A comparative study from Monte Carlo simulation,” *Langmuir*, vol. 23, pp. 659–666, jan 2007.
- [112] T. Düren, L. Sarkisov, O. M. Yaghi, and R. Q. Snurr, “Design of new materials for methane storage,” *Langmuir*, vol. 20, pp. 2683–2689, mar 2004.

- [113] H. Frost, T. Düren, and R. Q. Snurr, “Effects of surface area, free volume, and heat of adsorption on hydrogen uptake in metal-organic frameworks.,” *The Journal of Physical Chemistry B*, vol. 110, pp. 9565–70, may 2006.
- [114] C. E. Wilmer, M. Leaf, C. Y. Lee, O. K. Farha, B. G. Hauser, J. T. Hupp, and R. Q. Snurr, “Large-scale screening of hypothetical metal organic frameworks,” *Nature Chemistry*, vol. 4, pp. 83–89, nov 2011.
- [115] A. Gupta, L. A. Clark, and R. Q. Snurr, “Grand Canonical Monte Carlo simulations of nonrigid molecules: Siting and segregation in silicalite zeolite,” *Langmuir*, vol. 16, pp. 3910–3919, apr 2000.
- [116] O. I. Lebedev, F. Millange, C. Serre, G. Van Tendeloo, and G. Férey, “First direct imaging of giant pores of the metal-organic framework mil-101,” *Chemistry of Materials*, vol. 17, pp. 6525–6527, dec 2005.
- [117] X. Yue and X. Yang, “Molecular simulation study of adsorption and diffusion on silicalite for a benzene/CO₂ mixture,” *Langmuir*, vol. 22, pp. 3138–3147, mar 2006.
- [118] J. R. Karra and K. S. Walton, “Effect of open metal sites on adsorption of polar and nonpolar molecules in metal-organic framework Cu–BTC,” *Langmuir*, vol. 24, pp. 8620–8626, aug 2008.
- [119] J. Karra and K. Walton, “Molecular simulations and experimental studies of CO₂, CO, and N₂ adsorption in metal organic frameworks,” *The Journal of Physical Chemistry C*, pp. 15735–15740, 2010.
- [120] C. Valente, E. Choi, M. E. Belowich, C. J. Doonan, Q. Li, T. B. Gasa, Y. Y. Botros, O. M. Yaghi, and J. F. Stoddart, “Metal-organic frameworks with designed chiral recognition sites.,” *Chemical communications (Cambridge, England)*, vol. 46, pp. 4911–3, jul 2010.

- [121] P. Vairaprakash, H. Ueki, K. Tashiro, and O. M. Yaghi, “Synthesis of metalorganic complex arrays,” *Journal of the American Chemical Society*, vol. 133, pp. 759–61, feb 2011.
- [122] Y. Peng, V. Krungleviciute, I. Eryazici, J. T. Hupp, O. K. Farha, and T. Yildirim, “Methane storage in metal-organic frameworks: current records, surprise findings, and challenges,” *Journal of the American Chemical Society*, vol. 135, pp. 11887–94, aug 2013.
- [123] H. Wu, J. M. Simmons, Y. Liu, C. M. Brown, X.-S. Wang, S. Ma, V. K. Peterson, P. D. Southon, C. J. Kepert, H.-C. Zhou, T. Yildirim, and W. Zhou, “Metal-organic frameworks with exceptionally high methane uptake: where and how is methane stored?,” *Chemistry (Weinheim an der Bergstrasse, Germany)*, vol. 16, pp. 5205–14, may 2010.
- [124] J. Getzschmann, I. Senkovska, D. Wallacher, M. Tovar, D. Fairen-Jimenez, T. Düren, J. M. van Baten, R. Krishna, and S. Kaskel, “Methane storage mechanism in the metal-organic framework $\text{Cu}_3(\text{BTC})_2$: An in situ neutron diffraction study,” *Microporous and Mesoporous Materials*, vol. 136, pp. 50–58, dec 2010.
- [125] J. Cortés, “Gas-solid adsorption isotherms,” *Advances in Colloid and Interface Science*, vol. 22, pp. 151–176, jul 1985.
- [126] M. Khalfaoui, S. Knani, M. Hachicha, and A. Lamine, “New theoretical expressions for the five adsorption type isotherms classified by BET based on statistical physics treatment,” *Journal of Colloid and Interface Science*, vol. 263, pp. 350–356, jul 2003.
- [127] M. Donohue and G. Aranovich, “Classification of Gibbs adsorption isotherms,” *Advances in Colloid and Interface Science*, vol. 76-77, pp. 137–152, jul 1998.
- [128] W. Rudzinski and J. Jagiello, “Low-temperature adsorption of gases on

- heterogeneous solid surfaces: Surfaces with random topography,” *Journal of Low Temperature Physics*, vol. 45, pp. 1–19, oct 1981.
- [129] W. Rudzinski and M. Jaroniec, “Adsorption on heterogeneous surfaces,” *Surface Science*, vol. 42, pp. 552–564, apr 1974.
- [130] W. Rudzinski and T. Panczyk, “Kinetics of isothermal adsorption on energetically heterogeneous solid surfaces: A new theoretical description based on the statistical rate theory of interfacial transport,” *The Journal of Physical Chemistry B*, vol. 104, pp. 9149–9162, oct 2000.
- [131] M. Suzuki, *Adsorption Engineering*. Kodansha, 1990, illustrate ed., 1990.
- [132] T. L. Hill, “Statistical mechanics of multimolecular adsorption II. localized and mobile adsorption and absorption,” *The Journal of Chemical Physics*, vol. 14, no. 7, p. 441, 1946.
- [133] S. Sircar and J. R. Hufton, “Why does the linear driving force model for adsorption kinetics work?,” *Adsorption*, vol. 6, no. 2, pp. 137–147, 2000.
- [134] J. Crank, *The mathematics of diffusion*. Oxford University Press, USA, 1979.
- [135] A. Dabrowski, “Adsorption—from theory to practice,” *Advances in Colloid and Interface Science*, vol. 93, pp. 135–224, oct 2001.
- [136] T. Li, R. Wang, and H. Li, “Progress in the development of solid gas sorption refrigeration thermodynamic cycle driven by low-grade thermal energy,” *Progress in Energy and Combustion Science*, vol. 40, pp. 1–58, feb 2014.
- [137] M. Haerifar and S. Azizian, “An exponential kinetic model for adsorption at solid/solution interface,” *Chemical Engineering Journal*, vol. 215–216, pp. 65–71, 2012.
- [138] S. Azizian, “Kinetic models of sorption: a theoretical analysis,” *Journal of Colloid and Interface Science*, vol. 276, pp. 47–52, aug 2004.

- [139] A. W. Marczewski, A. Derylo-Marczewska, and A. Słota, “Adsorption and desorption kinetics of benzene derivatives on mesoporous carbons,” *Adsorption*, vol. 19, pp. 391–406, jan 2013.
- [140] W. S. Loh, K. A. Rahman, A. Chakraborty, B. B. Saha, Y. S. Choo, B. C. Khoo, and K. C. Ng, “Improved isotherm data for adsorption of methane on activated carbons,” *Journal of Chemical & Engineering Data*, vol. 55, pp. 2840–2847, aug 2010.
- [141] R. Babarao and J. Jiang, “Diffusion and separation of CO₂ and CH₄ in silicalite, C₁₆₈ schwarzite, and IRMOF-1: A comparative study from molecular dynamics simulation,” *Langmuir*, vol. 24, pp. 5474–5484, may 2008.
- [142] I. Glaznev and Y. Aristov, “Kinetics of water adsorption on loose grains of SWS-1L under isobaric stages of adsorption heat pumps: The effect of residual air,” *International Journal of Heat and Mass Transfer*, vol. 51, pp. 5823–5827, dec 2008.
- [143] K. Binder, *Monte Carlo and Molecular Dynamics Simulations in Polymer Science*. Oxford University Press, 1995.
- [144] S. Wolfram, “Cellular automaton fluids 1: Basic theory,” *Journal of Statistical Physics*, vol. 45, pp. 471–526, nov 1986.
- [145] P. Pfeifer, F. Ehrburger-Dolle, T. Rieker, M. González, W. Hoffman, M. Molina-Sabio, F. Rodríguez-Reinoso, P. Schmidt, and D. Voss, “Nearly space-filling fractal networks of carbon nanopores,” *Physical Review Letters*, vol. 88, p. 115502, feb 2002.
- [146] G. Rychlicki, “Fractal dimension of microporous activated carbon from henry’s law of adsorption,” *Polish Journal of Chemistry*, vol. 68, pp. 2671–2677, 1994.
- [147] D. Rothman and S. Zaleski, “Lattice-gas models of phase separation: interfaces, phase transitions, and multiphase flow,” *Reviews of Modern Physics*, 1994.

- [148] Y. Shi, “A mimetic porous carbon model by quench molecular dynamics simulation.,” *The Journal of chemical physics*, vol. 128, p. 234707, jun 2008.
- [149] S. D. C. Walsh and M. O. Saar, “Macroscale lattice-Boltzmann methods for low Peclet number solute and heat transport in heterogeneous porous media,” *Water Resources Research*, vol. 46, jul 2010.
- [150] M. Levesque, M. Duvail, and I. Pagonabarraga, “Accounting for adsorption and desorption in lattice Boltzmann simulations,” *Physical Review E*, pp. 1–6, 2013.
- [151] M.Zalzale and P.J.McDonald, “Lattice Boltzmann simulations of the permeability and capillary adsorption of cement model microstructures,” *Cement and Concrete Research*, pp. 1–52, 2012.
- [152] N. Manjhi, N. Verma, K. Salem, and D. Mewes, “Lattice Boltzmann modelling of unsteady-state 2D concentration profiles in adsorption bed,” *Chemical Engineering Science*, vol. 61, pp. 2510–2521, apr 2006.
- [153] N. Verma, K. Salem, and D. Mewes, “Simulation of micro- and macro-transport in a packed bed of porous adsorbents by lattice Boltzmann methods,” *Chemical Engineering Science*, vol. 62, pp. 3685–3698, jul 2007.
- [154] N. Verma and D. Mewes, “Lattice Boltzmann methods for simulation of micro and macrotransport in a packed bed of porous adsorbents under non-isothermal condition,” *Computers & Mathematics with Applications*, vol. 58, pp. 1003–1014, sep 2009.
- [155] S. Agarwal, N. Verma, and D. Mewes, “A lattice Boltzmann model for adsorption breakthrough,” *Heat and Mass Transfer*, vol. 41, pp. 843–854, mar 2005.
- [156] S. D. C. Walsh and M. O. Saar, “Interpolated lattice Boltzmann boundary conditions for surface reaction kinetics,” *Physical Review E*, vol. 82, p. 066703, dec 2010.

- [157] D. Wolf-Gladrow, *Lattice-Gas Cellular Automata and Lattice Boltzmann Models: An Introduction*. Berlin: Springer-Verlag Berlin Heidelberg, 2005.
- [158] T. Takei, J. Bernsdorf, N. Masuda, and H. Takahara, “Lattice Boltzmann simulation and its concurrent visualization on the SX-6 supercomputer,” in *Proceedings. Seventh International Conference on High Performance Computing and Grid in Asia Pacific Region, 2004.*, pp. 212–219, IEEE, 2004.
- [159] L. Richardson, “The adsorption of carbon dioxide and ammonia by charcoal,” *Journal of the American Chemical Society*, vol. 186, no. 1868, 1917.
- [160] W. Rogers and M. Sclar, “A modification of the Freundlich adsorption isotherm,” *The Journal of Physical Chemistry*, vol. 36, pp. 2284–2291, jan 1931.
- [161] T. L. Hill, “Statistical mechanics of adsorption. X. thermodynamics of adsorption on an elastic adsorbent,” *The Journal of Chemical Physics*, vol. 18, no. 6, p. 791, 1950.
- [162] T. L. Hill, “Statistical mechanics of adsorption. V. thermodynamics and heat of adsorption,” *The Journal of Chemical Physics*, vol. 17, no. 6, p. 520, 1949.
- [163] T. L. Hill, “Statistical mechanics of multimolecular adsorption. I,” *The Journal of Chemical Physics*, vol. 14, no. 4, p. 263, 1946.
- [164] T. L. Hill, “Statistical mechanics of adsorption. IX. adsorption thermodynamics and solution thermodynamics,” *The Journal of Chemical Physics*, vol. 18, no. 3, p. 246, 1950.
- [165] E. A. Ustinov, N. S. Polyakov, and G. A. Petukhova, “Statistical interpretation of the Dubinin-Radushkevich equation,” *Russian Chemical Bulletin*, vol. 48, pp. 261–265, feb 1999.
- [166] W. Rudzinski and J. Jagiello, “Low-temperature adsorption of gases on heterogeneous solid surfaces: Effects of surface topography,” *Journal of Low Temperature Physics*, vol. 48, pp. 307–320, aug 1982.

- [167] W. Rudzinski and B. W. Wojciechowski, “On the Jovanovic model of adsorption,” *Colloid and Polymer Science Kolloid-Zeitschrift & Zeitschrift für Polymere*, vol. 255, pp. 1086–1097, nov 1977.
- [168] V. Rudzinski and B. W. Wojciechowski, “On the Jovanovic model of adsorption I. An extension for mobile adsorbed layers,” *Colloid and Polymer Science Kolloid-Zeitschrift & Zeitschrift für Polymere*, vol. 255, pp. 869–880, sep 1977.
- [169] D. H. Everett, “The thermodynamics of adsorption. Part III. Analysis and discussion of experimental data,” *Transactions of the Faraday Society*, vol. 46, no. 0, p. 957, 1950.
- [170] D. H. Everett, “Thermodynamics of adsorption. Part I. General considerations,” *Transactions of the Faraday Society*, vol. 46, p. 453, 1950.
- [171] G. F. Cerofolini, M. Jaroniec, and S. Sokolovski, “A theoretical isotherm for adsorption on heterogeneous surface,” *Colloid and Polymer Science Kolloid-Zeitschrift & Zeitschrift für Polymere*, vol. 256, pp. 471–477, may 1978.
- [172] M. Vlad, G. Cerofolini, and J. Ross, “Statistical fractal adsorption isotherms, linear energy relations, and power-law trapping-time distributions in porous media,” *Physical Review E*, vol. 62, no. 1, 2000.
- [173] C. J. Anderson, W. Tao, J. Jiang, S. I. Sandler, G. W. Stevens, and S. E. Kentish, “An experimental evaluation and molecular simulation of high temperature gas adsorption on nanoporous carbon,” *Carbon*, vol. 49, pp. 117–125, jan 2011.
- [174] C. Chilev, F. Darkrim Lamari, E. Kirilova, and I. Pentchev, “Comparison of gas excess adsorption models and high pressure experimental validation,” *Chemical Engineering Research and Design*, vol. 90, pp. 2002–2012, nov 2012.
- [175] Y. Liu and J. Wilcox, “Molecular simulation of CO₂ adsorption in micro- and mesoporous carbons with surface heterogeneity,” *International Journal of Coal Geology*, vol. 104, pp. 83–95, dec 2012.

- [176] M. Mosquera, “Simple isotherm equations to fit type I adsorption data,” *Fluid Phase Equilibria*, vol. 337, pp. 174–182, jan 2012.
- [177] J. Tóth, “Thermodynamical correctness of gas/solid adsorption isotherm equations,” *Journal of Colloid and Interface Science*, vol. 163, no. 0021-9797, pp. 299–302, 1994.
- [178] J. Tóth, “A uniform interpretation of gas/solid adsorption,” *Journal of Colloid and Interface Science*, vol. 79, pp. 85–95, jan 1981.
- [179] M. Jaroniec and A. W. Marczewski, “Physical adsorption of gases on energetically heterogeneous solids I. Generalized Langmuir equation and its energy distribution,” *Monatshefte für Chemie - Chemical Monthly*, vol. 115, pp. 997–1012, aug 1984.
- [180] M. Jaroniec and A. W. Marczewski, “Physical adsorption of gases on energetically heterogeneous solids II. Theoretical extension of a generalized Langmuir equation and its application for analysing adsorption data,” *Monatshefte für Chemie - Chemical Monthly*, vol. 115, pp. 1013–1038, aug 1984.
- [181] M. Donohue and G. Aranovich, “A new classification of isotherms for Gibbs adsorption of gases on solids,” *Fluid Phase Equilibria*, vol. 158-160, pp. 557–563, jun 1999.
- [182] B. Sun and A. Chakraborty, “Thermodynamic frameworks of adsorption kinetics modeling: Dynamic water uptakes on silica gel for adsorption cooling applications,” *Energy*, vol. 84, pp. 296–302, 2015.
- [183] P. B. Balbuena and K. E. Gubbins, “Theoretical interpretation of adsorption behavior of simple fluids in slit pores,” *Langmuir*, vol. 9, pp. 1801–1814, jul 1993.
- [184] T. Hill, *An Introduction to Statistical Thermodynamics*. Dover, 1960.

- [185] D. Frenkel and B. Smit, *Understanding molecular simulation: from algorithms to applications*. San Diego: Academic Press, 1997.
- [186] J. Johnson, J. Zollweg, and K. Gubbins, “The Lennard-Jones equation of state revisited,” *Molecular Physics*, vol. 78, pp. 591–618, feb 1993.
- [187] H. Callen, *Thermodynamics & an Introduction to Thermostatistics*. 2nd Edition, John Wiley & Sons, 2006.
- [188] P. Kim and S. Agnihotri, “Application of water activated carbon isotherm models to water adsorption isotherms of single-walled carbon nanotubes,” *Journal of Colloid and Interface Science*, vol. 325, pp. 64–73, sep 2008.
- [189] D. Ramirez, S. Qi, M. J. Rood, and K. J. Hay, “Equilibrium and heat of adsorption for organic vapors and activated carbons,” *Environmental science & technology*, vol. 39, pp. 5864–71, aug 2005.
- [190] W. Rudzinski, S.-L. Lee, C.-C. S. Yan, and T. Panczyk, “A fractal approach to adsorption on heterogeneous solid surfaces. 1. the relationship between geometric and energetic surface heterogeneities,” *The Journal of Physical Chemistry B*, vol. 105, pp. 10847–10856, nov 2001.
- [191] M.-A. Richard, P. Bénard, and R. Chahine, “Gas adsorption process in activated carbon over a wide temperature range above the critical point. Part 1: modified Dubinin-Astakhov model,” *Adsorption*, vol. 15, pp. 43–51, feb 2009.
- [192] B. B. Saha, A. Chakraborty, S. Koyama, S.-H. Yoon, I. Mochida, M. Kumja, C. Yap, and K. C. Ng, “Isotherms and thermodynamics for the adsorption of n-butane on pitch based activated carbon,” *International Journal of Heat and Mass Transfer*, vol. 51, pp. 1582–1589, apr 2008.
- [193] P. Ravikovitch, A. Vishnyakov, and A. Neimark, “Density functional theories and molecular simulations of adsorption and phase transitions in nanopores,” *Physical Review E*, vol. 64, p. 011602, jun 2001.

- [194] T. Düren and R. Q. Snurr, “Assessment of isorecticular metal organic frameworks for adsorption separations: A molecular simulation study of methane/ n -butane mixtures,” *The Journal of Physical Chemistry B*, vol. 108, pp. 15703–15708, oct 2004.
- [195] B. Sun, W. Fan, and A. Chakraborty, “Adsorption kinetics emulation with lattice gas cellular automata (Accepted),” *Heat Transfer Engineering*, 2015.
- [196] K. Hata, D. N. Futaba, K. Mizuno, T. Namai, M. Yumura, and S. Iijima, “Water-assisted highly efficient synthesis of impurity-free single-walled carbon nanotubes.,” *Science (New York, N.Y.)*, vol. 306, pp. 1362–1364, nov 2004.
- [197] S. Wang, L. Bromberg, H. Schreuder-Gibson, and T. A. Hatton, “Organophosphorous ester degradation by chromium(III) terephthalate metal-organic framework (MIL-101) chelated to N, N-dimethylaminopyridine and related aminopyridines,” *ACS Applied Materials and Interfaces*, vol. 5, no. 4, pp. 1269–1278, 2013.
- [198] S. H. Jhung, J. H. Lee, J. W. Yoon, C. Serre, G. Férey, and J. S. Chang, “Microwave synthesis of chromium terephthalate MIL-101 and its benzene sorption ability,” *Advanced Materials*, vol. 19, no. 1, pp. 121–124, 2007.
- [199] K. A. Rahman, W. S. Loh, H. Yanagi, A. Chakraborty, B. B. Saha, W. G. Chun, and K. C. Ng, “Experimental adsorption isotherm of methane onto activated carbon at sub- and supercritical temperatures,” *Journal of Chemical & Engineering Data*, vol. 55, pp. 4961–4967, nov 2010.
- [200] P. Chowdhury, S. Mekala, F. Dreisbach, and S. Gumma, “Adsorption of CO, CO₂ and CH₄ on Cu-BTC and MIL-101 metal organic frameworks: Effect of open metal sites and adsorbate polarity,” *Microporous and Mesoporous Materials*, vol. 152, pp. 246–252, 2012.
- [201] I. Senkovska and S. Kaskel, “High pressure methane adsorption in the metal-

- organic frameworks $\text{Cu}_3(\text{btc})_2$, $\text{Zn}_2(\text{bdc})_2\text{dabco}$, and $\text{Cr}_3\text{F}(\text{H}_2\text{O})_2\text{O}(\text{bdc})_3$,” *Microporous and Mesoporous Materials*, vol. 112, pp. 108–115, jul 2008.
- [202] J. Moellmer, a. Moeller, F. Dreisbach, R. Glaeser, and R. Staudt, “High pressure adsorption of hydrogen, nitrogen, carbon dioxide and methane on the metal-organic framework HKUST-1,” *Microporous and Mesoporous Materials*, vol. 138, no. 1-3, pp. 140–148, 2011.
- [203] N. C. Jeong, B. Samanta, C. Y. Lee, O. K. Farha, and J. T. Hupp, “Coordination-chemistry control of proton conductivity in the iconic metal-organic framework material HKUST-1,” *Journal of the American Chemical Society*, vol. 134, no. 1, pp. 51–54, 2012.
- [204] B. Sun, S. Kayal, and A. Chakraborty, “Study of HKUST (Copper benzene-1,3,5-tricarboxylate, Cu-BTC MOF)-1 metal organic frameworks for CH_4 adsorption: An experimental Investigation with GCMC (grand canonical Monte-carlo) simulation,” *Energy*, vol. 76, pp. 419–427, sep 2014.
- [205] R. B. Getman, Y.-S. Bae, C. E. Wilmer, and R. Q. Snurr, “Review and analysis of molecular simulations of methane, hydrogen, and acetylene storage in metal organic frameworks,” *Chemical Reviews*, vol. 112, pp. 703–723, feb 2012.
- [206] T. R. Zeitler, M. D. Allendorf, and J. A. Greathouse, “Grand Canonical Monte Carlo simulation of low-pressure methane adsorption in nanoporous framework materials for sensing applications,” *The Journal of Physical Chemistry C*, vol. 116, pp. 3492–3502, feb 2012.
- [207] A. Gupta, S. Chempath, M. J. Sanborn, L. a. Clark, and R. Q. Snurr, “Object-oriented programming paradigms for molecular modeling,” *Molecular Simulation*, vol. 29, pp. 29–46, jan 2003.
- [208] I. Kühn, “A generalized potential theory of adsorption,” *Journal of Colloid and Interface Science*, vol. 23, pp. 563–571, apr 1967.

- [209] A. Rappé and C. Casewit, “UFF, a full periodic table force field for molecular mechanics and molecular dynamics simulations,” *Journal of the American Chemical Society*, vol. 2, pp. 10024–10035, 1992.
- [210] M. G. Martin and J. I. Siepmann, “Transferable potentials for phase equilibria. 1. united-atom description of n -alkanes,” *Journal of Physical Chemistry B*, vol. 5647, no. 97, pp. 2569–2577, 1998.
- [211] H.-C. Guo, F. Shi, Z.-F. Ma, and X.-Q. Liu, “Molecular simulation for adsorption and separation of CH₄/H₂ in zeolitic imidazolate frameworks,” *The Journal of Physical Chemistry C*, pp. 12158–12165, 2010.
- [212] T. Düren, F. Millange, G. Férey, K. S. Walton, and R. Q. Snurr, “Calculating geometric surface areas as a characterization tool for metal organic frameworks,” *The Journal of Physical Chemistry C*, vol. 111, pp. 15350–15356, oct 2007.
- [213] R. Snurr, A. Bell, and D. Theodorou, “Prediction of adsorption of aromatic hydrocarbons in silicalite from Grand Canonical Monte Carlo simulations with biased insertions,” *The Journal of Physical Chemistry*, pp. 13742–13752, 1993.
- [214] B. N. Okunev, a. P. Gromov, L. I. Heifets, and Y. I. Aristov, “Dynamics of water sorption on a single adsorbent grain caused by a large pressure jump: Modeling of coupled heat and mass transfer,” *International Journal of Heat and Mass Transfer*, vol. 51, no. 25-26, pp. 5872–5876, 2008.
- [215] L. X. Gong, R. Z. Wang, Z. Z. Xia, and C. J. Chen, “Design and performance prediction of a new generation adsorption chiller using composite adsorbent,” *Energy Conversion and Management*, vol. 52, no. 6, pp. 2345–2350, 2011.
- [216] B. B. Saha, I. I. El-Sharkawy, a. Chakraborty, and S. Koyama, “Study on an activated carbon fiber-ethanol adsorption chiller: Part I - system description and modelling,” *International Journal of Refrigeration*, vol. 30, no. 1, pp. 86–95, 2007.

- [217] N. D. Banker, M. Prasad, P. Dutta, and K. Srinivasan, “Development and transient performance results of a single stage activated carbon - HFC 134a closed cycle adsorption cooling system,” *Applied Thermal Engineering*, vol. 30, no. 10, pp. 1126–1132, 2010.
- [218] A. Freni, L. Bonaccorsi, E. Proverbio, G. Maggio, and G. Restuccia, “Zeolite synthesised on copper foam for adsorption chillers: A mathematical model,” *Microporous and Mesoporous Materials*, vol. 120, pp. 402–409, apr 2009.
- [219] L. Z. Zhang and L. Wang, “Effects of coupled heat and mass transfers in adsorbent on the performance of a waste heat adsorption cooling unit,” *Applied Thermal Engineering*, vol. 19, no. 2, pp. 195–215, 1999.
- [220] B. Dawoud, M. I. Sohel, a. Freni, S. Vasta, and G. Restuccia, “On the effective thermal conductivity of wetted zeolite under the working conditions of an adsorption chiller,” *Applied Thermal Engineering*, vol. 31, no. 14-15, pp. 2241–2246, 2011.
- [221] I. I. El-Sharkawy, “On the linear driving force approximation for adsorption cooling applications,” *International Journal of Refrigeration*, vol. 34, no. 3, pp. 667–673, 2011.
- [222] Y. I. Aristov, “Adsorptive transformation of heat: Principles of construction of adsorbents database,” *Applied Thermal Engineering*, vol. 42, pp. 18–24, 2012.
- [223] Y. I. Aristov, G. Restuccia, G. Cacciola, and V. N. Parmon, “A family of new working materials for solid sorption air conditioning systems,” *Applied Thermal Engineering*, vol. 22, no. 2, pp. 191–204, 2002.
- [224] L. Gordeeva and Y. Aristov, “Dynamic study of methanol adsorption on activated carbon ACM-35.4 for enhancing the specific cooling power of adsorptive chillers,” *Applied Energy*, vol. 117, pp. 127–133, 2014.
- [225] I. Ponomarenko, I. Glaznev, a.V. Gubar, Y. Aristov, and S. Kirik, “Synthesis and water sorption properties of a new composite CaCl_2 confined into SBA-15

- pores,” *Microporous and Mesoporous Materials*, vol. 129, no. 1-2, pp. 243–250, 2010.
- [226] Y. I. Aristov, “Experimental and numerical study of adsorptive chiller dynamics: Loose grains configuration,” *Applied Thermal Engineering*, vol. 61, no. 2, pp. 841–847, 2013.
- [227] A. Chakraborty, B. B. Saha, and Y. I. Aristov, “Dynamic behaviors of adsorption chiller: Effects of the silica gel grain size and layers,” *Energy*, vol. 78, no. 3, pp. 304–312, 2014.
- [228] B. J. Schindler and M. D. LeVan, “The theoretical maximum isosteric heat of adsorption in the Henrys law region for slit-shaped carbon nanopores,” *Carbon*, vol. 46, pp. 644–648, apr 2008.

Appendices

Appendix A

Calibration of Pressure Transducer

Pressure transducers (Kyowa-PGS-200KA) used in Figure 4.14 transfer the measured pressure analog signal into digital voltage outputs. It is necessary to conduct the calibration to establish the relation between the input pressure value and output voltage sampled by the Agilent 34972A LXI data acquisition.

Figure A.1: Pressure transducer (Kyowa-PGS-200KA) calibration with the hydraulic deadweight tester.

Figure A.1 illustrates the hydraulic deadweight tester used to calibrate all three

pressure transducers in Figure 4.14. Disc standard weights are used to induce force on the transducers to obtain the voltage reading corresponding to the recorded pressures. The set of disc weights comes in range of 1 to 35 bar to cover the whole experimental pressure condition. The calibration results are illustrated in Figure A.2.

Figure A.2: Calibration and linear fitting analysis converting voltage to pressure value for Kyowa-PGS-200KA pressure transducers.

Appendix B

Cryostat Standard Operating Procedure

B.1 Experimental Apparatus Components

Figure B.1: Experimental apparatus components.

B.2 Operating Procedures

B.2.1 Disassemble and Sample Preparation

1. cut off methane gas, and close all vacuum pumps.
2. remove gas inlet hose, temperature sensor and controller plugs
3. switch ON the evacuation valve and remove vacuum B hose
4. remove pressure transducer and open the Vacuum jacket
5. pull up vertically and gently the chamber part from the shroud, and one person hold it up side down steadily
6. remove 12 chamber screws one at a time
7. If the chamber cover cannot be removed after removing the screws, screw in 2 into the taped holes to elevate the cover
8. purge contaminates in chamber with air gun, and NEVER touch the temperature sensor inside the chamber
9. prepare the adsorbent materials and measure its dry mass on A&D MX 50 Moisture Analyzer.
10. place the adsorbent materials inside the chamber by funnel and place another metal mesh wafer upon it, and lastly with the plate
11. place the indium wire in the cleaned groove and flatten the overlap with blade or spoon
12. put in the spring and the cover followed by installing all 12 screws with hand torque 3 to 4 rounds
13. place back the rubber gasket and gently install the chamber back into the vacuum shroud

14. adjust the direction of the chamber align to the edge of the desk, and fasten the vacuum jacket
15. assemble back the connection pins of temperature controller, pressure transducer and vacuum pump B hose.
16. fasten the adsorbate gas inlet hose with spanner
17. insert the liquid nitrogen hose into the guide tube and fasten all knobs

B.2.2 Void Volume Calibration and Regeneration

1. vacuum the cryostat by turning on pump A and B
2. turn on the temperature controller and set the controlled point up to 400 K by discrete steps of 10 K
3. after at least 3 to 4 hours, channel helium gas at around 3 bar into the chamber for at least 2 hours, and calibrate the void volume of the cryostat chamber
4. switch off the gas inlet valve and turn off pump A
5. subsequently, stop the temperature controller and wait for the chamber temperature to drop back to room temperature, which normally takes no less than 24 hours.

B.2.3 Adsorption Cycle

1. switch on the vacuum pump A and B to vacuum the setup
2. channel the liquid nitrogen to the setup
3. manipulate the setting of PID controller with liquid nitrogen cooling to reach the desired experimental temperature
4. after normally 30 mins, close all the valves and start up the data logger softwares

5. switch off the pump A and keep pump B working throughout the experiment
6. once temperature is set, open the methane source and regulate the experimental pressure into the charging cell
7. momentarily open gas inlet valve to introduce adsorbate gas into the cryostat chamber
8. repeat the adsorption cycle from step 5 to until all experimental pressure values are completed
9. monitor the experiment from the Agilent Data acquisition, GS4200-USB pressure transducer and 22C temperature controller

B.2.4 Housekeeping

1. switch off the adsorbate supply
2. vacuum the setup by turning on pump A
3. stop temperature controller
4. close the liquid nitrogen supply from the dewar
5. after around 30 mins, charge in about 3 bar helium into the setup and switch off all valves and pump A
6. wait for the temperature reach back to the room temperature, which would take approximately 12 hours.
7. turn off all pumps and cut off all gas sources

Appendix C

Experimental Data Processing

To process the adsorption experimental raw data and generate the adsorption isotherms information, a program that interfaces with REFPROP *NIST Standard Reference Database* of Version 8.0, is written in Mathematica 9.0[®].

The density of adsorbate with respect to temperature and pressure, are retrieved from REFPROP and compiled in spreadsheet. With Mathematica programming, the interpolation function is established, which enables quick execution during the calculation of adsorbate's mass.

Clear Cache

```
ClearSystemCache;  
ClearAll["Global`*"];  
<<JLink`;  
InstallJava[];  
ReinstallJava[JVMArguments -> "-Xmx1024m"];
```

Interpolation adsorbate density properties from REFPROP

```
(*Import data from spreadsheet containing density properties from REFPROP,  
e.g. 295 K*)
```



```

dataTemp295 = Drop[Import[NotebookDirectory[] <>
  "/RefProp.xlsx",{"Data",5,All,1}],3];
dataPres295 = Drop[Import[NotebookDirectory[] <>
  "/RefProp.xlsx",{"Data",5,All,2}],3];
dataDen295 = Drop[Import[NotebookDirectory[] <>
  "/RefProp.xlsx",{"Data",5,All,3}],3];

(* Creation of function for a temperature at 1 to 10 bar*)
prop295=Through@{Most,Last}[#]&/@
Thread[{dataTemp295,dataPres295,dataDen295}];

(*Collating all data from 120 to 298 K*)
plotData=Join[
Thread[{dataTemp120,dataPres120,dataDen120}],
Thread[{dataTemp130,dataPres130,dataDen130}],
Thread[{dataTemp140,dataPres140,dataDen140}],
Thread[{dataTemp150,dataPres150,dataDen150}],
Thread[{dataTemp295,dataPres295,dataDen295}],
Thread[{dataTemp296,dataPres296,dataDen296}],
Thread[{dataTemp297,dataPres297,dataDen297}],
Thread[{dataTemp298,dataPres298,dataDen298}]];
refProp=Join[prop120,prop130,prop140,prop150,
prop295,prop296,prop297,prop298
(*Interpolation of intermedia points*)
intepolationFunction=Interpolation[refProp];

(*Graphical illustration*)
Show[
  ListPointPlot3D[plotData],
  Plot3D[
    intepolationFunction[x,y],
    {x,120,298},
    {y,0,11}]
]

```

Figure C.1: Thermal property surface of adsorbate from REFPROP and reconstructed with Mathematica.

Import charging cell readings from Agilent Data Acquisition, and adsorption cell readings from the cryostat pressure transducer

```
(*Import charging cell data*)
chargingFile = SystemDialogInput["FileOpen"];
TempCharging = Drop[Import[chargingFile,{"Data",1,All,5}],16];
presV2 = Drop[Import[chargingFile,{"Data",1,All,13}],16];
presV3 = Drop[Import[chargingFile,{"Data",1,All,15}],16];
(*Import adsorption cell data*)
presRec = Drop[Import[SystemDialogInput["FileOpen"],{"Data",1,All,2}],1];
(*convert voltage readings into pressure value*)
pt2[voltage_] := 9982.6 voltage + 0.9111;
charPres[voltage2_, voltage3_] := pt2[voltage2];
```

Input calibrated void volume and experimental temperatures of both charging and adsorption chambers. User should also input the number of adsorption experiment cycles

An information dialog box with a title bar and standard window controls. It contains six input fields with labels and units, and an OK button at the bottom.

Field Label	Value	Unit
Charging Cell Temperature	298.15	K
Reacting Cell Temperature	125	K
Charging Cell Volume	0.000612206358	m ³
Reacting Cell Volume	0.00010005	m ³
Mass of Solid Material	0.0030348	kg
Number of Sample Points	6	Unity

Figure C.2: Information dialog.

Figure C.3: Adsorption cell pressure profile.

Figure C.4: Charging cell temperature profile.

Figure C.5: Charging cell pressure profile.

Convert both charging and adsorption cells pressure readings into mass with interpolated data in partitions of each adsorption cycle

```

(*partition of charging cell*)
dataIndex=MapIndexed[{First[#2],#1}&,massCharg];
localMinIndex=MapIndexed[{First[#2],#1}&,Differences[massCharg]];
localMin = Pick[localMinIndex,MinDetect[localMinIndex[[All,2]]],1];
chargingIndex =
Partition[
  PadLeft[
    Append[
      Sort[
        First/@Take[SortBy[localMin,Last],sampleNum]
      ],
      Length@massCharg],
    sampleNum+2,1],
  2,1];
partitionCharging = Map[Take[massCharg,#]&,chargingIndex];
(*partition of reacting cell*)
chamberdataIndex = MapIndexed[{First[#2],#1}&,denRect];
chamberlocalMaxIndex = MapIndexed[{First[#2],#1}&,Differences[denRect]];
chamberlocalMax =
  Pick[chamberlocalMaxIndex,MaxDetect[chamberlocalMaxIndex[[All,2]]],1];

```

```

reactIndex =
Partition[
  PadLeft[
    Append[
      Sort[
        First/@Take[SortBy[chamberlocalMax,Last],-sampleNum]
      ],
      Length@denRect],
    sampleNum+2,1],
  2,1];
partitionChamber = Map[Take[denRect,#]&,reactIndex];
(*Take the first 200 and last 300 point for the average for charging cell*)
chargingVolPrior = Map[Mean@Take[#,200]&,partitionCharging];
chargingVolPost = Map[Mean@Take[#,-300]&,partitionCharging];
chargingVolPrior = chargingVolPrior - Min@chargingVolPrior
chargingVolPost = chargingVolPost - Min@chargingVolPrior
(*Take the last 500 point for the average for charging cell*)
reactMass = Map[Mean@Take[#,-500]&,partitionChamber]*recVol;
reactMass = reactMass - Min@reactMass

```

Adsorption uptake determination and excess isotherm results illustration and saving

```

partitionChamberPressure = Map[Take[presRec,#]&,reactIndex];
reactPressure = Map[Mean@Take[#,-200]&,partitionChamberPressure];
reactPressure = reactPressure - Min@reactPressure;
chargingMassPrior2 = Delete[chargingMassPrior,1];
chargingMassPost2 = Delete[chargingMassPost,-1];
chargingMass = chargingMassPost2 - chargingMassPrior2 + Drop[reactMass,-1];
uptake = Accumulate[chargingMass - Drop[reactMass,1]]/massSolid;
ListPlot[

```

```

Thread[{Drop[reacPressure,1],uptake}]
]
Export[SystemDialogInput["FileSave"],
Thread[{Drop[reacPressure,1],uptake}], "xlsx"]

```

Figure C.6: Typical excess adsorption isotherm data processing result.

Appendix D

Configurations for Grand Canonical Monte Carlo Simulation

To successfully implement the MuSic package as discussed in Chapter 5, it is essential to configure all the files correctly and accurately. The obtained results are absolute adsorption uptake against fugacity. To compare the simulation results with experimental measured data, the GCMC results should be convert to excess uptake against pressure. MuSic package also provides programs to calculate fugacity, to convert absolute uptake to excess results, to display potential maps, and to measure solid adsorbent's specific area and specific volumes. The configuration files used for CH₄ adsorption with HKUST-1 MOF is listed below for instance, as well as Mathematica programs the author has been using for (1) UFF parameters calculation (Equation 5.1), (2) acentric factor determination, and (3) Peng-Robinson equation for fugacity conversion.

Mathematica programs

```
(*UFF parameters calculation*)  
Clear[dis, ener]  
{dis,ener} = DialogInput[{x = 3.851, d = 0.105},  
Column[
```

```

{
Row[{"distance \!\(\)*
StyleBox[SubsuperscriptBox["x", "i", "a"],\nFontSlant->"Italic"]\)\)
", InputField[Dynamic[x], Number]]],
Row[{"energy \!\(\)*
StyleBox[SubsuperscriptBox["D", "i", "c"],\nFontSlant->"Italic"]\)\)
", InputField[Dynamic[d], Number]]],

Button["OK",
If[NumberQ[x] && NumberQ[d],
DialogReturn[{x, d}]
],
ImageSize->Automatic]]]
];

Block[{[Sigma]i=dis/2^(1/6),[Epsilon]i=ener/0.0019872
,[Sigma]ch4=3.73,[Epsilon]ch4=148,[Sigma]ij,[Epsilon]ij},
{[Sigma]i,[Epsilon]i,[Sigma]ij=([Sigma]i+[Sigma]ch4)/2,
[Epsilon]ij=Sqrt[Epsilon]i*[Epsilon]ch4]}
]

(*Acentric factor*)
acentricCH4:=(pres at T whereas T/Subscript[T, c]=0.7. For methane,
Subscript[T, c]=190.56K,T=133.39,Pc=45.992bar,P=4.4791bar*)
With[{pres=4.4791bar,presCritical=45.992bar},
-Log10[pres/presCritical]-1
]

(*Peng-Robinson equation*)
fugacity[temp_,pres_,tempCri_:190.56 k,presCri_:45.992 bar, mass_:16.043
g/mol, [Omega]_:0.01142,gasConstant_:8.3144621*10^-5 (m^3 bar)/(k
mol)]:=
Block[

```



```

{\[Gamma], \[Beta], \[Phi], compres, density, fuga,
z,
\[Alpha]=(1+(0.37464+1.54226\[Omega]\[Minus]0.26992\[Omega]^2)*
(1-Sqrt[temp/tempCri]))^2,
a=(0.457235*gasConstant^2*tempCri^2)/presCri,
b=(0.077796*gasConstant*tempCri)/presCri
},
{
\[Gamma]=(a*\[Alpha]*pres)/(gasConstant*temp)^2,
\[Beta]=(b*pres)/(gasConstant*temp),
compres=FindRoot[z^3+(\[Beta]-1)z^2+(\[Gamma]-2\[Beta]-3\[Beta]^2)z+
(\[Beta]^3+\[Beta]^2-\[Gamma]*\[Beta])==0,{z,1}],
density=mass*pres/(z*gasConstant*temp/.compres),
\[Phi]=Exp[(z-1)-Log[z-\[Beta]]-\[Gamma]/(2Sqrt[2]\[Beta])
Log[(z+(1+Sqrt[2])\[Beta])/(z+(1-Sqrt[2])\[Beta])]],
fuga=\[Phi]*pres/.compres
};
Return[{density, fuga, compres}]
]
property[temp_, pres_] := MapAt[UnitConvert[
Quantity[#1 m^3/g, ("Grams")/("Meters")^3], ("Grams")/("Centimeters")^3]&,
fugacity[temp, pres], 1]

```

Environment variables

```

#!/bin/sh

export ATOMSDIR=~ /BaiChuan/library/atoms
export MOLSDIR=~ /BaiChuan/library/molecules
export PMAPDIR=~ /BaiChuan/library/pmaps

```

Atom file

Basic Atom [Information](#)

Atom_Name: Carbon

Atom_Symbol: [C](#)

Atom_SS_Charge: 0.0

Atom_SZ_Charge: 0.0

Atom_Mass: 12.0

Atom_Valency: 4

Atom_Name: Copper

Atom_Symbol: Cu

Atom_SS_Charge: 0.0

Atom_SZ_Charge: 0.0

Atom_Mass: 63.546

Atom_Valency: 2

Atom_Name: Hydrogen

Atom_Symbol: H

Atom_SS_Charge: 0.4

Atom_SZ_Charge: 0.4

Atom_Mass: 1.0

Atom_Valency: 1

Atom_Name: Methane

Atom_Symbol: CH4

Atom_SS_Charge: 0.0

Atom_SZ_Charge: 0.0

Atom_Mass: 16.0

Atom_Valency: 0

Atom_Name: Oxygen

Atom_Symbol: O

Atom_SS_Charge: 0

Atom_SZ_Charge: 0

Atom_Mass: 16.0

Atom_Valency: 2

Molecule file

Methane Molecule File

Molecule_Name: Methane

Coord_Info: Listed Cartesian Rigid

1 # number of atoms in molecule

1 0.000000 0.000000 0.000000 Methane 0.0 0 0

#x,y,z,name,set,type

Molecule_Name: HKUST1

Coord_Info: Listed Cartesian None

624 # number of atoms in molecule

1 8.172679424 4.394035682 24.06384957 Carbon 0.00 0 0

2 7.506857937 5.061566285 25.2753491 Carbon 0.00 0 0

3 8.872625784 17.50952516 10.71167321 Carbon 0.00 0 0

4 7.95907823 18.43753587 11.45879751 Carbon 0.00 0 0

5 18.34386461 21.94336538 23.83755825 Carbon 0.00 0 0

6 18.93578254 21.31352983 25.10654864 Carbon 0.00 0 0

7 17.51273232 8.872902653 10.70569393 Carbon 0.00 0 0

8 18.44252046 7.959209074 11.44968184 Carbon 0.00 0 0

9 4.393579897 8.178248026 24.06515116 Carbon 0.00 0 0

10 5.065304067 7.50645035 25.27098876 Carbon 0.00 0 0
 11 17.74803366 4.045664168 2.157327569 Carbon 0.00 0 0
 12 18.36890216 4.756653914 0.950402209 Carbon 0.00 0 0
 13 17.57121492 17.55305962 15.72590871 Carbon 0.00 0 0
 14 18.47413868 18.44593693 14.91766145 Carbon 0.00 0 0
 15 4.23581013 4.23662648 16.1370704 Carbon 0.00 0 0
 16 5.028039175 5.029685461 15.12205533 Carbon 0.00 0 0
 17 8.390765246 22.32109517 2.387379801 Carbon 0.00 0 0
 18 7.866835442 21.64814187 1.117223495 Carbon 0.00 0 0
 19 8.88410934 8.881665368 15.66715934 Carbon 0.00 0 0
 20 7.976865515 7.975272874 14.89081534 Carbon 0.00 0 0
 21 24.06129382 8.182055755 4.394239189 Carbon 0.00 0 0
 22 25.26999878 7.516292321 5.066757773 Carbon 0.00 0 0
 23 10.70906308 8.871402186 17.51341433 Carbon 0.00 0 0
 24 11.45563804 7.959821771 18.44268772 Carbon 0.00 0 0
 25 23.82944251 18.34434086 21.94642557 Carbon 0.00 0 0
 26 25.10029004 18.93322702 21.31509562 Carbon 0.00 0 0
 27 24.06107571 4.394700968 8.176246073 Carbon 0.00 0 0
 28 25.26836946 5.067712867 7.507929575 Carbon 0.00 0 0
 29 10.70903419 17.50863006 8.874009834 Carbon 0.00 0 0
 30 11.45463953 18.4371877 7.959675115 Carbon 0.00 0 0
 31 2.154001979 17.74605685 4.04595519 Carbon 0.00 0 0
 32 0.948591708 18.36604712 4.758359559 Carbon 0.00 0 0
 33 15.72664004 17.56487419 17.57038508 Carbon 0.00 0 0
 34 14.92226 18.46714342 18.46619331 Carbon 0.00 0 0
 35 16.13096385 4.239371529 4.234712193 Carbon 0.00 0 0
 36 15.11417897 5.032646156 5.027090412 Carbon 0.00 0 0
 37 2.384729318 8.398385672 22.32640887 Carbon 0.00 0 0
 38 1.113205441 7.876815676 21.65430238 Carbon 0.00 0 0
 39 15.66335938 8.886615308 8.884954366 Carbon 0.00 0 0
 40 14.89150153 7.979020877 7.977048239 Carbon 0.00 0 0

41 4.396067591 24.05967165 8.17890917 Carbon 0.00 0 0
 42 5.070640849 25.26579487 7.509936098 Carbon 0.00 0 0
 43 4.445291463 10.04365816 22.18489203 Carbon 0.00 0 0
 44 5.145116599 11.17749365 21.45764731 Carbon 0.00 0 0
 45 21.9440861 23.84034304 18.33759377 Carbon 0.00 0 0
 46 21.30984515 25.10809215 18.92946761 Carbon 0.00 0 0
 47 22.18215597 10.04677491 4.442868512 Carbon 0.00 0 0
 48 21.45688565 11.1826063 5.142546877 Carbon 0.00 0 0
 49 8.177893935 24.0625891 4.395568349 Carbon 0.00 0 0
 50 7.514189031 25.2736417 5.0668052 Carbon 0.00 0 0
 51 4.043782001 2.15780373 17.75057302 Carbon 0.00 0 0
 52 4.754334438 0.948556038 18.36553991 Carbon 0.00 0 0
 53 4.23132144 16.13218616 4.238629465 Carbon 0.00 0 0
 54 5.021766897 15.1144321 5.032037148 Carbon 0.00 0 0
 55 22.32300262 2.384248971 8.39342929 Carbon 0.00 0 0
 56 21.6512004 1.113194009 7.870061287 Carbon 0.00 0 0
 57 21.9562572 16.4657919 21.97013962 Carbon 0.00 0 0
 58 21.33193279 15.22415976 21.34440519 Carbon 0.00 0 0
 59 8.881473626 15.66500114 8.886713983 Carbon 0.00 0 0
 60 7.969245949 14.89967374 7.978678477 Carbon 0.00 0 0
 61 4.053178237 8.586436874 2.166538201 Carbon 0.00 0 0
 62 4.760955242 7.977390264 0.953406848 Carbon 0.00 0 0
 63 4.441957918 22.17641777 16.30354958 Carbon 0.00 0 0
 64 5.140837976 21.45071865 15.16906069 Carbon 0.00 0 0
 65 22.3224222 17.94105564 2.375047525 Carbon 0.00 0 0
 66 21.64940274 18.46745076 1.105643057 Carbon 0.00 0 0
 67 22.17351021 4.443075015 16.30393192 Carbon 0.00 0 0
 68 21.44904014 5.143023292 15.16842592 Carbon 0.00 0 0
 69 8.590384263 4.04440124 2.162866653 Carbon 0.00 0 0
 70 7.982850164 4.750984363 0.948658569 Carbon 0.00 0 0
 71 4.393753169 18.17188476 24.0540638 Carbon 0.00 0 0

72 5.074038487 18.85406562 25.2498133 Carbon 0.00 0 0
73 4.233488794 4.236958527 10.21071428 Carbon 0.00 0 0
74 5.024204388 5.027284839 11.23077827 Carbon 0.00 0 0
75 21.94734719 8.007211774 23.84257405 Carbon 0.00 0 0
76 21.32716273 7.424956286 25.12074027 Carbon 0.00 0 0
77 21.97590163 21.95841978 9.887836157 Carbon 0.00 0 0
78 21.35205266 21.32521457 11.12606344 Carbon 0.00 0 0
79 8.903215292 8.904548872 10.74031779 Carbon 0.00 0 0
80 7.978597984 7.980799428 11.47357425 Carbon 0.00 0 0
81 8.010684252 23.83187262 21.95210612 Carbon 0.00 0 0
82 7.433817953 25.11118133 21.32728495 Carbon 0.00 0 0
83 8.900967094 10.74043213 8.910225337 Carbon 0.00 0 0
84 7.974312079 11.46972913 7.986758669 Carbon 0.00 0 0
85 18.17394726 24.04855864 4.391535095 Carbon 0.00 0 0
86 18.85973998 25.24291698 5.071732864 Carbon 0.00 0 0
87 17.5398464 10.67634454 17.54949335 Carbon 0.00 0 0
88 18.45498758 11.44393285 18.46355347 Carbon 0.00 0 0
89 4.234150004 10.21353344 4.239779146 Carbon 0.00 0 0
90 5.02172896 11.23586959 5.03328565 Carbon 0.00 0 0
91 17.93836982 2.377117396 22.32527368 Carbon 0.00 0 0
92 18.46434667 1.108270509 21.65031777 Carbon 0.00 0 0
93 17.52829086 15.6920292 8.851344894 Carbon 0.00 0 0
94 18.4416052 14.90398931 7.957470768 Carbon 0.00 0 0
95 4.048540064 2.1670134 8.583918498 Carbon 0.00 0 0
96 4.75388826 0.952155417 7.976987593 Carbon 0.00 0 0
97 8.590877141 2.159922772 4.04776906 Carbon 0.00 0 0
98 7.981255406 0.946302514 4.754019654 Carbon 0.00 0 0
99 8.848502321 15.69254293 17.53591196 Carbon 0.00 0 0
100 7.952570514 14.90778929 18.44800802 Carbon 0.00 0 0
101 24.05253815 4.391172864 18.16987709 Carbon 0.00 0 0
102 25.24922333 5.070511171 18.85158186 Carbon 0.00 0 0

103 10.21380543 4.234790225 4.235816329 Carbon 0.00 0 0
 104 11.23324645 5.027129697 5.026941055 Carbon 0.00 0 0
 105 23.8410622 21.95386987 8.007498902 Carbon 0.00 0 0
 106 25.11661243 21.3307236 7.424891402 Carbon 0.00 0 0
 107 9.887045553 21.95808733 21.97434171 Carbon 0.00 0 0
 108 11.12640432 21.33423432 21.34528969 Carbon 0.00 0 0
 109 10.73555305 8.907568178 8.906697687 Carbon 0.00 0 0
 110 11.46520813 7.982621458 7.980745524 Carbon 0.00 0 0
 111 2.162428192 4.050344527 8.5843621 Carbon 0.00 0 0
 112 0.948469539 4.7559411 7.97472354 Carbon 0.00 0 0
 113 16.30486054 4.446555868 22.17974199 Carbon 0.00 0 0
 114 15.1695548 5.146087478 21.45567917 Carbon 0.00 0 0
 115 2.375765693 22.32363324 17.94008764 Carbon 0.00 0 0
 116 1.108048542 21.64802478 18.46820407 Carbon 0.00 0 0
 117 2.16376866 8.589208936 4.046724573 Carbon 0.00 0 0
 118 0.948625553 7.98145483 4.750753639 Carbon 0.00 0 0
 119 16.30417497 22.17278809 4.442192661 Carbon 0.00 0 0
 120 15.16580734 21.45069435 5.140101942 Carbon 0.00 0 0
 121 17.94126662 22.31661702 2.375079071 Carbon 0.00 0 0
 122 18.46618321 21.64407991 1.103854601 Carbon 0.00 0 0
 123 17.5329477 8.847069051 15.69769155 Carbon 0.00 0 0
 124 18.44277106 7.953241781 14.90443811 Carbon 0.00 0 0
 125 8.849199329 17.53262411 15.7008955 Carbon 0.00 0 0
 126 7.960546291 18.44828531 14.91079623 Carbon 0.00 0 0
 127 8.006527289 21.94861948 23.84175027 Carbon 0.00 0 0
 128 7.423209476 21.32797127 25.1189648 Carbon 0.00 0 0
 129 18.16955311 4.391371508 24.05915316 Carbon 0.00 0 0
 130 18.85226982 5.071169211 25.25507505 Carbon 0.00 0 0
 131 17.54182173 17.54879742 10.67165801 Carbon 0.00 0 0
 132 18.45569677 18.46631563 11.43448608 Carbon 0.00 0 0
 133 2.376958053 17.94016623 22.3226995 Carbon 0.00 0 0

134 1.107442328 18.46627514 21.64868021 Carbon 0.00 0 0
135 15.69093083 17.53068877 8.846178327 Carbon 0.00 0 0
136 14.90359852 18.44559165 7.95561125 Carbon 0.00 0 0
137 15.6932008 8.846428041 17.53470101 Carbon 0.00 0 0
138 14.90575972 7.950876893 18.4461215 Carbon 0.00 0 0
139 23.82967173 8.008017641 21.95247182 Carbon 0.00 0 0
140 25.10677839 7.425879306 21.32798262 Carbon 0.00 0 0
141 24.0529498 18.17228286 4.391714243 Carbon 0.00 0 0
142 25.24672378 18.85864004 5.071659943 Carbon 0.00 0 0
143 10.68049135 17.53751964 17.54864558 Carbon 0.00 0 0
144 11.44441495 18.45639484 18.4617035 Carbon 0.00 0 0
145 22.32083128 2.375183375 17.94012336 Carbon 0.00 0 0
146 21.64604131 1.106946228 18.46824729 Carbon 0.00 0 0
147 22.17335413 16.30683052 4.442893275 Carbon 0.00 0 0
148 21.44607242 15.17364293 5.142274248 Carbon 0.00 0 0
149 4.443064839 16.30279831 22.17989164 Carbon 0.00 0 0
150 5.142338595 15.16729703 21.45699316 Carbon 0.00 0 0
151 21.94981878 23.83477355 8.009444726 Carbon 0.00 0 0
152 21.32568608 25.1145114 7.431091536 Carbon 0.00 0 0
153 21.95907331 9.889659281 21.97725598 Carbon 0.00 0 0
154 21.33263196 11.1293834 21.3491113 Carbon 0.00 0 0
155 4.393856983 24.0537477 18.17061292 Carbon 0.00 0 0
156 5.074869203 25.24923569 18.85321318 Carbon 0.00 0 0
157 21.94564266 18.34752483 23.83597485 Carbon 0.00 0 0
158 21.32062091 18.93824853 25.10798978 Carbon 0.00 0 0
159 22.18166467 4.441705585 10.04210557 Carbon 0.00 0 0
160 21.45480461 5.139026898 11.17741671 Carbon 0.00 0 0
161 4.441327976 22.1796941 10.04477532 Carbon 0.00 0 0
162 5.145938648 21.45591754 11.17773742 Carbon 0.00 0 0
163 22.3229905 8.397313291 2.383395151 Carbon 0.00 0 0
164 21.65366528 7.87384659 1.110146312 Carbon 0.00 0 0

165 21.96446741 21.97083265 16.45647671 Carbon 0.00 0 0
 166 21.33748033 21.34692902 15.21491562 Carbon 0.00 0 0
 167 4.039057119 17.74454105 2.157238114 Carbon 0.00 0 0
 168 4.749687637 18.36167282 0.948850857 Carbon 0.00 0 0
 169 17.74519197 2.158188062 4.044466214 Carbon 0.00 0 0
 170 18.36313 0.949423689 4.755142464 Carbon 0.00 0 0
 171 17.56163375 15.7198852 17.57264041 Carbon 0.00 0 0
 172 18.46080656 14.91837515 18.46974934 Carbon 0.00 0 0
 173 8.390659866 2.387902178 22.32132242 Carbon 0.00 0 0
 174 7.870149759 1.11574692 21.64870303 Carbon 0.00 0 0
 175 8.873910563 10.70937549 17.51241573 Carbon 0.00 0 0
 176 7.96235363 11.45897562 18.4410255 Carbon 0.00 0 0
 177 18.33977991 23.83044477 21.95145979 Carbon 0.00 0 0
 178 18.92553834 25.10429283 21.32358901 Carbon 0.00 0 0
 179 17.51024578 10.70921017 8.86871933 Carbon 0.00 0 0
 180 18.43759161 11.45392596 7.953761302 Carbon 0.00 0 0
 181 2.382208768 22.32635364 8.397643995 Carbon 0.00 0 0
 182 1.111225332 21.65529176 7.873387529 Carbon 0.00 0 0
 183 16.46205929 21.95752557 21.97097479 Carbon 0.00 0 0
 184 15.2191038 21.33761441 21.34404234 Carbon 0.00 0 0
 185 2.159522373 4.047331922 17.75499275 Carbon 0.00 0 0
 186 0.951537873 4.759004403 18.37228584 Carbon 0.00 0 0
 187 23.83313133 21.95568928 18.33835065 Carbon 0.00 0 0
 188 25.10466284 21.32737943 18.92849249 Carbon 0.00 0 0
 189 10.04034436 22.18010977 4.444088785 Carbon 0.00 0 0
 190 11.17291215 21.45611065 5.147618643 Carbon 0.00 0 0
 191 10.03689573 4.448819315 22.18270935 Carbon 0.00 0 0
 192 11.1751357 5.145718543 21.45877038 Carbon 0.00 0 0
 193 9.354100028 5.102809014 23.38753971 Carbon 0.00 0 0
 194 10.18499287 18.06385864 10.18663218 Carbon 0.00 0 0
 195 17.08786505 21.32127815 23.21629012 Carbon 0.00 0 0

196 16.19955112 8.317672583 10.18699349 Carbon 0.00 0 0
 197 3.083569313 21.66493111 9.580612422 Carbon 0.00 0 0
 198 16.64689258 4.790361105 2.910555153 Carbon 0.00 0 0
 199 16.26692793 18.12596551 16.26354895 Carbon 0.00 0 0
 200 2.709027118 18.30354143 2.714424953 Carbon 0.00 0 0
 201 9.573702425 21.66104111 3.089182255 Carbon 0.00 0 0
 202 10.18687507 8.313239994 16.20275447 Carbon 0.00 0 0
 203 23.38583669 9.365679216 5.09849203 Carbon 0.00 0 0
 204 23.19779672 23.20834276 18.97603169 Carbon 0.00 0 0
 205 10.18576502 10.18447708 18.0669541 Carbon 0.00 0 0
 206 23.20245875 17.08860246 21.32895023 Carbon 0.00 0 0
 207 23.52694659 3.03317886 7.679252892 Carbon 0.00 0 0
 208 9.570933781 3.094564704 21.66103274 Carbon 0.00 0 0
 209 2.908669452 16.64722165 4.790494018 Carbon 0.00 0 0
 210 2.715500143 2.716235655 18.3126757 Carbon 0.00 0 0
 211 3.090291171 9.578674267 21.66547349 Carbon 0.00 0 0
 212 3.032470955 23.52962668 7.683789082 Carbon 0.00 0 0
 213 5.099959286 23.38168853 9.362120472 Carbon 0.00 0 0
 214 18.98047996 23.19665937 23.20285783 Carbon 0.00 0 0
 215 18.06651858 10.18522586 10.18047664 Carbon 0.00 0 0
 216 21.3252441 23.2154091 17.08162755 Carbon 0.00 0 0
 217 21.66241305 9.58009059 3.086888705 Carbon 0.00 0 0
 218 7.678240144 23.52663378 3.035579644 Carbon 0.00 0 0
 219 4.787535714 2.912099489 16.65019073 Carbon 0.00 0 0
 220 18.30560645 2.714884849 2.714685283 Carbon 0.00 0 0
 221 21.66332709 3.086494796 9.576309494 Carbon 0.00 0 0
 222 7.677983669 3.032182244 23.52846506 Carbon 0.00 0 0
 223 4.791324992 9.694391035 2.917548034 Carbon 0.00 0 0
 224 18.09721915 10.15215891 16.23630971 Carbon 0.00 0 0
 225 21.65614513 16.76718639 3.08537099 Carbon 0.00 0 0
 226 8.280230142 16.22867562 16.23341946 Carbon 0.00 0 0

227 8.024295801 2.720199873 2.723559089 Carbon 0.00 0 0
 228 5.10141407 16.99046555 23.37895384 Carbon 0.00 0 0
 229 4.788275022 2.916267094 9.690958999 Carbon 0.00 0 0
 230 18.09458658 16.23337263 10.15319746 Carbon 0.00 0 0
 231 21.3275999 9.265929768 23.22458832 Carbon 0.00 0 0
 232 8.346296027 10.21639044 10.2207767 Carbon 0.00 0 0
 233 9.265244483 23.20361299 21.33473704 Carbon 0.00 0 0
 234 10.21265326 10.21968804 8.351855824 Carbon 0.00 0 0
 235 16.99210059 23.37302964 5.099906036 Carbon 0.00 0 0
 236 16.22795165 10.15101696 18.10157331 Carbon 0.00 0 0
 237 2.910494999 9.69685736 4.787532612 Carbon 0.00 0 0
 238 16.76456205 3.08928954 21.66032286 Carbon 0.00 0 0
 239 16.22357623 16.2243757 8.281838286 Carbon 0.00 0 0
 240 2.725336013 2.728137938 8.016136537 Carbon 0.00 0 0
 241 9.696399768 2.911497719 4.788854742 Carbon 0.00 0 0
 242 10.15526893 16.22463551 18.10131968 Carbon 0.00 0 0
 243 23.37384382 5.100840707 16.99098027 Carbon 0.00 0 0
 244 23.52998939 18.65316636 3.019985649 Carbon 0.00 0 0
 245 9.696236642 4.785898154 2.91270693 Carbon 0.00 0 0
 246 23.2247464 21.33196717 9.264789426 Carbon 0.00 0 0
 247 23.19112459 7.361772277 23.19848118 Carbon 0.00 0 0
 248 10.21435881 8.348691216 10.21724378 Carbon 0.00 0 0
 249 2.910495726 4.789362964 9.693221303 Carbon 0.00 0 0
 250 3.023716943 18.65527313 23.52805003 Carbon 0.00 0 0
 251 3.083386559 21.66052346 16.76282011 Carbon 0.00 0 0
 252 2.728782138 8.019547651 2.72592989 Carbon 0.00 0 0
 253 16.76571498 21.65285998 3.08557173 Carbon 0.00 0 0
 254 16.22867342 8.278979528 16.23100303 Carbon 0.00 0 0
 255 10.15570403 18.0941092 16.23674981 Carbon 0.00 0 0
 256 9.263140952 21.32593618 23.22255981 Carbon 0.00 0 0
 257 16.99152032 5.102543168 23.38096015 Carbon 0.00 0 0

258 16.22850206 18.09997763 10.148415 Carbon 0.00 0 0
 259 3.085626762 16.762525 21.66102882 Carbon 0.00 0 0
 260 3.022639144 23.53010945 18.65337915 Carbon 0.00 0 0
 261 23.20520263 9.266037372 21.3365025 Carbon 0.00 0 0
 262 23.19736489 23.19886439 7.363440071 Carbon 0.00 0 0
 263 23.37524795 16.99197761 5.100449647 Carbon 0.00 0 0
 264 23.52837946 3.020328705 18.65244539 Carbon 0.00 0 0
 265 21.65663244 3.084615153 16.76380422 Carbon 0.00 0 0
 266 18.6501838 3.019867369 23.53462456 Carbon 0.00 0 0
 267 21.33283943 23.20501714 9.265474432 Carbon 0.00 0 0
 268 7.364415951 23.19540735 23.19930915 Carbon 0.00 0 0
 269 5.101709848 23.37544806 16.9905896 Carbon 0.00 0 0
 270 18.65534298 23.52344132 3.020435489 Carbon 0.00 0 0
 271 21.32207889 17.09223974 23.21505432 Carbon 0.00 0 0
 272 8.315530219 16.19863383 10.19004494 Carbon 0.00 0 0
 273 5.100115455 9.361849242 23.39018015 Carbon 0.00 0 0
 274 8.31742354 10.18654636 16.20078578 Carbon 0.00 0 0
 275 4.784781445 16.64682154 2.913999528 Carbon 0.00 0 0
 276 18.13004349 16.24883584 16.26587307 Carbon 0.00 0 0
 277 16.64590281 2.915115736 4.788532002 Carbon 0.00 0 0
 278 16.2591913 16.25959195 18.1375499 Carbon 0.00 0 0
 279 10.18699526 16.19634264 8.318978738 Carbon 0.00 0 0
 280 9.361475334 23.38580577 5.099476206 Carbon 0.00 0 0
 281 17.08679424 23.20179632 21.33071738 Carbon 0.00 0 0
 282 16.19679407 10.18960065 8.31604626 Carbon 0.00 0 0
 283 3.030967776 7.68435598 23.53151602 Carbon 0.00 0 0
 284 2.914350041 4.791309848 16.65501394 Carbon 0.00 0 0
 285 23.20874679 21.332695 17.08380489 Carbon 0.00 0 0
 286 23.52740269 7.684183684 3.032979223 Carbon 0.00 0 0
 287 23.38570884 5.098611793 9.360786983 Carbon 0.00 0 0
 288 23.19648196 18.98548648 23.19799814 Carbon 0.00 0 0

289 7.293721327 7.286281679 -0.338919157 Copper 0.00 0 0
 290 7.409243342 20.89014493 13.17567827 Copper 0.00 0 0
 291 20.88919756 7.408330369 13.16985292 Copper 0.00 0 0
 292 20.74703585 20.74574619 -0.446193155 Copper 0.00 0 0
 293 19.11596241 19.11033717 -0.201810492 Copper 0.00 0 0
 294 19.10586949 5.513259276 13.16898025 Copper 0.00 0 0
 295 5.504606067 19.09706397 13.17636085 Copper 0.00 0 0
 296 5.657655093 5.652895249 -0.545906093 Copper 0.00 0 0
 297 19.1413827 7.304675654 -0.269741516 Copper 0.00 0 0
 298 19.05679752 20.91576007 13.17343515 Copper 0.00 0 0
 299 5.523257046 7.364684411 13.17630716 Copper 0.00 0 0
 300 5.628479489 20.72652944 -0.487665147 Copper 0.00 0 0
 301 7.302744919 19.13375483 -0.261530642 Copper 0.00 0 0
 302 7.361263942 5.526589796 13.17445058 Copper 0.00 0 0
 303 20.88992243 19.07147506 13.16893125 Copper 0.00 0 0
 304 20.73489896 5.630682458 -0.491387279 Copper 0.00 0 0
 305 -0.344926018 7.287924438 7.282391144 Copper 0.00 0 0
 306 -0.442484253 20.74578593 20.74685271 Copper 0.00 0 0
 307 13.17147741 7.41132354 20.89253266 Copper 0.00 0 0
 308 13.17198484 20.88867857 7.409655766 Copper 0.00 0 0
 309 -0.19690832 19.11240455 19.11396716 Copper 0.00 0 0
 310 -0.54374369 5.653611183 5.64614673 Copper 0.00 0 0
 311 13.16932223 19.09798947 5.501548862 Copper 0.00 0 0
 312 13.17200007 5.511416836 19.11035776 Copper 0.00 0 0
 313 -0.266539969 19.14139742 7.308242302 Copper 0.00 0 0
 314 -0.492474343 5.638545462 20.73377119 Copper 0.00 0 0
 315 13.17384215 19.08126888 20.88455327 Copper 0.00 0 0
 316 13.17307735 5.525980414 7.368131049 Copper 0.00 0 0
 317 -0.263062869 7.310797023 19.13940547 Copper 0.00 0 0
 318 -0.489180828 20.73208936 5.631801533 Copper 0.00 0 0
 319 13.17125663 7.369352068 5.53583142 Copper 0.00 0 0

320 13.17303129 20.9277464 19.04912884 Copper 0.00 0 0
321 7.286087865 -0.34229785 7.288060677 Copper 0.00 0 0
322 7.40927841 13.17477674 20.89229395 Copper 0.00 0 0
323 20.74321876 -0.443437528 20.74880129 Copper 0.00 0 0
324 20.88691292 13.1758209 7.408719958 Copper 0.00 0 0
325 19.1111656 -0.194218921 19.11538135 Copper 0.00 0 0
326 19.10301767 13.1739295 5.509904444 Copper 0.00 0 0
327 5.651949329 -0.543590891 5.652147159 Copper 0.00 0 0
328 5.508040593 13.17441509 19.10526528 Copper 0.00 0 0
329 7.307203062 -0.262148977 19.1337461 Copper 0.00 0 0
330 7.364703837 13.17595244 5.526093997 Copper 0.00 0 0
331 20.72929313 -0.489084551 5.630304392 Copper 0.00 0 0
332 20.93184574 13.17438364 19.04395135 Copper 0.00 0 0
333 19.13713806 -0.266323903 7.305407112 Copper 0.00 0 0
334 19.08156696 13.17613676 20.88148127 Copper 0.00 0 0
335 5.634304063 -0.493288317 20.72728361 Copper 0.00 0 0
336 5.53851528 13.17650501 7.372586226 Copper 0.00 0 0
337 9.714021187 6.113755058 23.77264551 Hydrogen 0.00 0 0
338 10.6328547 19.01201757 10.63401876 Hydrogen 0.00 0 0
339 16.619299 20.39170448 23.68107224 Hydrogen 0.00 0 0
340 15.75507497 7.366768878 10.63177216 Hydrogen 0.00 0 0
341 2.607618893 20.76640804 10.09613966 Hydrogen 0.00 0 0
342 16.24614874 5.778749616 2.50767396 Hydrogen 0.00 0 0
343 15.82244972 19.07470099 15.81395452 Hydrogen 0.00 0 0
344 2.166021851 19.14627168 2.171981443 Hydrogen 0.00 0 0
345 10.0879886 20.76054774 2.61555547 Hydrogen 0.00 0 0
346 10.63095923 7.361526546 15.75926107 Hydrogen 0.00 0 0
347 23.76989994 9.728006814 6.108849757 Hydrogen 0.00 0 0
348 23.6582345 23.67036799 19.91085838 Hydrogen 0.00 0 0
349 10.63392235 10.632421 19.01463692 Hydrogen 0.00 0 0
350 23.66401765 16.61673736 20.39920645 Hydrogen 0.00 0 0

351	24.0094914	2.518869945	6.783723125	Hydrogen	0.00	0	0
352	10.08553456	2.623697439	20.75921324	Hydrogen	0.00	0	0
353	2.508031455	16.24743417	5.780090086	Hydrogen	0.00	0	0
354	2.173921597	2.174216049	19.15659109	Hydrogen	0.00	0	0
355	2.618622924	10.09296016	20.7639273	Hydrogen	0.00	0	0
356	2.517909533	24.01418197	6.789477757	Hydrogen	0.00	0	0
357	6.112484908	23.76233467	9.722579741	Hydrogen	0.00	0	0
358	19.91559811	23.65850562	23.66283867	Hydrogen	0.00	0	0
359	19.01541418	10.63273396	10.62655346	Hydrogen	0.00	0	0
360	20.3949797	23.67746627	16.61160449	Hydrogen	0.00	0	0
361	20.76201884	10.09499685	2.613363055	Hydrogen	0.00	0	0
362	6.782570254	24.00934715	2.52165239	Hydrogen	0.00	0	0
363	5.775371658	2.509570063	16.24758165	Hydrogen	0.00	0	0
364	19.14931044	2.17229975	2.173295355	Hydrogen	0.00	0	0
365	20.76353488	2.612575558	10.09166702	Hydrogen	0.00	0	0
366	6.785641895	2.51405462	24.01284594	Hydrogen	0.00	0	0
367	5.778141709	10.09896417	2.514251679	Hydrogen	0.00	0	0
368	19.04498201	10.60121303	15.78901523	Hydrogen	0.00	0	0
369	20.75300724	16.25402839	2.615465932	Hydrogen	0.00	0	0
370	7.328009035	15.78613826	15.78981935	Hydrogen	0.00	0	0
371	7.175482502	2.181988023	2.185776375	Hydrogen	0.00	0	0
372	6.115887864	16.63514675	23.75905536	Hydrogen	0.00	0	0
373	5.774926275	2.512044965	10.09472602	Hydrogen	0.00	0	0
374	19.04237675	15.78644906	10.60194131	Hydrogen	0.00	0	0
375	20.40184844	9.737819612	23.69341431	Hydrogen	0.00	0	0
376	7.396013731	10.66033896	10.66718439	Hydrogen	0.00	0	0
377	9.738143901	23.66516076	20.40569585	Hydrogen	0.00	0	0
378	10.65709079	10.66582068	7.401473773	Hydrogen	0.00	0	0
379	16.63670862	23.75359735	6.114200462	Hydrogen	0.00	0	0
380	15.77856182	10.5982391	19.04888079	Hydrogen	0.00	0	0
381	2.502407517	10.10258758	5.771602316	Hydrogen	0.00	0	0

382 16.25021663 2.620588235 20.7571857 Hydrogen 0.00 0 0
 383 15.77823215 15.77693546 7.332539761 Hydrogen 0.00 0 0
 384 2.189275703 2.191470672 7.165290736 Hydrogen 0.00 0 0
 385 10.10039013 2.507250017 5.775400892 Hydrogen 0.00 0 0
 386 10.60327464 15.77378979 19.04769026 Hydrogen 0.00 0 0
 387 23.75267938 6.116181181 16.63681132 Hydrogen 0.00 0 0
 388 24.01861127 19.54124288 2.498542547 Hydrogen 0.00 0 0
 389 10.10013719 5.771921206 2.507176636 Hydrogen 0.00 0 0
 390 23.69552899 20.40653552 9.735380585 Hydrogen 0.00 0 0
 391 23.64739924 6.420969996 23.65240156 Hydrogen 0.00 0 0
 392 10.65927847 7.397153486 10.660331 Hydrogen 0.00 0 0
 393 2.504231756 5.774212732 10.09930722 Hydrogen 0.00 0 0
 394 2.504411804 19.54635625 24.01344274 Hydrogen 0.00 0 0
 395 2.611184211 20.76019347 16.24684741 Hydrogen 0.00 0 0
 396 2.193429074 7.168194557 2.189355994 Hydrogen 0.00 0 0
 397 16.2508089 20.75073983 2.615701413 Hydrogen 0.00 0 0
 398 15.78437345 7.328282864 15.78565553 Hydrogen 0.00 0 0
 399 10.60509467 19.04153493 15.78909527 Hydrogen 0.00 0 0
 400 9.73304225 20.398689 23.69077599 Hydrogen 0.00 0 0
 401 16.6379264 6.117733527 23.76058553 Hydrogen 0.00 0 0
 402 15.78068724 19.04901585 10.59399889 Hydrogen 0.00 0 0
 403 2.614779484 16.24591248 20.76036477 Hydrogen 0.00 0 0
 404 2.503050437 24.01721571 19.54337537 Hydrogen 0.00 0 0
 405 23.66843413 9.738631016 20.40794812 Hydrogen 0.00 0 0
 406 23.65202438 23.65705582 6.423898609 Hydrogen 0.00 0 0
 407 23.75454976 16.63673387 6.115243249 Hydrogen 0.00 0 0
 408 24.0160322 2.499866717 19.54164195 Hydrogen 0.00 0 0
 409 20.75534099 2.613513351 16.24852566 Hydrogen 0.00 0 0
 410 19.53749508 2.4971519 24.02327424 Hydrogen 0.00 0 0
 411 20.40263367 23.665054 9.737869451 Hydrogen 0.00 0 0
 412 6.426091658 23.65490371 23.65507065 Hydrogen 0.00 0 0

413 6.117343719 23.75306615 16.63595747 Hydrogen 0.00 0 0
 414 19.5447305 24.01019281 2.499451136 Hydrogen 0.00 0 0
 415 20.39254554 16.62419539 23.68024569 Hydrogen 0.00 0 0
 416 7.36427956 15.75454185 10.63422949 Hydrogen 0.00 0 0
 417 6.111124108 9.722331995 23.77469121 Hydrogen 0.00 0 0
 418 7.367945197 10.63246978 15.7545255 Hydrogen 0.00 0 0
 419 5.774503169 16.24683633 2.513300772 Hydrogen 0.00 0 0
 420 19.07698343 15.79653781 15.82046311 Hydrogen 0.00 0 0
 421 16.24468508 2.514498578 5.777713339 Hydrogen 0.00 0 0
 422 15.81072077 15.81347146 19.08579109 Hydrogen 0.00 0 0
 423 10.6319098 15.75004877 7.368921878 Hydrogen 0.00 0 0
 424 9.725186008 23.77027368 6.109358506 Hydrogen 0.00 0 0
 425 16.6167656 23.66251669 20.39973577 Hydrogen 0.00 0 0
 426 15.75032052 10.6341283 7.365981214 Hydrogen 0.00 0 0
 427 2.514276115 6.790568598 24.01476153 Hydrogen 0.00 0 0
 428 2.514222886 5.781422054 16.25571 Hydrogen 0.00 0 0
 429 23.6716834 20.40169763 16.6161351 Hydrogen 0.00 0 0
 430 24.01091888 6.788983205 2.519031 Hydrogen 0.00 0 0
 431 23.76947757 6.109279996 9.722911853 Hydrogen 0.00 0 0
 432 23.65770808 19.92175343 23.65625513 Hydrogen 0.00 0 0
 433 8.092346269 6.339023658 25.8265607 Oxygen 0.00 0 0
 434 8.451964737 19.84394304 11.74011745 Oxygen 0.00 0 0
 435 22.01987434 6.437117066 11.73576395 Oxygen 0.00 0 0
 436 21.94396924 20.14140927 25.7692789 Oxygen 0.00 0 0
 437 18.28346477 20.08828238 25.70115152 Oxygen 0.00 0 0
 438 17.98541279 6.544861824 11.77111752 Oxygen 0.00 0 0
 439 4.531471928 20.17719965 11.7014272 Oxygen 0.00 0 0
 440 4.440501666 6.293886298 25.91411832 Oxygen 0.00 0 0
 441 17.82611394 6.168663251 0.593966721 Oxygen 0.00 0 0
 442 17.97965251 19.84377866 14.57660717 Oxygen 0.00 0 0
 443 4.462998045 6.35965835 14.63817043 Oxygen 0.00 0 0

444 4.215337008 19.67154564 0.32183966 Oxygen 0.00 0 0
 445 8.514509697 20.29782416 0.706910785 Oxygen 0.00 0 0
 446 8.457596609 6.56905863 14.57711275 Oxygen 0.00 0 0
 447 21.9591152 20.08083717 14.63076844 Oxygen 0.00 0 0
 448 22.14995585 6.561778572 0.455540274 Oxygen 0.00 0 0
 449 25.81357036 8.098929766 6.348996735 Oxygen 0.00 0 0
 450 25.77184739 21.95150522 20.12805942 Oxygen 0.00 0 0
 451 11.73536036 8.454457991 19.84988218 Oxygen 0.00 0 0
 452 11.73358678 22.01675102 6.441185906 Oxygen 0.00 0 0
 453 25.69928591 18.27625612 20.09420517 Oxygen 0.00 0 0
 454 25.91094275 4.447865386 6.292649584 Oxygen 0.00 0 0
 455 11.77771541 17.97961289 6.545262752 Oxygen 0.00 0 0
 456 11.69988041 4.512145924 20.17081051 Oxygen 0.00 0 0
 457 0.595853121 17.8252682 6.172273195 Oxygen 0.00 0 0
 458 0.322800591 4.225871972 19.68206324 Oxygen 0.00 0 0
 459 14.61298323 18.00052991 19.87906633 Oxygen 0.00 0 0
 460 14.63418574 4.468981656 6.35820198 Oxygen 0.00 0 0
 461 0.704929075 8.523232045 20.30299469 Oxygen 0.00 0 0
 462 0.459036226 22.14839682 6.559143282 Oxygen 0.00 0 0
 463 14.58340442 8.459353479 6.570436306 Oxygen 0.00 0 0
 464 14.65536242 21.95923192 20.0680117 Oxygen 0.00 0 0
 465 6.352771791 25.80980225 8.092013946 Oxygen 0.00 0 0
 466 6.441207067 11.73770418 22.02195256 Oxygen 0.00 0 0
 467 20.12244017 25.77508912 21.9489055 Oxygen 0.00 0 0
 468 19.84409121 11.73572405 8.446483007 Oxygen 0.00 0 0
 469 20.08430687 25.70130665 18.27599393 Oxygen 0.00 0 0
 470 20.16733357 11.7033636 4.512882226 Oxygen 0.00 0 0
 471 6.302939942 25.9218976 4.444984308 Oxygen 0.00 0 0
 472 6.548593244 11.78291227 17.98370677 Oxygen 0.00 0 0
 473 6.166295485 0.596870332 17.82015978 Oxygen 0.00 0 0
 474 6.3514919 14.63390328 4.467452782 Oxygen 0.00 0 0

475 19.67328822 0.323603161 4.219604538 Oxygen 0.00 0 0
 476 19.85777873 14.57746206 17.96974378 Oxygen 0.00 0 0
 477 20.3014444 0.701204361 8.517818336 Oxygen 0.00 0 0
 478 20.08832133 14.61509739 21.97949636 Oxygen 0.00 0 0
 479 6.560334186 0.456097721 22.14369323 Oxygen 0.00 0 0
 480 6.560490051 14.60423787 8.454832791 Oxygen 0.00 0 0
 481 6.150316132 8.558925929 0.574094039 Oxygen 0.00 0 0
 482 6.43898699 22.01672024 14.61255148 Oxygen 0.00 0 0
 483 19.84322788 8.454292355 14.60300566 Oxygen 0.00 0 0
 484 19.76216534 22.16294103 0.438073335 Oxygen 0.00 0 0
 485 20.27540468 17.85599048 0.718346287 Oxygen 0.00 0 0
 486 20.1600474 4.512918314 14.64464577 Oxygen 0.00 0 0
 487 6.564931445 17.9980329 14.56901947 Oxygen 0.00 0 0
 488 6.658701856 4.238919282 0.330492528 Oxygen 0.00 0 0
 489 6.38273584 18.30636206 25.76721603 Oxygen 0.00 0 0
 490 6.351478336 4.460912825 11.71946972 Oxygen 0.00 0 0
 491 19.86125961 17.98596825 11.75002735 Oxygen 0.00 0 0
 492 20.04481744 4.429320773 25.91798677 Oxygen 0.00 0 0
 493 20.1355886 8.110755897 25.7446624 Oxygen 0.00 0 0
 494 20.07706845 21.94507525 11.69221461 Oxygen 0.00 0 0
 495 6.568232314 8.459183384 11.77447044 Oxygen 0.00 0 0
 496 6.19807794 21.92677705 25.76222702 Oxygen 0.00 0 0
 497 8.121684367 25.73008124 20.13389365 Oxygen 0.00 0 0
 498 8.452957503 11.77411286 6.578021873 Oxygen 0.00 0 0
 499 21.92510631 25.76886612 6.211192137 Oxygen 0.00 0 0
 500 21.95499235 11.69203612 20.07174886 Oxygen 0.00 0 0
 501 18.31546816 25.76029289 6.381735623 Oxygen 0.00 0 0
 502 17.99713474 11.73787305 19.87947467 Oxygen 0.00 0 0
 503 4.431961513 25.91283683 20.0447288 Oxygen 0.00 0 0
 504 4.452275801 11.74260763 6.353904892 Oxygen 0.00 0 0
 505 17.85539624 0.724920925 20.2740276 Oxygen 0.00 0 0

506 17.98218059 14.56902895 6.547212018 Oxygen 0.00 0 0
 507 4.240130309 0.335853752 6.65291114 Oxygen 0.00 0 0
 508 4.510550133 14.64381713 20.169289 Oxygen 0.00 0 0
 509 8.561487001 0.56597745 6.143771494 Oxygen 0.00 0 0
 510 8.451794612 14.61060088 19.84808834 Oxygen 0.00 0 0
 511 22.16190949 0.441800468 19.76631012 Oxygen 0.00 0 0
 512 22.01036056 14.61816961 6.441701703 Oxygen 0.00 0 0
 513 25.76016443 6.384434482 18.31052377 Oxygen 0.00 0 0
 514 25.90395213 20.05378796 4.428801816 Oxygen 0.00 0 0
 515 11.72764983 6.352798928 4.460223206 Oxygen 0.00 0 0
 516 11.77078587 19.85805207 17.96882735 Oxygen 0.00 0 0
 517 25.73657604 20.13634628 8.109853223 Oxygen 0.00 0 0
 518 25.74779042 6.19594027 21.9200507 Oxygen 0.00 0 0
 519 11.73404716 20.08793487 21.98117262 Oxygen 0.00 0 0
 520 11.77038521 6.573961121 8.459516187 Oxygen 0.00 0 0
 521 0.565971049 6.144330577 8.556510144 Oxygen 0.00 0 0
 522 0.442775206 19.76380923 22.16528844 Oxygen 0.00 0 0
 523 14.60904605 6.443809443 22.02258673 Oxygen 0.00 0 0
 524 14.60962798 19.8438116 8.450945797 Oxygen 0.00 0 0
 525 0.722766457 20.27204724 17.85890524 Oxygen 0.00 0 0
 526 0.334827113 6.656888101 4.235692386 Oxygen 0.00 0 0
 527 14.64017326 20.16365051 4.507841339 Oxygen 0.00 0 0
 528 14.56564228 6.541837444 17.98286241 Oxygen 0.00 0 0
 529 17.85774167 20.26847743 0.715759611 Oxygen 0.00 0 0
 530 17.97818848 6.547427763 14.55981226 Oxygen 0.00 0 0
 531 4.509065869 20.16086242 14.64766392 Oxygen 0.00 0 0
 532 4.246736893 6.654077184 0.335112028 Oxygen 0.00 0 0
 533 8.566176828 6.139687564 0.570038591 Oxygen 0.00 0 0
 534 8.454191467 19.84511945 14.61159262 Oxygen 0.00 0 0
 535 22.01623666 6.440562566 14.60952584 Oxygen 0.00 0 0
 536 22.16539343 19.76555967 0.441476722 Oxygen 0.00 0 0

537 8.10832693 20.13608527 25.74347431 Oxygen 0.00 0 0
538 8.451930819 6.568600148 11.7679026 Oxygen 0.00 0 0
539 21.98896667 20.07881889 11.73256277 Oxygen 0.00 0 0
540 21.92629066 6.200745806 25.76600836 Oxygen 0.00 0 0
541 18.30690566 6.381749608 25.76991163 Oxygen 0.00 0 0
542 17.97215559 19.87290219 11.75625971 Oxygen 0.00 0 0
543 4.46133789 6.357542713 11.71576849 Oxygen 0.00 0 0
544 4.432385916 20.04690718 25.91190827 Oxygen 0.00 0 0
545 0.720592343 17.85606145 20.27375757 Oxygen 0.00 0 0
546 0.334416346 4.242267711 6.649208501 Oxygen 0.00 0 0
547 14.5622575 17.99732229 6.560340859 Oxygen 0.00 0 0
548 14.64711363 4.519267044 20.17268864 Oxygen 0.00 0 0
549 0.565506592 8.562885641 6.139363424 Oxygen 0.00 0 0
550 0.443493938 22.16439961 19.76576459 Oxygen 0.00 0 0
551 14.60777352 8.452572654 19.84696692 Oxygen 0.00 0 0
552 14.60943567 22.01558698 6.438278011 Oxygen 0.00 0 0
553 25.73395429 8.115233793 20.13987386 Oxygen 0.00 0 0
554 25.76230403 21.92874568 6.201056735 Oxygen 0.00 0 0
555 11.75230289 8.453239076 6.566891954 Oxygen 0.00 0 0
556 11.68860858 21.95435819 20.06976367 Oxygen 0.00 0 0
557 25.76677569 18.31397517 6.380439564 Oxygen 0.00 0 0
558 25.91834248 4.422952251 20.03757232 Oxygen 0.00 0 0
559 11.73850485 17.99648627 19.8791469 Oxygen 0.00 0 0
560 11.71414067 4.465026686 6.358662159 Oxygen 0.00 0 0
561 20.27051433 0.722589141 17.85877277 Oxygen 0.00 0 0
562 20.16081718 14.64980855 4.513839383 Oxygen 0.00 0 0
563 6.656085808 0.331938294 4.240073338 Oxygen 0.00 0 0
564 6.552310321 14.56906687 17.99278308 Oxygen 0.00 0 0
565 6.14196064 0.570487044 8.560195846 Oxygen 0.00 0 0
566 6.440985044 14.61040452 22.023295 Oxygen 0.00 0 0
567 19.76063263 0.441301912 22.16738401 Oxygen 0.00 0 0

568 19.84351933 14.60782227 8.458552363 Oxygen 0.00 0 0
569 20.13164712 25.73292886 8.117671556 Oxygen 0.00 0 0
570 20.08800379 11.73887723 21.98238983 Oxygen 0.00 0 0
571 6.211603783 25.76257052 21.92382646 Oxygen 0.00 0 0
572 6.560959692 11.75235908 8.456696824 Oxygen 0.00 0 0
573 6.384963023 25.76518036 18.30736205 Oxygen 0.00 0 0
574 6.352026557 11.71669642 4.468442559 Oxygen 0.00 0 0
575 20.05353591 25.90309845 4.429126178 Oxygen 0.00 0 0
576 19.85707648 11.77093138 17.97070254 Oxygen 0.00 0 0
577 20.09874531 18.28479421 25.70823888 Oxygen 0.00 0 0
578 20.16540943 4.510162285 11.69841248 Oxygen 0.00 0 0
579 6.544711769 17.9781322 11.78356435 Oxygen 0.00 0 0
580 6.297322388 4.435207748 25.92248794 Oxygen 0.00 0 0
581 6.347017003 8.086425296 25.81815992 Oxygen 0.00 0 0
582 6.439513812 22.0158227 11.73592598 Oxygen 0.00 0 0
583 19.849497 8.451758051 11.73144279 Oxygen 0.00 0 0
584 20.13887235 21.93444508 25.77014233 Oxygen 0.00 0 0
585 20.30371348 8.51983832 0.696700565 Oxygen 0.00 0 0
586 20.06956222 21.973949 14.63875173 Oxygen 0.00 0 0
587 6.572123892 8.459539974 14.57529967 Oxygen 0.00 0 0
588 6.554234462 22.14211452 0.462886054 Oxygen 0.00 0 0
589 6.162969339 17.81889521 0.597603216 Oxygen 0.00 0 0
590 6.356020545 4.464704954 14.63475509 Oxygen 0.00 0 0
591 19.88683203 17.97978422 14.60693615 Oxygen 0.00 0 0
592 19.68012389 4.221480262 0.326266053 Oxygen 0.00 0 0
593 17.82121599 0.59506226 6.168126104 Oxygen 0.00 0 0
594 17.99547581 14.61183406 19.8795903 Oxygen 0.00 0 0
595 4.221071008 0.31979 19.67503113 Oxygen 0.00 0 0
596 4.452850875 14.61065192 6.353993873 Oxygen 0.00 0 0
597 8.517670518 0.707945027 20.29774031 Oxygen 0.00 0 0
598 8.453347783 14.5809069 6.57392288 Oxygen 0.00 0 0

599 22.14522101 0.460027312 6.556927908 Oxygen 0.00 0 0
 600 21.95584571 14.65746601 20.06996211 Oxygen 0.00 0 0
 601 8.102387714 25.82266368 6.344177688 Oxygen 0.00 0 0
 602 8.454726351 11.73992477 19.84885103 Oxygen 0.00 0 0
 603 21.92537726 25.7707254 20.13605135 Oxygen 0.00 0 0
 604 22.02240836 11.74279471 6.441179589 Oxygen 0.00 0 0
 605 18.27441308 25.69706917 20.09663621 Oxygen 0.00 0 0
 606 17.9812919 11.77955763 6.544479014 Oxygen 0.00 0 0
 607 4.446937768 25.91431151 6.299688623 Oxygen 0.00 0 0
 608 4.524481549 11.69718197 20.17385242 Oxygen 0.00 0 0
 609 0.699373924 20.30588664 8.521359278 Oxygen 0.00 0 0
 610 0.455888073 6.566130548 22.14968632 Oxygen 0.00 0 0
 611 14.60969658 20.09300567 21.98166743 Oxygen 0.00 0 0
 612 14.57577006 6.573879897 8.459916341 Oxygen 0.00 0 0
 613 0.598750501 6.170701112 17.82680585 Oxygen 0.00 0 0
 614 0.324164454 19.67596051 4.222030476 Oxygen 0.00 0 0
 615 14.618866 6.358031279 4.460974668 Oxygen 0.00 0 0
 616 14.57656763 19.86044551 17.96748094 Oxygen 0.00 0 0
 617 25.69880162 20.10050263 18.27846386 Oxygen 0.00 0 0
 618 25.92110157 6.308546056 4.441235732 Oxygen 0.00 0 0
 619 11.69315843 20.17811976 4.531963131 Oxygen 0.00 0 0
 620 11.77853883 6.550824939 17.99195021 Oxygen 0.00 0 0
 621 25.81874712 6.345013033 8.094929387 Oxygen 0.00 0 0
 622 25.76166708 20.14027659 21.9308126 Oxygen 0.00 0 0
 623 11.73378918 6.44455396 22.0229641 Oxygen 0.00 0 0
 624 11.73792541 19.84229456 8.452809662 Oxygen 0.00 0 0

Fundcell_Info: Listed

26.34300	26.34300	26.34300	# unit cell edge lengths
90.00000	90.00000	90.00000	# unit cell angles
0.00000	0.00000	0.00000	# origin of unit cell

26.34300 26.34300 26.34300 # effective bound box size

Intramolecular interaction file

Intra: Methane

Intra: HKUST1

Atom-atom interaction file

Methane Methane LJ SIG@3.730 EPS@148.0 HICUT@13.17

Methane Carbon LJ SIG@3.580 EPS@88.431 HICUT@13.17

Methane Hydrogen LJ SIG@3.151 EPS@57.245 HICUT@13.17

Methane Oxygen LJ SIG@3.424 EPS@66.848 HICUT@13.17

Methane Copper LJ SIG@3.422 EPS@19.297 HICUT@13.17

Molecule-molecule interaction file

#!without potential map

Methane Methane NCOUL BASIC LJ FAST

Methane Methane COUL OFF

Methane HKUST1 NCOUL BASIC LJ FAST

Methane HKUST1 COUL OFF

HKUST1 HKUST1 NCOUL OFF

HKUST1 HKUST1 COUL OFF

#!with potential map

Methane Methane NCOUL BASIC LJ FAST

Methane Methane COUL OFF

Methane HKUST1 NCOUL MAP@HKUST1 FAST Methane@PMAP@HKUST1.CH4.UFF.pmap

Methane HKUST1 COUL OFF

HKUST1 HKUST1 NCOUL OFF

HKUST1 HKUST1 COUL OFF

Map control file

----- General Information -----

Methane in IRMOF1

1 # No. of iterations
1 # No. of steps between writes to output/log file
1 # No. of steps between writes to crash file
1 # No. of steps between writes to config. file
2 # Start numbering simulations from .
1892134 # Iseed
4 # specifies contents of config file,
Methane.res # Restart File to write to
Methane.con # Configuration File

----- Atomic Types -----

5 # number of atomic types

Methane # atom type

Methane.atm # basic atom info file

Carbon # atom type

Carbon.atm # basic atom info file

Oxygen # atom type

Oxygen.atm # basic atom info file

```

Hydrogen                # atom type
Hydrogen.atm            # basic atom info file

Copper                  # atom type
Copper.atm              # basic atom info file

----- Molecule Types -----
2                        # number of sorbate types

Methane                 # sorbate
Methane.mol             # sorbate coordinates file

HKUST1                  # sorbate
HKUST1.mol              # sorbate coordinates file

----- Simulation Cell Information -----
HKUST1                  # Fundamental cell type
1, 1, 1                 # No. of unit cells in x, y, z direction
1, 1, 1                 # (1 = Periodic) in x, y, z

----- Forcefield Information -----
BASIC
SPC
atom_atom_file_Methane_UFF      # atom-atom interaction file
sorb_sorb_file_Methane          # sorbate-sorbate interaction file (optional)
intramolecular_file             # intramolecular interactions

----- Mapmaker Information -----
1                                # Number of maps to make

HKUST1                          # Sorbate to map
Methane                         # Sorbate to probe map with
NCOUL LJ                        # Interaction type to map
0.2                             # Approximate grid spacing (Ang)

```

```

100.0          # High end potential cutoff (kJ/mol)
HKUST1.CH4.UFF.pmap      # Map filename or AUTO
----- Configuration Initialization -----
Methane                # Sorbate_Type
GCMC NULL              # Source Filename
HKUST1                 # Sorbate_Type
Fixed NULL             # Source Filename

```

GCMC control file

```

----- General Information -----
Methane molecule in IRMOF1
20000000          # No. of iterations
2000000          # No. of steps between writes to output/log file
2000000          # No. of steps between writes to crash file
10000            # No. of steps between writes to config. file
1                # Start numbering simulations from .
10283            # Iseed
3                # specifies contents of config file,
HKUST1.Methane.res      # Restart File to write to
HKUST1.Methane.con      # Configuration File
----- Atomic Types -----
5                # number of atomic types

Methane          # atom type
Methane.atm      # basic atom info file

Carbon          # atom type
Carbon.atm      # basic atom info file

Oxygen          # atom type

```

```

Oxygen.atm          # basic atom info file

Hydrogen            # atom type
Hydrogen.atm        # basic atom info file

Copper
Copper.atm

----- Molecule Types -----
2                  # number of sorbate types

Methane             # sorbate
Methane.mol         # sorbate coordinates file

HKUST1              # sorbate
HKUST1.mol          # sorbate coordinates file

----- Simulation Cell Information -----
HKUST1              # Fundamental cell file
1, 1, 1             # No. of unit cells in x, y, z direction
1, 1, 1             # (1 = Periodic) in x, y, z

----- Forcefield Information -----
BASIC
SPC
atom_atom_file_Methane_UFF  # atom-atom interaction file
sorb_sorb_file_UFF         # sorbate-sorbate interaction file
intramolecular_file # intramolecular interaction file/specification

----- Ideal Parameters -----
Ideal                # Equation of State
1                   # no. of sorbates
Methane              # Sorbate Name

----- GCMC Information -----

```

```

1                # No. of iterations
140.             # temperature
Ideal Parameters # Tag for the equation of state (NULL = Ideal Gas)
1                # No. of simulation points
5000             # Block size for statistics
1                # no. of sorbates

-----

Methane          # Sorbate Name
fugacity_verification.dat #pressure
HKUST1.CH4.UFF.pmap      # sitemap filename (Null = no sitemap)
3                  # no of gcmc movetypes
1.0, 1.0, 1.0      # move type weights
RINSERT           # type of move.1
RDELETE           # type of move.2
RTRANSLATE        # type of move.4
0.2, 0            # Delta Translate, adjust delta option (0=NO, 1=YES)
----- Configuration Initialization -----
Methane          # Sorbate_Type
GCMC NULL
HKUST1           # Sorbate_Type
FIXED NULL
----- Main Datafile Information -----
Energy, position, pair_energy # contents of datafile
----- Movie Information -----
movie.xyz #Movie filename
10000000, 20000000 #Starting step, ending step
10000 #Steps between frames
NO #Include MOF in movie
1,1,1 #number of unit cells to dump in x, y, z directions

```

Post processing

```
# this section is required for working with any post code
#
#
-----

    ### Required section #####
-- Post Processor Information -----

GCMC                # Type of simulation GCMC, NVTMC , MD ....
HKUST1.Methane.con   # basename for config files
1, 1                # first and last file numbers
new.ctr             # name for new ctrlfile that will regenerated
HKUST1.Methane.post  # Base name for output files
60,0                # Percentages of data to skipped at start and end


# The sections below are necessary only if you want the corresponding
# analysis performed
# ----- ALL OF THEM ARE OPTIONAL -----


####   This section is reqd for energy averages in your post code output
        files
####   as of now only total enrgies vs sim. step
----- Post : Energy Average Info -----
20      # Number of blocks into which data should be divided for stats


####   This section is reqd for Loading averages in your post code
        outputfiles
####   as of now only species loading vs sim. step (for all species)
```

----- Post : Loading Average Info -----
20 # **Number** of blocks into which data should be divided for stats

Bash file

```
#run the map
#!/bin/sh
cd ~/BaiChuan/gcmc.hkust1.ch4/run
source set_path
./music_mapmaker ctr.map.HKUST1.CH4 > mapHKUST1result.log

#run the gcmc
#!/bin/sh
cd ~/BaiChuan/gcmc.hkust1.ch4/run
source set_path
./music_gcmc gcmc.Methane.HKUST1 > gcmcHKUSTResult.log

#run the post processing
#!/bin/sh
cd ~/BaiChuan/gcmc.hkust1.ch4/run
source set_path
./music_post post.ctr > post.log

>qsub [above filename]
```

Typical GCMC results

```
#-----OVERALL ISOTHERM-----
# Molecule : Methane
# Pressure                   loading
# kpa(1 st gcmc species) (molec/uc)
```

1.00000000000000	139.1416667
1.45468000000000	155.7083333
2.11610000000000	166.1687500
3.07825000000000	170.7385417
4.47788000000000	173.5770833
6.51389000000000	177.4208333
9.47564000000000	178.4687500
13.78405000000000	180.8177083
20.05141000000000	182.0114583
29.16843000000000	183.1093750
42.43079000000000	184.8072917
61.72332000000000	185.4187500
89.78781000000000	186.1250000
130.61272000000000	186.6645833
190.00000000000000	187.8916667

Results of a Langmuir **Fit**, $fug = K * z / (z_{max} - z)$

Where **K** is is kPa, z , and z_{max} are zeo-loadings in molec/uc

K =0.3149469740890 ; z_{max} 186.46799

% Error in loading 0.92314

Appendix E

Publications Arising From This Thesis

The author is grateful to his supervisor Asst. Prof. Anutosh Chakraborty to be co-author for the following publications.

Award

“Best Poster” Award in commendation for the outstanding poster presented at the 6th International Meeting on Advanced Thermofluids, IMAT 2013, NUS Singapore during 18-19 Nov. 2013 with the paper *“Adsorption Characteristics of Various MOFs for Gas Storage Applications”*.

Journals Papers

1. **B. Sun**, A. Chakraborty, “Thermodynamic frameworks of adsorption kinetics modeling: Dynamic water uptakes on silica gel for adsorption cooling applications,” *Energy*, 2015, 84, 296-302.
2. **B. Sun**, S. Kayal, A. Chakraborty, “Study of HKUST-1 Metal Organic Frameworks for CH₄ Adsorption: An Experimental Investigation with GCMC simulation, ” *Energy*, 2014, 76, 419-427.

3. **B. Sun**, A. Chakraborty, “Thermodynamic formalism of water uptakes on solid porous adsorbents for adsorption cooling applications,” *Applied Physics Letters*, 2014, 104, 201901.
4. **B. Sun**, A. Chakraborty, S. M. Ali, S. Kayal, “Design and development of a volumetric apparatus for the measurement of methane uptakes under cryogenic conditions” *Applied Thermal Engineering*, In Press, 2015.
5. A. Chakraborty, **B. Sun**, “An adsorption isotherm equation for multi-types adsorption with thermodynamic correctness,” *Applied Thermal Engineering*, 2014, 72, 190-199.
6. S. Kayal, **B. Sun**, A. Chakraborty, “A robust metal-organic framework MIL-101(Cr) for high capacity natural gas storage,” *Energy*, 2015, 91, 772-781.
7. **B. Sun**, W. Fan, A. Chakraborty, “Adsorption kinetics emulation with lattice gas cellular automata,” *Heat Transfer Engineering*, Accepted.

Conference Papers

1. A. Chakraborty, **B. Sun**, S.M. Ali, Wu Fan, “Design and development of cryo-adsorption chamber for the measurement of methane uptakes on activated carbons and MOFs,” *7th Asian Conference on Refrigeration and Air Conditioning*, ACRA 2014, Jeju Island, South Korea.
2. **B. Sun**, A. Chakraborty, “A Single Component Adsorption Isotherm for Multi-types Heterogeneous Surfaces based on Fermi-Dirac Distribution Law,” *International Symposium on Innovative Materials for Process in Energy Systems 2013*, Fukuoka, Japan. (Selected paper for *Applied Thermal Engineering*)
3. **B. Sun**, A. Chakraborty, “Adsorption Kinetics Emulation with Lattice Gas Cellular Automata,” *The 6th International Meeting on Advanced Thermofluids 2013*, Singapore. (Selected paper for *Heat Transfer Engineering*)

4. **B. Sun**, Wu Fan, A. Chakraborty, “Adsorption Characteristics of Various MOFs for Gas Storage Applications,” *The 6th International Meeting on Advanced Thermofluids 2013*, Singapore. (Best Poster)