UNIVERSIDADE FEDERAL DO PARANÁ



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EXPLORING SCHWARZITES: CARBON-BASED POROUS STRUCTURES FOR CARBON DIOXIDE CAPTURE

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RESUMO

Neste trabalho, é apresentada a metodologia utilizada para estudar a adsorção de gás em Schwarzites. Essas estruturas cristalinas de carbono únicas possuem curvaturas gaussianas negativas e foram originalmente desenvolvidas por Mackay e Terrones em 1991, por meio do uso de ligações do tipo sp2 para povoar Superfícies Minimais Triplamente Periódicas (TPMS) com anéis contendo seis ou mais átomos de carbono. Para calcular as propriedades de tais sistemas, foi empregada a dinâmica molecular, uma abordagem computacional que resolve as equações de movimento de Newton para derivar a temperatura e outras grandezas como funções das posições e velocidades das partículas. As simulações foram realizadas utilizando o software de código aberto Lammps, uma ferramenta essencial para modelar sistemas de partículas de diferentes escalas e a principal ferramenta de simulação utilizada neste trabalho. Para as simulações de dinâmica molecular, utilizou-se o ensemble grande canônico, uma vez que o número de partículas no sistema era a quantidade de interesse. As interações entre as partículas foram calculadas usando um potencial de Lennard-Jones com um termo adicional de interação par a par de Coulomb. O campo de força UFF foi utilizado para descrever a estrutura de carbono, e TraPPE, uma coleção de formas funcionais e parâmetros de interação, foi utilizado para modelar as moléculas de CO₂ em nossas simulações.

Palavras-chave: Schwarzitas. Adsorção. Dióxido de carbono.

ABSTRACT

This work presents the methodology used to study the gas adsorption in Schwarzites. These unique crystalline carbon structures possess negative Gaussian curvatures, and were originally developed by Mackay and Terrones in 1991 through the use of sp2-type bonds to populate Triply Periodic Minimal Surfaces (TPMS) with rings containing six or more carbon atoms. To calculate the properties of such systems, molecular dynamics simulations were employed, a computational approach that solves Newton's equations of motion to derive temperature and other observables as functions of particle positions and velocities. The simulations were performed using the open-source software Lammps, which is an essential tool for modeling particle systems of different scales and was the primary simulation tool used in this work. For the molecular dynamics simulations, the Grand Canonical ensemble was utilized since the number of particles in our system was not only variable but also the quantity of interest. The interactions between particles were computed using a Lennard-Jones potential with an additional Coulomb pairwise interaction term. The non-reactive force field UFF was used to describe the carbon structure, and TraPPE, a collection of functional forms and interaction parameters, was employed to model the CO_2 molecules in our simulations.

Keywords: Schwarzites. Adsorption. Carbon Dioxide.

LIST OF FIGURES

2.1	Vostok Ice Core Data	15
2.2	When immersed in hot water, the gas molecules exhibit elevated kinetic energies, competing with the attractive forces present. This increased kinetic energy facilitates the overcoming of the attractive forces, thereby making it easier for the gas molecules to escape from their respective attractions.	16
2.3	Vostok Ice Core Data of the last 20,000 years	17
2.4	The blue line represents the global proxy temperature. The red line illustrates an Antarctic ice-core temperature record. The yellow dots correspond to atmo- spheric CO ₂ concentration. The intervals of the Holocene, Younger Dryas (YD), Bølling–Allerød (B–A), Oldest Dryas (OD), and Last Glacial Maximum (LGM) are marked on the graph. Error bars, represented by 1σ , indicate the margin of error in the measurements.	18
2.5	Figure illustrating the three distinct orbital movements that are intricately associ- ated with the Milankovitch cycles.	18
2.6	A comparison between global surface temperature changes (depicted by the red line) and the Sun's received energy by Earth (represented by the yellow line) in watts per square meter since 1880	19
2.7	Monthly mean concentrations of carbon dioxide measured globally over marine surface sites by the Global Monitoring Laboratory.	20
2.8	The figure serves as an illustration for adsorption, a surface phenomenon where molecules or ions adhere to the surface of a solid or liquid material. The figure also provides a visual representation of the nomenclature associated with the adsorbate and adsorbent.	22
2.9	Figure illustrating the two possible types of adsorption. Physical adsorption, also known as physisorption, involves the relatively weak van der Waals forces and occurs primarily on the surface of the adsorbent material. In contrast, chemical adsorption, or chemisorption, involves stronger chemical bonds forming between the adsorbate and the adsorbent.	23
2.10	Types of physisorption isotherms	25
2.11	The figure provides a visual representation of discretized adsorption sites. Adsorption sites denote particular regions or points on the surface of an adsorbent material where adsorbate molecules or ions adhere. In this depiction, each circle represents an adsorption site, with those marked in red indicating sites occupied by an adsorbate, while the blue circles signify available, unoccupied sites	27
3.1	Metal-organic frameworks (MOFs) are assembled from metal "clusters" and or- ganic molecules referred to as "linkers." The organic linkers coordinate with the metal clusters, leading to the formation of three-dimensional structures of various topologies	30

3.2	Illustration of the gaussian curvature for a surface, a normal vector is defined at a point P and the intersection of the collection of normal planes containing this vector and the surface establishes a normal curvature. The curves k_1 and k_2 denote the maximum and minimum normal curvatures at this point.	31
3.3	Examples of Triply Periodic Minimal Surfaces, surface (P) is the basis for the structures studied here, giving rise to the P-family Schwarzites. Figure sourced from Oraib Al-Ketan et al	32
3.4	The P-family of schwarzites is illustrated, (a) depicting the unit cells of the struc- tures to scale with each other. The red unit cell represents P8-1, the grey unit cell corresponds to P8-3, and the orange unit cell signifies P8-7. The replicated supercells utilized in the simulations are also displayed. Panels (b), (c), and (d) showcase the 2x2x2 supercells for P8-1, P8-3, and P8-7, respectively.	34
4.1	The illustration demonstrates periodic boundary conditions, where the interaction between the orange circle and the image of the red circle is depicted	36
4.2	The diagram illustrates the grand canonical ensemble or μ VT ensemble, wherein the system has the ability to exchange particles with an ideal gas reservoir. Within this depiction, the smaller rectangle symbolizes the system under investigation, while the larger rectangle denotes the ideal gas reservoir.	37
4.3	The figure depicts various interactions outlined by the potential energy of the system. Bond vibration, angle vibration, and torsion potentials are categorized as bonded interactions, while van der Waals and electrostatic interactions fall under the non-bonded interactions category.	44
5.1	Snapshots of the P8-3 converging at 10 bars and 300K, in grey is the carbon structure while the small molecules of grey and red atoms are the CO_2 molecules, showcasing steps (a) 30000, (b) 60000 and (c) 90000. From step 30000 to step 90000 there's been a total of 825 atoms added to the system. Here the blue outlines represent the simulation box.	49
5.2	Convergence curves for all three samples of each schwarzite at 300K, in the y-axis the amount of adsorbate per molar mass of the adsorbent is displayed in mmol g^{-1} , the x-axis shows the simulations steps, the figures show the (a) P8-1 at 0.8 bars, (b) P8-1 at 30 bars, (c) P8-3 at 0.8 bars, (d) P8-3 at 30 bars, (e) P8-7 at 0.8 bars and (f) P8-7 at 30 bars.	50
5.3	Adsorption isotherms of all three samples of all structures, this time the y-axis remains as the amount of adsorbate per molar mass of adsorbent in mmol g^{-1} while the x-axis displays the pressure of the gas reservoir in bars, the figures show the (a) P8-1 at 200K, (b) P8-1 at 300K, (c) P8-1 at 400K,(d) P8-3 at 200K, (e) P8-3 at 300K, (f) P8-3 at 400K,(g) P8-7 at 200K, (h) P8-7 at 300K and (i) P8-7 at 400K.	51

5.4	Adsorption isotherms for the schwarzites at different temperatures, each pair of figures shows the same data within different pressure ranges, here the y-axis remains as the amount of adsorbate per molar mass of adsorbent in mmol g^{-1} while the x-axis displays the pressure of the gas reservoir in bars, (a) shows the P8-1 at pressures ranging from 0.01 bars to 50 bars, (b) shows The P8-1 at pressures ranging from 0.01 bars to 1.0 bar, (c) shows the P8-3 at pressures ranging from 0.01 bars to 50 bars, (d) shows The P8-3 at pressures ranging from 0.01 bars to 1.0 bar, (e) shows the P8-7 at pressures ranging from 0.01 bars to 50 bars.	52
5.5	Snapshots of the P8-3 at 300K and (a) 0.1 bars, (b) 1.0 bars and (c) 10 bars. Here the blue outlines represent the simulation box	53
5.6	Adsorption isotherms for all three schwarzites compared at different temperatures, where dots represent the simulated values while the dashed lines represent the fitted curves. Figure (a) shows 200K with pressures ranging from 0.01 bars to 50 bars, (b) shows 200K with pressures ranging from 0.01 bars to 1.0 bars, (c) shows 300K with pressures ranging from 0.01 bars to 50 bars, (d) shows 300K with pressures ranging from 0.01 bars to 50 bars, (d) shows 300K with pressures ranging from 0.01 bars to 50 bars, intersection of the pressures ranging from 0.01 bars to 50 bars, (d) shows 300K with pressures ranging from 0.01 bars to 1.0 bars, (e) shows 400K with pressures ranging from 0.01 bars to 50 bars and (f) shows 400K with pressures ranging from 0.01 bars to 1.0 bars.	54
6.1	Figure presents the adsorption capacity of the P-Family of Schwarzites at 300K, the y-axis presents the adsorption capacity as the number of adsorbate molecules per molar mass of each adsorbent, while the x-axis presents the pressure of the gas reservoir. The region highlighted in red shows the range of the adsorption capacity of MOF-74	57

LIST OF ACRONYMS

LAMMPS	Large-scale Atomic/Molecular Massively Parallel Simulator
GCMC	Grand Canonical Monte Carlo
IUPAC	International Union of Pure and Applied Chemistry
EEIC	English East India Company
NASA	National Aeronautics and Space Administration
CCS	Carbon Capture and Storage
MOF	Metal-Organic Frameworks
BET	Brunauer-Emmett-Teller
CA	Cellulose Acetate
PSF	Polysulfone
PVDF	Polyvinylidene Fluoride
TPMS	Triply Periodic Minimal Surfaces
MD	Molecular Dynamics
UFF	Universal Force Field
MC	Monte Carlo
PBC	Periodic Boundary Conditions
DNA	Deoxyribonucleic Acid
OPLS	Optimized Potentials for Liquid Simulations
TraPPE	Transferable Potentials for Phase Equilibria
VESTA	Visualization for Electronic and Structural Analysis
VMD	Visual Molecular Dynamics

CONTENTS

1	INTRODUCTION AND OBJECTIVES	12
2	BASIC CONCEPTS	14
2.1	TEMPERATURE HISTORY AND CO2	14
2.2	MILANKOVITCH CYCLES	16
2.3	WHAT CHANGED?	19
2.4	CARBON CAPTURE AND STORAGE	21
2.5	ADSORPTION	21
2.5.1	Physisorption	23
2.5.2	Chemisorption	24
2.5.3	Isotherms (IUPAC)	24
2.5.4	Freundlich Adsorption Isotherm	26
2.5.5	Langmuir Adsorption Isotherm	26
2.5.6	BET Isotherm	28
3	STRUCTURES	29
3.1	MOFS	29
3.2	MEMBRANES	30
3.3	ZEOLITES	30
3.4	NEGATIVE GAUSSIAN CURVATURES	31
3.5	TRIPLY PERIODIC MINIMAL SURFACES	32
3.6	SCHWARZITES	32
4	SIMULATION TECHNIQUES AND CONCEPTS	35
4.1	PERIODICITY	35
4.2	ENSEMBLES	37
4.3	FUGACITY AND CHEMICAL POTENTIAL	38
4.4	MOLECULAR DYNAMICS	38
4.5	MONTE CARLO	39
4.6	THERMOSTATS	40
4.6.1	Andersen Thermostat	40
4.6.2	Nosé-Hoover Thermostat	40
4.6.3	Berendsen Thermostat	41
4.6.4	Langevin Thermostat	41
4.7	BONDED AND NON-BONDED INTERACTIONS.	42
4.8	INTERACTION POTENTIALS.	42
4.8.1	Universal Force Field	43

4.8.2	TraPPE	44
4.8.3	LAMMPS	45
4.8.4	Grand Canonical Monte Carlo	45
4.9	DATA PROCESSING	47
4.9.1	VESTA	47
4.9.2	VMD	47
5	RESULTS AND ANALYSIS	48
6	CONCLUSIONS	56
	REFERENCES	58

1 INTRODUCTION AND OBJECTIVES

From the start of the industrial revolution the combustion of fossil fuels for energy production, industrial processes, deforestation, and various other human-induced activities release vast amounts of CO_2 into the atmosphere. The effect of this surge in greenhouse gas emissions can be clearly measured and even observed on a daily basis, being the driving force behind the global climate change, causing a rise in global temperature [1] as well as more frequent and severe weather events [2, 3, 4]. In the last decade or so it has become increasingly clear the need for sustainable environmental practices and transitioning towards cleaner energy sources [5]. One measure currently used to prevent a further increase in greenhouse gas emissions is the practice of post-combustion CO_2 capture and storage [6].

The process of capturing and storing gas is achieved through adsorption, a mechanism in which gas molecules adhere to the surface of a solid material [7]. This method is particularly relevant in the context of gas storage and separation applications. Adsorption relies on the affinity between the gas molecules and the surface of the adsorbent material. The adsorbent, often a porous material like activated carbon [8] or metal-organic frameworks [9], provides a large surface area with sites where gas molecules can bind. The attractive forces between the gas molecules and the adsorbent surface, such as van der Waals forces (physisorption) or chemical interactions (chemisorption), facilitate the adsorption process.

In order to study the properties useful for the capture and storage of CO₂ the use of computer simulations [10] was employed. Computer simulations are widely employed to model and study physical systems. These simulations use numerical methods and algorithms to approximate the behavior of complex systems that may be difficult or impossible to study analytically or experimentally. It is important to note that while computer simulations provide valuable insights and predictions, they are not without limitations. Simulations often rely on approximations and assumptions in order to reduce their computational cost. The accuracy of a simulation is directly dependent on the approximations used and their effect on the property of interest [11]. One interesting aspect of computer simulations is its ability to study systems that have not been synthesized or observed experimentally. This scenario often occurs in materials science, where researchers aim to explore the properties and behaviors of hypothetical systems that may one day become reality.

As mentioned before, computer simulations rely on numerical methods and algorithms to study complex systems. A numerical model is crafted by selecting essential characteristics based on the properties and systems to be analysed. These models are developed through laws and principles translated into mathematical language.

In practice, computer simulations are a computational approach used to model and analyze complex systems or processes. They involve a series of steps, typically guided by algorithms, which are executed sequentially to solve a particular problem or obtain specific properties of interest. The simulation process proceeds through discrete steps, each representing a unit of time or another relevant increment. During each step, the algorithm is applied to update the system's state based on current conditions. Throughout the simulation, data is collected, including variables of interest and performance metrics. After completion, the collected data is analyzed, often involving statistical methods or visualization.

One option for simulating complex systems using molecular dynamics is through the use of LAMMPS, a widely used open-source molecular dynamics simulation software [12]. LAMMPS, which stands for Large-scale Atomic/Molecular Massively Parallel Simulator, is designed for

simulating molecular and atomic systems. It employs parallel computing techniques, making it efficient for large-scale simulations on high-performance computing platforms. In each simulation step, starting from a defined set of initial conditions, LAMMPS iteratively solves Newton's Laws for every atom, enabling the calculation of a comprehensive set of properties based on classical physics.

Implementing the desired analysis through LAMMPS involved several key steps. First, a system was defined, through the use of parameters available in the literature [13], to describe the adsorbents to be studied. Subsequently, a process was established using LAMMPS, ensuring that the resultant system represented the adsorbent under analysis filled to its maximum capacity with guest molecules, considering specific values of pressure and temperature. For this reason, a Grand Canonical Monte Carlo (GCMC) ensemble was selected in our simulation approach. The GCMC ensemble is a statistical mechanical ensemble used to model systems under constant chemical potential, temperature, and volume. Here, it provides a suitable framework for studying systems where the number of particles fluctuates, such as adsorption or desorption processes.

The adsorbents chosen for analysis belong to the P-family of Schwarzites [14]. Schwarzites are distinctive three-dimensional porous carbon structures that exhibit intriguing properties for various applications, particularly in adsorption processes. These structures are characterized by their negative gaussian curvatures, a characteristic to be further explained on another section, creating a network of voids and channels within the carbon framework. The P-family of Schwarzites specifically refers to a subgroup with unique geometric features and pore arrangements. These properties make them well-suited for adsorption studies, as the complex and tunable structure of Schwarzites can influence the adsorption capacity and selectivity of different molecules.

From the simulations, curves known as adsorption isotherms are derived, and these can be classified according to the guidelines set by the International Union of Pure and Applied Chemistry (IUPAC) [15, 16]. IUPAC provides a standardized classification system for adsorption isotherms based on the shape of the curve, which reflects the interaction between the adsorbent material and the adsorbed gas molecules, an overview of this classification can be seen in the section regarding isotherms.

2 BASIC CONCEPTS

2.1 TEMPERATURE HISTORY AND CO2

The rise in global temperature attributed to greenhouse gas emissions can be assessed through a comprehensive examination of temperature measurements conducted over an extended period of history. By analyzing data collected over time, scientists and researchers can track and quantify the correlation between the increase in greenhouse gases and the corresponding changes in temperature. This historical perspective allows for a more nuanced understanding of the impact of greenhouse gas emissions on global temperature and supports efforts to model and predict future climate trends. The careful scrutiny of temperature records spanning thousands of years enables the discerning of patterns, trends, and the overall trajectory of temperature changes, contributing to a more substantiated comprehension of the consequences of human activities on the Earth's climate system.

The English East India Company (EEIC) emerges as a notable entity for its meticulous collection and preservation of measurement results. The archives of the EEIC, subjected to digitization and comprehensive analysis by P. Brohan et al. [17], provide a valuable historical repository. This extensive examination of EEIC records offers insights into climatic conditions, allowing for a deeper understanding of historical temperature patterns.

In conjunction with these historical records, data derived from in-depth ice analysis [18, 19, 20] contributes a complementary dimension to the study. The examination of ice cores provides a unique and natural archive of environmental data, offering glimpses into past climatic conditions. By integrating information from both historical archives and natural proxies like ice cores, researchers gain a more comprehensive perspective on long-term climate trends. This interdisciplinary approach enhances the ability to unravel the complexities of Earth's climate history, drawing connections between human activities, historical climatic variations, and the broader environmental context.

Figure 2.1 illustrates the carbon dioxide and temperature data spanning 400,000 years obtained from Vostok, an Antarctic ice-core analysis site [21]. The process of ice-core analysis involves scrutinizing specific layers within ice cores. By drilling deeply into these ice cores, researchers uncover encapsulated air bubbles, each representing a distinct epoch in Earth's history. The data reveals synchronous patterns in Antarctic temperature and carbon dioxide levels: when CO₂ levels are high, the Earth experiences warmer periods, and when CO₂ levels are low, cooler periods prevail. It's crucial to note that correlation does not imply causation, does CO_2 cause warming or does warming cause CO_2 to increase? Both statements are valid; the ice core data indicates that a modest warming initiates an increase in CO₂ which in turn causes warming, creating a reinforcing feedback loop, that both starts and ends due to external factors. Misinterpretations of ice core records have spawned the misconception that since warming causes CO_2 to rise, CO_2 cannot cause warming — an example of a false dichotomy. In reality, both phenomena can coexist. Understanding the mechanism behind the increase in CO_2 levels during global warming involves considering the impact of a warmer Earth on the oceans. As water warms, gases like carbon dioxide are expelled because warm water holds less gas than cold water as illustrated in figure 2.2. Consequently, a warmer ocean releases a significant amount of carbon dioxide into the atmosphere, given the vast carbon reservoir held by the ocean. This initiates a feedback loop wherein a warmer Earth prompts the ocean to release more CO2, leading to further warming. The question then arises: what initiated this feedback loop?



Figure 2.1: Vostok Ice Core Data [21].

To explore the origins of this feedback loop, one must pay attention to the end of the last ice age [25], approximately 20,000 years ago. Over a span of 7-8 thousand years, the Earth transitioned from this ice age to its current temperature. The Antarctica ice-core data from the Vostok site mentioned earlier can be seen again in figure 2.3, but this time the focus is on the past 20,000 years. This data reveals that Antarctica seemingly began warming before a substantial increase in carbon dioxide occurred. This observation aligns with the myth suggesting that temperature rose before CO2, seemingly challenging CO2's role as a cause of warming. However, a global analysis combining data from various other sites at the end of the last ice age, seen in figure 2.4, paints a more comprehensive picture. The data underscores that the warming was not uniform across the globe [26]. The melting of glaciers in the northern hemisphere altered ocean circulation, trapping heat in the southern hemisphere. Consequently, Antarctica began warming first, while Greenland simultaneously experienced a slight cooling.

The data also indicates that the dramatic increase in CO₂ preceded most of the planet's warming, with global temperature increases lagging behind due to the substantial heat absorption



Figure 2.2: When immersed in hot water, the gas molecules exhibit elevated kinetic energies, competing with the attractive forces present. This increased kinetic energy facilitates the overcoming of the attractive forces, thereby making it easier for the gas molecules to escape from their respective attractions.

by the oceans, which, given their vast size, take hundreds of years to warm. This clear temporal sequence implicates CO_2 as the primary driver of global warming. Yet, two interconnected questions persist: what initiated this feedback loop?

The answers to these questions lie in changes to the Earth's orbit, which initiated warming in the northern hemisphere [27, 28]. This warming prompted the oceans to release stored CO2, gradually building up its concentration. The feedback loop strengthened as CO2-induced warming led to further CO_2 release from the oceans.

2.2 MILANKOVITCH CYCLES

The discernible patterns in past climate variations find an explanation in the Milankovitch cycles [29, 30, 31]. The intricate interplay of multiple parameters can account for the observed shifts in global temperatures and atmospheric CO_2 concentrations. Milankovitch cycles initiate changes in the distribution of solar radiation on Earth's surface, impacting regional climates and influencing the feedback loops that govern the carbon cycle.

A century ago, the Serbian scientist Milutin Milankovitch proposed that Earth's long-term climate is intricately linked to changes in its position relative to the Sun [32]. He delved into three specific orbital movements illustrated in figure 2.5 — eccentricity, obliquity, and precession —



Figure 2.3: Vostok Ice Core Data [21] of the last 20,000 years.

that collectively give rise to what is now recognized as Milankovitch cycles. These cycles, with their cyclical variations, play a pivotal role in shaping the climatic conditions of our planet over extended periods.

Eccentricity refers to the shape of Earth's orbit, which, influenced by gravitational forces from Jupiter and Saturn, fluctuates from nearly circular to slightly elliptical over time. This variation affects the distance between Earth and the Sun, leading to subtle differences in the length of seasons. As Earth's eccentricity slowly decreases, the seasons gradually even out. Despite the modest impact of eccentricity on seasonal variations, it plays a role in the long-term climate cycle, with Earth's current eccentricity approaching its least elliptic state in a cycle spanning about 100,000 years.

Obliquity, the tilt of Earth's axis as it orbits the Sun, is a key factor in the development of seasons. Over the past million years, the axial tilt has varied between 22.1 and 24.5 degrees, impacting the intensity of seasons. Currently at 23.4 degrees, this tilt is slowly decreasing, contributing to milder seasons and fostering the accumulation of snow and ice at high latitudes. The obliquity cycle spans about 41,000 years.

Precession, the wobbling of Earth's rotational axis, introduces variations in seasonal contrasts. As Earth wobbles slightly upon its axis, a phenomenon known as axial precession, the direction of this wobble relative to fixed positions of stars changes. Currently, perihelion, Earth's closest approach to the Sun, occurs during the Northern Hemisphere's winter and the Southern Hemisphere's summer. This arrangement moderates Northern Hemisphere seasonal variations. However, in about 13,000 years, axial precession will reverse these conditions. The precession



Figure 2.4: The blue line represents the global proxy temperature stack, depicting temperature deviations from the early Holocene mean (11.5–6.5 thousand years ago). The red line illustrates an Antarctic ice-core composite temperature record [22]. The yellow dots correspond to atmospheric CO₂ concentration [23, 24]. The intervals of the Holocene, Younger Dryas (YD), Bølling–Allerød (B–A), Oldest Dryas (OD), and Last Glacial Maximum (LGM) are marked on the graph. Error bars, represented by 1σ , indicate the margin of error in the measurements. Figure from Shakun et al. [25].



Figure 2.5: Figure illustrating the three distinct orbital movements that are intricately associated with the Milankovitch cycles.

cycle spans about 25,771.5 years, influencing seasonal timing relative to Earth's closest and farthest points around the Sun.

2.3 WHAT CHANGED?

The Milankovitch cycles, while influential in shaping Earth's long-term climate patterns over tens of thousands to hundreds of thousands of years, fall short in explaining recent rapid warming. Milankovitch cycles operate on extended time scales, whereas the current warming has occurred over decades to centuries. Contrary to the cycles' influence, NASA satellite observations reveal a slight decrease in solar radiation over the last 40 years seen in figure 2.6, discounting significant changes in the amount of solar energy absorbed by Earth.



Figure 2.6: A comparison between global surface temperature changes (depicted by the red line) and the Sun's received energy by Earth (represented by the yellow line) in watts per square meter since 1880. The thinner lines depict yearly variations, while the thicker lines present 11-year average trends, employed to mitigate year-to-year natural fluctuations and highlight underlying patterns. Notably, the solar energy received by Earth has adhered to the Sun's natural 11-year cycle, exhibiting minor fluctuations with no overall increase since the 1950s. In contrast, the global temperature has experienced a substantial rise during the same period. This observation strongly suggests that the Sun's variability is highly unlikely to be the driving force behind the observed warming trend in global temperatures over the past five decades. Image sourced from NASA-JPL/Caltech [33].

Moreover, Milankovitch cycles represent just one facet of climate change, both historically and presently. Ice sheet extent [35, 36, 37], atmospheric carbon dioxide concentration, and their interactions significantly influence temperature fluctuations. In the past, carbon dioxide concentrations fluctuated within a range of 180 to 280 parts per million (ppm) during Milankovitch-driven climate changes, as seen in figure 2.4. However, the recent surge to over 400 ppm as seen in figure 2.7, a 50 percent increase since the Industrial Age, is directly linked to human



Figure 2.7: The graph depicts monthly mean concentrations of carbon dioxide measured globally over marine surface sites by the Global Monitoring Laboratory. The laboratory has been collecting data on carbon dioxide and other greenhouse gases for several decades across a network of air sampling sites worldwide. The graph includes data from all years since 1980. The carbon dioxide levels are reported as dry air mole fractions, representing the ratio of carbon dioxide molecules to the total number of molecules in air (excluding water vapor). The dashed red line represents monthly mean values, centered on the middle of each month. The black line with square symbols reflects the same data after correction for the average seasonal cycle. The correction involves a moving average of seven adjacent seasonal cycles centered on the month being corrected, with exceptions for the first and last three and a half years. Figure from the Global Monitoring Laboratory [34].

activities, with fossil fuel combustion leaving a distinct carbon "fingerprint" [38, 39], the carbon isotope chemistry.

Carbon isotope chemistry highlights unique features in fossil fuels, including a carbon-13 to 12 ratio inherited from ancient plants and animals. Plants, in particular, prefer the lighter carbon-12 isotope, resulting in a low carbon-13 to 12 ratio, which then extends through food chains. Studies of carbon isotope ratios in the atmosphere from geological sources like ice cores show that these ratios are currently at their lowest in the last 10,000 years. This decline started precisely when CO_2 levels began increasing after 1850 AD, providing strong evidence that the higher CO_2 is linked to fossil fuel combustion. The presence of another isotope carbon-14, with its short half-life, adds weight to this argument, as its dilution due to fossil fuel burning has been observed for over 50 years. Due to the short half-life of this isotope it is mostly absent in the burning of fossil fuels, explaining it's dilution. In essence, human activities, especially burning fossil fuels, are the key reason behind the recent 50% surge in atmospheric CO_2 levels.

The rapid warming due to human-induced carbon dioxide emissions is occurring alongside the slower changes caused by Milankovitch cycles. Climate models indicate that humandriven factors, particularly the concentration of carbon dioxide exceeding 350 ppm, overpower any potential impact from Milankovitch cycles.

The increase in greenhouse gases from burning fossil fuels has resulted in over 50 times more warming since 1750 than the slight additional warming from the Sun during the same period. This substantial warming is inconsistent with a solar-driven scenario, as observations show warming in the lower atmosphere and surface while the stratosphere has cooled.

Lastly, Earth's current interglacial period contradicts the Milankovitch-predicted cooling trend [40]. If not for human influences, the orbital positions within Milankovitch cycles would anticipate Earth cooling, maintaining a long-term trend that began 6,000 years ago. In essence, while Milankovitch cycles offer insights into historical climate variations, the current trajectory of climate change is unequivocally tied to human-induced factors, particularly the elevated levels of carbon dioxide in the atmosphere.

2.4 CARBON CAPTURE AND STORAGE

Given the evident necessity to regulate and limit CO_2 emissions resulting from human activities, one of the viable solutions to address this concern is known as postcombustion CO_2 capture and storage (CCS) [41, 42]. This technology plays a crucial role in mitigating the impact of anthropogenic carbon dioxide emissions on the environment. Postcombustion CCS involves capturing CO_2 emissions produced during the combustion of fossil fuels in power plants and industrial facilities. The captured CO_2 is then transported and securely stored underground in geological formations, preventing its release into the atmosphere.

This approach is instrumental in reducing the overall carbon footprint of industries and power generation [43, 44]. By implementing postcombustion CCS, it is possible to manage and mitigate the environmental consequences of our carbon-intensive activities, moving toward a more sustainable and environmentally friendly future. The adoption of such advanced technologies is pivotal for achieving emission reduction targets and fostering a cleaner, greener approach to energy production and industrial processes.

Carbon capture and storage encompasses a range of technologies aimed at mitigating the release of carbon dioxide into the atmosphere. Among these technologies, absorption processes, primarily utilizing commercial technologies, are deemed the most mature for postcombustion capture. Adsorption, employing various adsorbents like zeolites [45] and metal organic frameworks (MOFs) [46], represents another approach. The third method involves membrane processes [47]. While absorption dominates current post-combustion CCS applications, ongoing research explores alternative methods. The captured CO_2 must be compressed and transported for sequestration, with underground storage identified as a potent solution. As the global movement to reduce emissions intensifies, a combination of CCS technologies holds the potential to play a crucial role in addressing climate change.

2.5 ADSORPTION

Adsorption, illustrated in figure 2.8, is a surface process that involves the accumulation and adherence of molecules or particles onto the surface of a solid or liquid material [48, 49]. Unlike absorption, which entails the penetration and incorporation of substances into the bulk of a material, adsorption occurs exclusively on the material's outer surface. This phenomenon is driven by attractive forces between the adsorbate (substance being accumulated) and the adsorbent (material with the surface). The interactions responsible for adsorption can include van der Waals forces, electrostatic attractions, and chemical bonding.



Figure 2.8: The figure serves as an illustration for adsorption, a surface phenomenon where molecules or ions adhere to the surface of a solid or liquid material. The figure also provides a visual representation of the nomenclature associated with the adsorbate and adsorbent.

Depending on the nature of the interactions between the adsorbate and adsorbent this process can be identified as physisorption or chemisorption [50], both illustrated in figure 2.9. Physisorption, also known as physical adsorption, primarily involves van der Waals forces. In this type of adsorption, the molecules of the adsorbate are attracted to the surface of the adsorbent through relatively weak forces. Physisorption is generally reversible and is influenced by factors like temperature and pressure. On the other hand, chemisorption, or chemical adsorption, involves stronger chemical bonds formed between the adsorbate and the adsorbent. This interaction often results in the formation of new chemical species on the surface. Unlike physisorption, chemisorption is typically characterized by covalent bonds, in which, electrons are shared between atoms creating a stable molecular structure, and the process is often more specific and selective.

In adsorption, the surface of the adsorbent acts as a substrate for the adsorbate to cling to, creating a layer or film of accumulated molecules. The extent of adsorption is influenced by factors such as the nature of the adsorbent, the characteristics of the adsorbate, temperature, and pressure. Various materials, including activated carbon, zeolites, and certain metals, are commonly employed as adsorbents due to their ability to provide a large surface area for effective adsorption [51].

When studying adsorption, the focus is often on the isotherms, which are graphical representations depicting the relationship between the amount of adsorbate molecules adsorbed onto a surface and the equilibrium conditions, typically represented by temperature and pressure [52]. Isotherms provide crucial insights into the adsorption behavior of a material and are



Figure 2.9: Figure illustrating the two possible types of adsorption. Physical adsorption, also known as physisorption, involves the relatively weak van der Waals forces and occurs primarily on the surface of the adsorbent material. In contrast, chemical adsorption, or chemisorption, involves stronger chemical bonds forming between the adsorbate and the adsorbent.

fundamental in characterizing its adsorption capacity and affinity. The isotherm data reveal important information about the adsorption process, such as the maximum adsorption capacity, the strength of adsorbate-adsorbent interactions, and the nature of the adsorption mechanism. Researchers use these insights to optimize adsorption systems for various applications, including gas separation, water purification, and catalysis. Understanding the intricacies of adsorption isotherms is essential for designing and improving materials and processes that utilize adsorption as a key mechanism, contributing to advancements in diverse fields, from environmental science to materials engineering.

This surface-centric process finds applications in diverse fields, ranging from gas separation and purification to wastewater treatment and catalysis. Understanding and manipulating adsorption processes are essential in optimizing the performance of adsorption-based technologies and harnessing their potential for practical applications.

2.5.1 Physisorption

Physisorption involves intermolecular forces between the adsorbent and solute molecules [53]. The critical condition for physisorption is that these attractive forces must surpass the intermolecular forces between solute molecules, making it comparable to condensation—an exothermic process with heat dissipation. The enthalpy change (ΔH) associated with physical adsorption is expressed by the equation $\Delta H = \Delta G + T\Delta S$, where ΔG represents the change in Gibbs free energy, and ΔS denotes the entropy change of the adsorbate. Because the adsorbed state is more ordered than the unadsorbed state, ΔS is inherently negative.

Negative enthalpy changes characterize physical adsorption, indicating its exothermic nature. The rise in adsorption temperature leads to a continuous decrease in uptake, influenced by the heat of physical adsorption, which can vary in magnitude and change with the extent of adsorption. Physisorption occurs rapidly, as it doesn't require activation energy. However, in finely porous adsorbents like zeolites and certain carbons, slow uptake may occur due to diffusion limitations rather than the sorption process itself.

For gases above their critical temperature, physisorption is limited to a monolayer, while below the critical temperature, it may involve multilayer coverage. Physisorption is a reversible process, and the density of the physisorbed phase aligns with that of the liquid phase rather than the vapor phase.

It is crucial to highlight that, in the context of this specific adsorption, there is a potential occurrence of the adsorbate forming multiple layers. This implies that the adsorption process may involve the stacking or accumulation of adsorbate molecules in more than one distinct layer.

In summary, physisorption is a complex and reversible process driven by intermolecular forces, exhibiting distinct characteristics such as negative enthalpy changes, rapid occurrence, and temperature-dependent uptake behavior. Understanding these nuances is essential for optimizing materials in applications such as hydrogen storage and other physisorption-related processes.

2.5.2 Chemisorption

Chemisorption is a distinct adsorption phenomenon characterized by the transfer of electrons between the adsorbate and the adsorbent [53]. Unlike physisorption, which relies on intermolecular forces, chemisorption involves a more intimate interaction through chemical bonding. This bonding occurs as a result of shared electrons, creating a stronger and more permanent attachment between the adsorbate and the surface of the adsorbent.

One notable feature of chemisorption is its propensity to occur at elevated temperatures, often surpassing the critical temperature of the adsorbate. This temperature requirement is a consequence of the chemical nature of the interaction, as chemical bonding typically demands higher energy input, which is provided by the increased temperature.

Similar to most chemical reactions, chemisorption necessitates activation energy. This energy threshold is essential to overcome the barrier to the formation of chemical bonds between the adsorbate and the adsorbent.

In this context, it is crucial to emphasize that, unlike physisorption, the occurrence of multiple layers is not possible in chemisorption. This distinction is fundamental in understanding the unique characteristics and limitations associated with chemisorption compared to physisorption.

2.5.3 Isotherms (IUPAC)

There is a diverse array of isotherm models, each designed to capture and represent specific aspects of adsorption behavior on solid surfaces [52, 54]. These models are essential tools in the field of adsorption science, offering frameworks to understand and quantify the complex interplay between adsorbates and adsorbents. Among the myriad isotherm models, the choice depends on the specific characteristics of the adsorption system under investigation. Researchers often select models based on factors such as the nature of adsorbent-adsorbate interactions, the type of adsorption (physical or chemical), and the structural properties of the adsorbent material. These isotherm models encompass a spectrum of mathematical expressions, including the Langmuir, Freundlich, BET (Brunauer–Emmett–Teller), Dubinin-Radushkevich, and Toth models, among others. The diversity of isotherm models reflects the intricacies of adsorption phenomena and

allows scientists and engineers to tailor their analyses to the unique features of different adsorption processes. The continuous refinement and development of these models contribute to a deeper understanding of adsorption mechanisms and enhance the precision of predictions in various industrial and environmental applications.

IUPAC (International Union of Pure and Applied Chemistry) classifies physisorption isotherms into six main types, each revealing distinct characteristics associated with the adsorption process [15, 16]. Figure 2.10 illustrates these types, offering a visual representation of their behaviors. The reversible Type I isotherm is commonly observed in microporous solids such as activated carbons and zeolites. The limiting uptake in Type I is governed by the accessible micropore volume rather than the internal surface area and limited to single layer adsorption. Type II isotherms are typical for non-porous or macroporous adsorbents, representing unrestricted monolayer-multilayer adsorption. Point B, marking the completion of monolayer coverage, signals the onset of multilayer adsorption. Type III isotherms, which are convex over their entire range, lack a distinct Point B and are relatively uncommon. Type IV isotherms display hysteresis loops associated with capillary condensation in mesopores, and they exhibit a limiting uptake. This type is characteristic of many mesoporous industrial adsorbents. The less common Type V isotherm is related to Type III, indicating weak adsorbent-adsorbate interactions. Finally, the Type VI isotherm represents stepwise multilayer adsorption on a uniform non-porous surface, with step-height reflecting the monolayer capacity for each adsorbed layer.



Figure 2.10: Types of physisorption isotherms [55].

The IUPAC classification comprehensively describe gas-solid adsorption isotherms, encompassing a wide range of adsorption systems. However, there exist instances where isotherms deviate from these classifications, presenting unique behaviors not covered by IUPAC classes or intermediate between them. For the isotherms examined here, the IUPAC classification proves adequate.

2.5.4 Freundlich Adsorption Isotherm

Proposing an empirical relationship [56], Freundlich formulated an equation expressed as:

$$\frac{w}{m} = kP^{\frac{1}{n}} \tag{2.1}$$

In this equation, w denotes the mass of gas adsorbed on a mass m of adsorbent at a pressure P, while k and n represent constants influenced by the specific gas, adsorbent characteristics, and temperature. Typically visualized as a curve, this relationship depicts the mass of gas adsorbed per unit mass of adsorbent against equilibrium pressure. Looking at this equation and comparing to the IUPAC classifications this curve best fits the Type I isotherm, although only at low values of pressure, it is essential to emphasize that the Freundlich isotherm lacks applicability under high pressures.

In this scenario, it is assumed that there is negligible interaction between the adsorbate molecules, and it is allowed the formation of multiple layers.

Taking logarithms on both sides of the Freundlich equation transforms it into:

$$\log \frac{w}{m} = \log k + \frac{1}{n} \log P \tag{2.2}$$

forming a linear equation. Plotting $\log \frac{w}{m}$ against $\log P$ theoretically results in a straight line with a slope of $\frac{1}{n}$ and an intercept of $\log k$. However, experimental observations reveal that while the plots exhibit linearity at low pressures, a slight curvature emerges at higher pressures, particularly at low temperatures. This departure implies that the Freundlich equation serves as an approximation and does not accurately describe gas adsorption by solids under elevated pressures.

2.5.5 Langmuir Adsorption Isotherm

The Langmuir isotherm model, introduced as one of the earliest proposed isotherms [57, 58], operates under the assumption of an ideal interaction between the adsorbate and adsorbent, specifically suitable for homogeneous surfaces. A key feature of this model is its application to systems where adsorption and desorption processes are reversible.

The model makes certain approximations, including the assumption that adsorption occurs in a monolayer, the surface is energetically homogeneous, and there is no interaction among the adsorbed particles. These assumptions give rise to the concept of discretized adsorption sites, as depicted in Figure 2.11. In other words, there is a finite number of potential locations for the adsorbate, serving as a constraining factor for the adsorption capacity. This isotherm is considered a Type I isotherm by the IUPAC classification seen before.

Langmuir envisioned a dynamic equilibrium between adsorption and desorption processes, where the fraction of the surface covered by adsorbed molecules (θ) plays a pivotal role. The rates of desorption (R_d) and adsorption (R_a) are given by:

$$R_d = k_d \theta \tag{2.3}$$

$$R_a = k_a (1 - \theta) P \tag{2.4}$$

where k_d is the rate constant for desorption, k_a is the rate constant for adsorption, θ is the fraction of the total surface covered by adsorbed molecules, and P is the gas pressure.

At equilibrium, the rate of desorption equals the rate of adsorption:



Figure 2.11: The figure provides a visual representation of discretized adsorption sites. Adsorption sites denote particular regions or points on the surface of an adsorbent material where adsorbate molecules or ions adhere. In this depiction, each circle represents an adsorption site, with those marked in red indicating sites occupied by an adsorbate, while the blue circles signify available, unoccupied sites.

$$\theta = \frac{k_a P}{k_d + k_a P} \tag{2.5}$$

$$\theta = \frac{\frac{k_a}{k_d}P}{1 + \frac{k_a}{k_d}P}$$
(2.6)

Rearranging and introducing a constant $K = \frac{k_a}{k_d}$:

$$\theta = \frac{KP}{1+KP} \tag{2.7}$$

The amount of gas adsorbed per gram of the adsorbent, x, is proportional to θ .

$$x \propto \frac{KP}{1+KP} \tag{2.8}$$

$$x = K' \frac{KP}{1 + KP} \tag{2.9}$$

Where K' is a new constant identified as the maximum adsorption capacity of the material. Equation 2.9 is known as the Langmuir Adsorption Isotherm. At low pressures, the isotherm approximates x = KP, showing a direct proportionality. At high pressures, the isotherm approximates x = K', indicating saturation. Rearranging in a way that facilitates obtaining the adsorption coefficient, which indicates the affinity between the single layer and the adsorbate:

$$\frac{x}{K'} = \frac{KP}{1+KP} \tag{2.10}$$

In summary, Langmuir's Adsorption Isotherm elegantly describes the equilibrium adsorption of gas on a solid surface, and its linear form allows for easy verification through experimental data.

2.5.6 BET Isotherm

The BET isotherm, proposed by Brunauer, Emmett, and Teller (BET) in 1938 [59], revolutionized adsorption science with its introduction of a multilayered (physisorption) isotherm. This model was groundbreaking for quantifying substance adsorption in the first layer, a unique concept at the time. Unlike the Langmuir equation, BET addressed the calculation of specific surface areas of adsorbents and incorporated kinetic considerations, earning its reputation as a generalization of the Langmuir model.

The BET isotherm assumes that adsorption of multimolecular layers is attributed to condensation forces in the adsorbent's capillaries. It accounts for the energy of multimolecular adsorption, with features like the formation of the first adsorption layer on sites with uniform energy, identical rates of adsorption and desorption in each molecular layer, and, from the second layer onward, the heat of adsorption being equal to the substrate's condensation heat.

Despite its contributions, the BET isotherm has limitations, including the coarseness of the capillary condensation theory for porous structures and inaccuracies in specific surface area calculations in the presence of adsorbate molecules. It deviates from experimental data at certain relative pressures, and extreme pressure conditions may yield unrealistic results.

The BET theory equation is expressed as:

$$V_a = \frac{(V_m C_t P)}{((P^0 - P)[1 + (C_t - 1)\frac{P}{P^0}])}$$
(2.11)

where C_t is the constant related to pore size, P is pressure, P^0 is the gas saturation pressure, V_A is the adsorbed gas quantity, and V_m is the monolayer adsorption capacity. This theory provides insights into multilayer adsorption by considering layer-by-layer deposition and the interaction energies between the adsorbent and adsorbed molecules.

3 STRUCTURES

When discussing adsorption, a large array of possible structures emerges as potential candidates for various applications. In this particular work, the primary focus is on Schwarzites, a distinctive class of materials with intriguing properties that make them relevant for adsorption studies. Schwarzites are three-dimensional, carbon-based structures featuring minimal surfaces [14], and their unique topology provides a platform for diverse adsorption phenomena.

However, to better understand the current state of the field, this chapter extends beyond Schwarzites to encompass three other noteworthy structures, each holding significance in the field of adsorption. These structures include Metal-Organic Frameworks (MOFs), Membranes, and Zeolites. MOFs are hybrid materials composed of metal ions or clusters coordinated to organic ligands, forming porous structures with tunable properties [60]. Their versatility makes MOFs valuable for various adsorption applications [61, 62, 63, 64, 65].

Membranes, another critical component, play a pivotal role in adsorption processes. Polymeric membranes, particularly those containing functional groups like oxygen-rich polymers and polymeric ionic liquids, contribute to the selective separation of gases such as CO2, H2, and CH4 [66]. Understanding the principles of gas separation through polymeric membranes is essential for advancements in carbon capture.

Zeolites, on the other hand, are a diverse class of materials known for their crystalline structures and porous nature [67]. With selective adsorption properties, zeolites are extensively explored for separating gas mixtures, such as CO2/CH4 and CO2/N2 [45]. The physicochemical properties of zeolites, including framework type, Si/AI ratio, and extra-framework cations, play a crucial role in their performance as adsorbents.

While Schwarzites take center stage in this study due to their unique characteristics, the exploration of MOFs, Membranes, and Zeolites adds depth and breadth to the understanding of adsorption processes. Each material brings its distinct advantages and challenges, contributing to the broader landscape of adsorption research and applications.

3.1 MOFS

The emergence of Metal–organic frameworks (MOFs) in the late 1990s marked a revolutionary development at the intersection of molecular coordination chemistry and materials science [60]. MOFs are characterized by a unique structure, where positively charged metal ions are intricately linked by organic 'linker' molecules, resulting in a regularly arranged crystalline porous material [68]. This distinctive architecture, illustrated in figure 3.1, imparts exceptional internal surface area to MOFs, exemplified by variants like DUT-60, which boast surface areas exceeding 7800 square meters per gram [69]. To put it in perspective, a teaspoon of this MOF material could cover an entire soccer field.

The versatile applications of MOFs extend across various fields, leveraging their cage-like structures for diverse purposes such as gas storage, separation, liquid purification, electrochemical energy storage, catalysis, and sensing [70, 71, 72, 73, 74, 75, 76]. Moreover, MOFs serve as precursors for the construction of inorganic functional materials, including carbons, metal-based compounds, and their composites, unlocking opportunities for innovative designs with unprecedented possibilities [77].

One remarkable example is Mg-MOF-74, an open metal site MOF [78, 79, 80], showcasing the broad applications and potential impact of MOFs. This specific MOF demonstrates promise



Figure 3.1: Metal-organic frameworks (MOFs) are assembled from metal "clusters" and organic molecules referred to as "linkers." The organic linkers coordinate with the metal clusters, leading to the formation of three-dimensional structures of various topologies.

in capturing and storing greenhouse gases, illustrating the pivotal role of MOFs in addressing critical global challenges.

3.2 MEMBRANES

Membrane technology has long been integral to liquid and gas separations [81], offering a combination of ease of fabrication, simplicity in usage, high selectivity, and the absence of sorbent regeneration requirements. Among the materials employed in membrane construction — polymeric, ceramic, and stainless-steel — polymeric membranes stand out as the most favored [66]. This preference is attributed to their high selectivity, operational ease, and the potential for functionalization and modification, prompting extensive research in this domain.

The spectrum of polymers explored for membrane fabrication encompasses both conventional and sustainable options. Conventional polymers like cellulose acetate (CA), polysulfone (PSf), and polyvinylidene fluoride (PVDF) have been extensively studied [82, 83, 84]. Notably, PVDF emerged as a groundbreaking choice due to its remarkable chemical and thermal resistance, coupled with substantial mechanical strength [85].

3.3 ZEOLITES

Zeolites, three-dimensional crystalline solids composed of aluminum silicate, exhibit microporous structures with fixed-size openings, often referred to as molecular sieves [67, 86]. Axel Fredrik Cronstedt, a Swedish mineralogist, coined the term "zeolite" in 1756 after observing steam produced during the rapid heating of stilbite, attributed to the water absorbed earlier [87]. Derived from the Greek words meaning "to boil" and "stone," zeolites have found significance in various applications due to their unique properties.

These microporous materials, available in over 50 types, can be naturally occurring or synthesized industrially. Natural zeolites are commonly found in volcanic and sedimentary rocks



Figure 3.2: Illustration of the gaussian curvature for a surface, a normal vector is defined at a point P and the intersection of the collection of normal planes containing this vector and the surface establishes a normal curvature. The curves k_1 and k_2 denote the maximum and minimum normal curvatures at this point.

[88]. Synthetic zeolites are produced through crystallization processes, allowing for precise control over their structures and properties [89]. The synthetic route also enables the incorporation of various elements, enhancing their chemical diversity and activity.

Zeolites exhibit stability under various environmental conditions, high melting points, and insolubility in water or inorganic solvents. Their open cage-like framework structure makes them effective for trapping water and ions, with natural and synthetic zeolites having distinct pore size characteristics.

In recent applications, zeolites have demonstrated their significance in carbon capture, storage, and utilization due to their selective CO_2 adsorption behavior [45]. Small-pore zeolites, play a crucial role in the separation of CO_2 from gas mixtures, emphasizing their diverse and evolving role in addressing contemporary challenges [90].

3.4 NEGATIVE GAUSSIAN CURVATURES

Gaussian curvature serves as a fundamental concept within the realm of differential geometry, providing insights into the local geometry of a surface. Figure 3.2 illustrates this concept, where at any given point on a surface, the normal vector perpendicular to the surface establishes a normal plane. The intersection of this normal plane with the surface gives rise to a curve referred to as a normal section, and the curvature of this curve is termed the normal curvature. Principal curvatures, denoted as k_1 and k_2 , denote the maximum and minimum values of normal curvature at a specific point.

The Gaussian curvature (K) is derived by multiplying these principal curvatures. The sign of the Gaussian curvature plays a pivotal role in delineating the surface's characteristics. In instances where both principal curvatures share the same sign, indicating $k_1k_2 > 0$, the Gaussian curvature is positive, resulting in the characterization of an elliptic point. Conversely, if the principal curvatures exhibit different signs ($k_1k_2 < 0$), the Gaussian curvature is negative, defining a hyperbolic or saddle point. In such cases, the surface adopts a saddle-shaped configuration.



Figure 3.3: Examples of Triply Periodic Minimal Surfaces, surface (P) is the basis for the structures studied here, giving rise to the P-family Schwarzites. Figure sourced from Oraib Al-Ketan et al. [91].

When one principal curvature is zero ($k_1k_2 = 0$), the Gaussian curvature assumes a value of zero, signifying a parabolic point.

Surfaces often manifest regions featuring positive Gaussian curvature (elliptical points), negative Gaussian curvature (saddle points), and are demarcated by a curve of points with zero Gaussian curvature known as a parabolic line. An instance of negative Gaussian curvature can be observed in saddle points, where the surface takes on a configuration resembling a saddle.

3.5 TRIPLY PERIODIC MINIMAL SURFACES

Triply Periodic Minimal Surfaces (TPMS) constitute a distinctive class of mathematical surfaces first elucidated by Schwarz [92] and later by Neovius [93]. These surfaces are characterized by their unique geometric properties, particularly their ability to achieve minimal area within repeating patterns. The term "triply periodic" denotes that these surfaces possess three-dimensional periodicity, repeating in three spatial directions. Minimal surfaces, in this context, refer to surfaces that achieve the smallest possible area for a given boundary. TPMS have become significant subjects of study in geometry, exploring the fundamental principles that govern their intricate structures and the mathematical elegance underlying their minimal surface characteristics.

3.6 SCHWARZITES

Schwarzites, a fascinating class of structures originally conceptualized by Mackay and Terrones in 1991 [14], draw inspiration from Triply Periodic Minimal Surfaces. These mathematical constructs provide the symmetrical foundation for the unique properties exhibited by Schwarzites.

Mackay and Terrones took these fascinatiting surfaces further in 1991 by introducing a groundbreaking concept: imbuing Triply Periodic Minimal Surfaces with rings composed of six or more carbon atoms, utilizing sp^2 hybridization. The introduction of carbon atoms into the intricate

network of minimal surfaces resulted in the creation of crystalline carbon structures with distinctive characteristics, notably negative Gaussian curvatures. This innovative approach paved the way for the development of Schwarzites, introducing a new dimension to carbon-based materials with unique symmetries and properties derived from the principles of minimal surfaces.

The complexities inherent in schwarzites give rise to fascinating structures with potentially remarkable applications, but they also introduce challenges to the synthesis process. Numerous projects have attempted to tackle this challenge [94, 95, 96], yet as of now, no successful synthesis of a schwarzite has been achieved.

This study centers on three structures belonging to the P-family of schwarzites, namely P8-1, P8-3, and P8-7, depicted in figure 3.4, along with their replicated 2x2x2 supercells. The unit cells were replicated as 2x2x2 supercells to enhance the statistical robustness of the simulations.



Figure 3.4: The P-family of schwarzites is illustrated, (a) depicting the unit cells of the structures to scale with each other. The red unit cell represents P8-1, the grey unit cell corresponds to P8-3, and the orange unit cell signifies P8-7. The replicated supercells utilized in the simulations are also displayed. Panels (b), (c), and (d) showcase the 2x2x2 supercells for P8-1, P8-3, and P8-7, respectively.

(d)

(c)

4 SIMULATION TECHNIQUES AND CONCEPTS

In the pursuit of understanding the adsorption behavior of CO_2 molecules on Schwarzites, a comprehensive simulation approach known as molecular dynamics (MD) was employed. Molecular dynamics is a powerful computational technique employed in materials science and chemistry to simulate the time-dependent behavior of interacting particles within a specified system [97]. The interactions among particles are described by force fields, which capture the forces between atoms and molecules. These force fields encompass both bonded and non-bonded interactions. Bonded interactions involve covalent bonds, angles, and dihedrals, whereas non-bonded interactions include van der Waals forces and electrostatic interactions.

Periodicity is a crucial consideration in MD simulations, and it is often implemented by enclosing the simulated system within a simulation box that replicates itself in three dimensions. This periodic boundary condition enables the study of systems that mimic an infinite and repeating lattice.

Two common ensembles used in MD simulations are the canonical (NVT) ensemble, which maintains constant particle number, volume, and temperature, and the microcanonical (NVE) ensemble, which conserves the number of particles, volume, and energy [98]. To control the temperature during MD simulations, thermostats are utilized [99] to simulate temperature by employing stochastic methods, introducing fictional interactions, or modifying the equations of motion.

In the context of MD simulations, interaction potentials describe the mathematical functions governing the forces between particles. The choice of an appropriate interaction potential is critical for accurately capturing the system's behavior. One notable example is the Universal Force Field (UFF) [100], a comprehensive force field that can be applied to a diverse range of chemical systems. The selection of this force field was based on its convenient accessibility, providing a user-friendly framework, and versatile applicability.

LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) [12] is a widely used software package for MD simulations that supports various force fields and simulation techniques. It enables the simulation of large-scale systems by efficiently utilizing parallel computing architectures.

In the realm of adsorption studies, the concept of fugacity or chemical potential is significant. Fugacity represents the escaping tendency of a component from a mixture, and chemical potential is a thermodynamic quantity closely related to fugacity [98, 101]. These concepts are particularly relevant when studying gas adsorption on surfaces.

For a more detailed exploration of gas adsorption, Monte Carlo [97] simulations in the Grand Canonical ensemble [102] (Monte Carlo Grand Canonico) can be implemented in LAMMPS. This ensemble allows for simulations at constant chemical potential, providing insights into adsorption processes under realistic conditions. The combination of molecular dynamics, ensembles, interaction potentials, and specialized techniques such as Monte Carlo Grand Canonico in LAMMPS forms a robust framework for studying complex adsorption phenomena at the molecular level.

4.1 PERIODICITY

In MD simulations, periodic boundary conditions are employed to mimic an infinite and repeating system. This approach creates a virtual simulation box that extends in three dimensions, and any



Figure 4.1: The illustration demonstrates periodic boundary conditions, where the interaction between the orange circle and the image of the red circle is depicted.



Figure 4.2: The diagram illustrates the grand canonical ensemble or μ VT ensemble, wherein the system has the ability to exchange particles with an ideal gas reservoir. Within this depiction, the smaller rectangle symbolizes the system under investigation, while the larger rectangle denotes the ideal gas reservoir.

molecule leaving one side of the box re-enters from the opposite side, an illustration of this can be seen in figure 4.1. PBC effectively eliminates edge effects and ensures that the simulated system resembles an infinite and homogeneous environment. This technique is particularly valuable when studying bulk materials, crystals, or large molecular ensembles.

Periodicity allows the replication of fundamental units within the simulation box. For instance, in crystal simulations, a small unit cell is repeated in three dimensions to create a larger simulation box, also called supercell. This periodic replication enables the study of collective phenomena, such as the propagation of waves, defects, or phase transitions, as they interact with neighboring units in a consistent and repetitive manner.

By incorporating periodicity, researchers can analyze macroscopic properties that emerge from the collective behavior of molecular units. This includes the study of diffusion, conductivity, and thermal properties in materials. Periodic systems are particularly relevant for understanding how molecular structures influence macroscopic behavior, providing valuable information for the design and optimization of materials with specific functionalities.

While periodicity is a powerful tool, it introduces challenges, especially at the boundaries of the simulation box. The treatment of long-range interactions, such as Coulombic forces, requires careful consideration to avoid artifacts. Special algorithms like the Ewald summation method are often employed to accurately calculate long-range interactions in periodic systems.

4.2 ENSEMBLES

In thermodynamics, an ensemble refers to a collection of multiple possible microscopic states that a system can occupy, each with an associated probability [102]. The idea of ensembles is a crucial theoretical framework for understanding the statistical behavior of large groups of particles, providing a bridge between the microscopic world of individual particles and the macroscopic properties of a system.

One fundamental type of thermodynamic ensemble is the microcanonical ensemble, often referred to as the "NVE ensemble," where N represents the number of particles, V is the volume, and E is the total energy of the system. In this ensemble, the system is isolated and exchanges neither energy nor particles with its surroundings. The microcanonical ensemble assumes the system's energy is precisely fixed, and all accessible microstates with that energy are equally probable.

Another important ensemble is the canonical ensemble or NVT ensemble, where the system is allowed to exchange energy with its surroundings, typically through heat transfer. In this ensemble, the temperature (T), volume (V), and the number of particles (N) are fixed. The probability distribution for different microstates depends on the system's temperature, reflecting the fact that energy exchange with the surroundings occurs.

Moving to the grand canonical ensemble or μ VT ensemble, illustrated in figure 4.2, this ensemble allows the system to exchange both energy and particles with its surroundings. Here, the chemical potential (μ), temperature (T), and volume (V) are fixed. It is particularly useful for describing systems in contact with a particle reservoir, allowing for variations in the number of particles.

In summary, thermodynamic ensembles offer distinct perspectives on systems, providing a comprehensive framework to analyze their statistical behavior under different conditions. Whether focusing on a fixed energy (microcanonical), allowing energy exchange (canonical), or permitting both energy and particle exchange (grand canonical), these ensembles help elucidate the complex interplay between microscopic states and macroscopic observables in the study of thermodynamics.

4.3 FUGACITY AND CHEMICAL POTENTIAL

Fugacity and chemical potential are essential concepts in the field of molecular simulations, providing valuable insights into the thermodynamic behavior of a system. Fugacity (f) represents a measure of the escaping tendency of a molecule from a given phase, akin to pressure but accounting for deviations from ideal gas behavior. It is particularly relevant in simulations involving gases, where deviations from ideal behavior become significant. Fugacity is a critical parameter when studying phase equilibria and adsorption phenomena.

Chemical potential (μ), on the other hand, is a fundamental thermodynamic quantity that reflects the potential energy of a molecular species in a given environment. It encompasses both internal energy and entropy contributions and serves as an indicator of the system's tendency to exchange particles with its surroundings. In molecular simulations, understanding the chemical potential is crucial for predicting phase transitions, solubility, and reaction equilibrium.

The relationship between fugacity and chemical potential is expressed by the equation:

$$f = P \exp \frac{\mu - \mu_0}{RT} \tag{4.1}$$

where *P* is pressure, *T* is temperature, *R* is the gas constant, and μ_0 is a reference chemical potential. This equation highlights the exponential dependence of fugacity on chemical potential, emphasizing the sensitivity of escaping tendencies to changes in the chemical potential.

4.4 MOLECULAR DYNAMICS

Molecular dynamics serves as a computational approach for determining the equilibrium and transport characteristics of a classical system comprising multiple bodies [97]. The process

entails selecting a model to characterize the system, which consists of N particles, and solving the Newtonian equations of motion for the system until it achieves equilibrium. Subsequently, relevant measurements are conducted after the system has stabilized.

Expressing an observable in molecular dynamics involves representing it as a function of the positions and velocities of the particles within our system. For instance, to characterize the temperature of a system comprising numerous particles, the equation 4.2 is employed:

$$\langle \frac{1}{2}m_{\alpha}\nu_{\alpha}^{2} \rangle = \frac{1}{2}k_{B}T$$

$$m_{\alpha} : \text{Mass of the particle}$$

$$\nu_{\alpha} : \text{Speed of the particle}$$

$$k_{B} : \text{Boltzmann's constant}$$

$$T : \text{Temperature}$$

$$(4.2)$$

In the course of a molecular dynamics simulation, fluctuations in temperature values are commonplace. Consequently, it is imperative to average the relevant observables across multiple fluctuations to attain more accurate and dependable results.

4.5 MONTE CARLO

Unlike molecular dynamics (MD), which tracks the time evolution of a system, Monte Carlo simulations [97] focuses on the probabilistic sampling of different molecular configurations based on defined statistical ensembles. Monte Carlo simulations often operate within specific ensembles, such as the canonical ensemble (NVT) or the grand canonical ensemble (μ VT).

In a Monte Carlo simulation, the system undergoes configurational changes through a series of trial moves, which could involve changes in molecular positions, orientations, or other degrees of freedom. Each trial move is accepted or rejected based on a Metropolis acceptance criterion, considering factors such as energy changes and temperature. This stochastic process allows the exploration of different regions of configurational space.

Monte Carlo simulation is particularly valuable for studying adsorption processes, such as the adsorption of gases on surfaces or within porous materials. Researchers can investigate how molecules adsorb, providing insights into the thermodynamics of adsorption, selectivity, and the effect of surface properties on adsorbate behavior.

In molecular dynamics packages, Monte Carlo methods are implemented to perform grand canonical simulations. The grand canonical ensemble allows the system to exchange particles with a reservoir, maintaining a specified chemical potential. In LAMMPS, the Monte Carlo grand canonical (GCMC) ensemble is employed to simulate systems with varying particle numbers, making it applicable to adsorption studies and other scenarios involving fluctuations in particle counts.

Monte Carlo simulations are advantageous for studying equilibrium properties and obtaining statistical averages. However, they are not suitable for capturing dynamic processes over time, as MD simulations do. The complementary use of both Monte Carlo and molecular dynamics techniques provides a comprehensive approach to understanding the thermodynamics and kinetics of molecular systems.

4.6 THERMOSTATS

In the realm of molecular dynamics simulations, maintaining a stable and realistic average temperature is crucial for accurately representing physical systems. This is where thermostats come into play. A thermostat is a computational tool employed to control and regulate the temperature of a simulated system, ensuring that it mimics the desired thermodynamic conditions.

The thermostat accomplishes this by interacting with the simulated particles, adjusting their velocities or energies to achieve the target temperature according to the Boltzmann distribution. Various types of thermostats exist, each designed to address specific simulation requirements and constraints.

One commonly used thermostat is the velocity rescaling thermostat, where particle velocities are rescaled to match a desired temperature distribution. Another popular choice is the Nosé-Hoover thermostat, which introduces additional degrees of freedom to the system to control its temperature dynamically.

The choice of thermostat depends on the specific characteristics of the system under investigation. Researchers must consider factors such as the system size, time scale of interest, and the physical phenomena being studied. The accurate representation of temperature in simulations is essential for obtaining meaningful insights into the thermodynamic properties and dynamic behavior of molecular systems.

4.6.1 Andersen Thermostat

Andersen's thermostat is a technique employed in molecular dynamics simulations to maintain a constant temperature in a canonical ensemble (NVT) [103]. To achieve this, Andersen couples the system to a heat bath, intermittently introducing stochastic collisions that act on randomly selected particles. The equations of motion for the particles follow Hamiltonian dynamics supplemented by stochastic collision terms, impacting the momentum of individual particles. The frequency of these collisions and the desired temperature are key parameters influencing the strength of the coupling to the heat bath.

In Andersen's method, a simulation proceeds by integrating the Hamiltonian equations of motion until a stochastic collision occurs. During a collision, the momentum of the affected particle is randomly chosen from a Boltzmann distribution at the specified temperature. This process repeats, resulting in a trajectory for the particles over time. Despite its effectiveness in maintaining constant temperature, a drawback of the Andersen thermostat is its impact on the physical realism of dynamics. The random decorrelation of velocities introduced by the algorithm can disrupt the true dynamical properties, making it less suitable for simulations aimed at accurately measuring dynamic behavior. Despite this limitation, Andersen's algorithm has been shown to generate a canonical distribution in phase space, ensuring the ensemble average aligns with the time average for quantities of interest in the canonical ensemble.

4.6.2 Nosé-Hoover Thermostat

The Nosé-Hoover thermostat is a technique utilized in molecular dynamics simulations to maintain a constant temperature in a canonical ensemble (NVT). In contrast to employing stochastic collisions on the simulated system, Nosé introduced an extended Lagrangian, which involves additional artificial coordinates and velocities. Initially introduced by Andersen in constant-pressure MD simulations, this extended-Lagrangian approach has become a stable and efficient method for simulations requiring expensive optimizations at each time step. When incorporated into molecular dynamics simulations, the extended-Lagrangian method is commonly referred to as the Nosé-Hoover thermostat.

In the Nosé-Hoover thermostat, an additional degree of freedom is introduced as an external system that acts on the simulated system. Virtual variables, including coordinates, momenta, and time, are introduced and related to real variables.

The equations of motion for the extended system involve the virtual variables and are derived from the extended Hamiltonian. Notably, the extended Hamiltonian is conserved during the evolution of the extended system, resulting in a microcanonical ensemble. By projecting the partition function of the extended system onto the original system, the canonical ensemble is recovered, ensuring correct results for static quantities.

4.6.3 Berendsen Thermostat

The Berendsen thermostat, also known as the proportional thermostat [104], was introduced as a solution to a limitation of the velocity-rescaling method, which does not allow for temperature fluctuations inherent in the canonical ensemble. To address this, Berendsen proposed a weak coupling method to an external bath, creating what is now known as the Berendsen thermostat. This thermostat aims to correct deviations of the actual temperature from the prescribed temperature by adjusting the velocities with a scaling factor. Unlike some other methods, the Berendsen thermostat permits temperature fluctuations, providing a more realistic representation of dynamic systems. The motivation behind Berendsen's thermostat lies in minimizing local disturbances of a stochastic thermostat while maintaining global effects. In Berendsen's method, velocities are scaled at each time step, leading to an exponential decay of the system toward the desired temperature, determined by a coupling time constant. Despite its advantages, a drawback of the Berendsen thermostat is its inability to be precisely mapped onto a specific thermodynamic ensemble. The resulting phase space distribution shows an interpolation between the canonical and microcanonical ensembles, providing a compromise between fixed temperature and energy conservation.

4.6.4 Langevin Thermostat

The Langevin thermostat is motivated by the need to simulate the motion of large particles through a continuum of smaller particles, where the smaller particles create damping forces and provide random kicks to the larger particles [105]. The Langevin equation, which incorporates a frictional drag force and random thermal fluctuations, is particularly useful for modeling solute-solvent systems, such as proteins, DNA, or nanoparticles in solution. The equation of motion includes a damping term, reflecting the damping of momenta due to collisions with smaller particles, and a random force term to account for thermal kicks from the smaller particles. The key idea behind the Langevin thermostat is to implicitly include the influence of many atoms through stochastic terms, leading to fewer computations per time step. While it allows for a larger time step, the thermostat has some drawbacks, such as excluding the volume effects of the solvent and facing challenges in implementing drag forces for non-spherical particles. Additionally, it requires that solvent molecules be small compared to the smallest molecules explicitly considered. Despite these limitations, the Langevin thermostat offers advantages, such as computational efficiency and stability in resolving slower degrees of freedom with larger time steps.

4.7 BONDED AND NON-BONDED INTERACTIONS

Bonded Interactions: Bonded interactions involve the forces between atoms that are directly connected by chemical bonds. These interactions are described by mathematical functions that capture the energy associated with bond stretching, angle bending, and dihedral angle rotation. Covalent bonds are characterized by their well-defined equilibrium lengths and bond angles, these parameters will be used by the chosen force field in order to ensure that these structural features are accurately represented during the simulation. The potential energy associated with bonded interactions is a function of the bond lengths, angles, and dihedral angles, influencing the overall geometry and conformational changes of the molecular system.

Non-Bonded Interactions: Non-bonded interactions encompass forces between atoms that are not connected by chemical bonds. These interactions can be broadly categorized into van der Waals (dispersion) forces and electrostatic forces. Van der Waals forces arise due to temporary fluctuations in electron distribution, leading to attractive forces between molecules. Electrostatic forces, on the other hand, result from the interaction between charged particles. The Coulombic potential is used to describe the electrostatic interactions, accounting for both attractive and repulsive forces based on the charge distribution of atoms. Non-bonded interactions significantly influence the overall stability, packing, and solvation behavior of molecules within the simulation environment.

In MD simulations, a careful selection of force field parameters for both bonded and non-bonded interactions is essential to accurately reproduce experimental observations. Force fields, such as UFF, CHARMM, AMBER, and OPLS, provide parameterizations for various chemical species, ensuring that the simulated interactions align with known physical and chemical properties. Achieving a balance between accurate representation of bonded and non-bonded interactions is critical for obtaining reliable insights into the behavior of molecular systems, whether they involve biological macromolecules, polymers, or nanomaterials.

4.8 INTERACTION POTENTIALS

In molecular dynamics, adequately characterizing a system involves not only selecting the suitable ensemble but also specifying the interactions among particles. The interaction among non-bonded particles is computed using a Lennard-Jones potential combined with a Coulomb pair interaction term, as illustrated in equation 4.3.

$$E_{lj} = 4\epsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6]$$
 $r < r_c$: Lennard-Jones Potential.
 $E_c = \frac{Cq_iq_j}{\epsilon r}$ $r < r_c$: Coulomb Pair Interaction.

- ϵ : Dielectric constant.
- σ : Particle size (Distance at which the potential is minimum). (4.3)
- r: Distance between two interacting particles.
- r_c : Cutoff distance.
- C: Energy conversion constant (Dependent on the energy unit used).
- q_i, q_j : Residual charges of the involved atoms.

The next step involves describing the bonded atoms in a manner that allows for the replication of the known properties of the specific system. Established models are chosen for

this purpose; for structural considerations, the Universal Force Field (UFF) is utilized [100], while for molecules, the Transferable Potentials for Phase Equilibria (TraPPE) is applied [106]. These models delineate the interactions among atoms and molecules, encompassing attractive and repulsive forces, electrostatic potentials, and other pertinent properties essential for characterizing the system. By employing these models, it becomes feasible to simulate the system's behavior under diverse conditions and extract valuable insights into its dynamics and thermodynamic properties.

4.8.1 Universal Force Field

In the Universal Force Field (UFF), parameters are determined through general rules that rely solely on the element, its hybridization, and connectivity (which describes the manner in which atoms are linked or bonded to one another within a molecular structure) [100]. It is important to highlight that UFF operates as a non-reactive force field, signifying that chemical bonds between atoms are treated as fixed, and there is no occurrence of bond formation or breaking during the simulation.

In UFF, atoms are separated by types, with 126 available atom types. A five-character nomenclature is used. The first two correspond to the chemical symbol, where an underscore is used if the element has only one letter (e.g., N_ is nitrogen, Rh is rhodium). The third term in the UFF nomenclature describes the hybridization or geometry of atoms, using the following codes: 1 for *linear*, 2 for *trigonal*, R for *resonant*, 3 for *tetrahedral*, 4 for *square planar*, 5 for *trigonal bipyramid*, and 6 for *octahedral*. For example, N_3 represents a nitrogen atom with tetrahedral geometry. The fourth and fifth terms are indicators of alternative parameters, such as the formal oxidation state. For instance, Rh6+3 indicates a rhodium atom with octahedral geometry and formally in the oxidation state +3.

The potential energy of the system is described by the superposition of various interactions among multiple bodies, illustrated in figure 4.3, as depicted in equation 4.4, were m stands for .

$$E = E_R + E_{\theta} + E_{\psi} + E_{vdw} + E_{el}$$

$$E_R = \frac{1}{2}k_{IJ}(r - r_{IJ})^2 : \text{Bond stretch}$$

$$E_{\theta} = K_{IJK} \sum C_n \cos(n\theta) : \text{Angle bend}$$

$$E_{\Phi} = K_{IJKL} \sum C_n \cos(n\phi_{IJKL}) : \text{Torsion}$$

$$E_w = K_{IJKL} (C_0 + C_1 \cos w_{IKJL} + C_2 \cos 2w_{IJKL}) : \text{Inversion}$$

$$E_{vdw} = D_{IJ} \left\{ -2 \left[\frac{x_{IJ}}{x} \right]^6 + \left[\frac{x_{IJ}}{x} \right]^{12} \right\} : \text{van der Waals}$$

$$E_{el} = 332.0637 (\frac{Q_I Q_J}{\epsilon R_{IJ}}) : \text{Electrostatic Interactions}$$

$$(4.4)$$

The potential binding energy E_R is described by an harmonic oscillator, where k_{IJ} represents the force constant expressed in $(kcal/mol)/\text{Å}^2$, and r_{IJ} represents the equilibrium bond length. It's important to note that the harmonic nature of this component in the force field excludes the consideration of bond breakage. This characteristic categorizes the force field as non-reactive, where all bonds are treated as simple harmonic oscillators. While this choice heavily



Figure 4.3: The figure depicts various interactions outlined by the potential energy of the system. Bond vibration, angle vibration, and torsion potentials are categorized as bonded interactions, while van der Waals and electrostatic interactions fall under the non-bonded interactions category.

impacts the computational cost of simulations, it does not compromise the accuracy of results for the specific application under consideration.

The term governing angle stretching, denoted as E_{θ} , is expressed through a Fourier series expansion centered on the equilibrium angle θ_0 . The coefficients C_n are selected to meet suitable boundary conditions, ensuring that the function attains a minimum at the natural angle position. The preference for this expansion over the more conventional harmonic expansion stems from its enhanced capacity to depict high amplitudes, particularly relevant in the context of molecular dynamics simulations, where angles between bonded atoms may experience significant deviations from their natural positions.

The torsion term associated with two bonds, IJ and KL, connected by a bond JK, is characterized by a Fourier expansion in terms of the dihedral angle ϕ . The coefficients K_{IJKL} and C_n are established based on the periodicity of the potential and the equilibrium angle.

The inversion term describes an atom I connected to exactly three other atoms J, K, and L through a Fourier expansion in w. The force constant is represented by K_{IJKL} in units of (kcal/mol), and w_{IJKL} is the angle between the IL axis and the IJK plane.

The van der Waals term is utilized to depict non-bonding interactions (van der Waals forces) and is expressed through a Lennard-Jones equation. In this equation, D_{IJ} denotes the well depth in kcal/mol, and x_{IJ} represents the van der Waals bonding distance in Å. The selection of the Lennard-Jones form is motivated by its numerical stability, particularly at small inter-nuclear separations.

The term characterizing electrostatic interactions encapsulates details regarding the partial charges of the relevant atoms. Within this expression, Q_I and Q_J denote the charges in electron units for atoms I and J, respectively, while R_{IJ} signifies the distance between them measured in Å. The dielectric constant ϵ is also taken into account in this term.

4.8.2 TraPPE

The choice of the TraPPE (Transferable Potentials for Phase Equilibria) force field for a Grand Canonical Monte Carlo (GCMC) adsorption study is justified by its well-established reputation for accurately characterizing thermo-physical properties in diverse chemical systems. Developed by Eggimann et al. in 2014 [106], the TraPPE force field has demonstrated exceptional accuracy in simulating complex chemical systems, making it highly valuable as a tool for applications ranging from industrial processes to material studies. The TraPPE force field has been extensively validated and applied across various compounds, states, compositions, and properties.

For CO_2 , the TraPPE model established by Potoff and Siepmann [107, 108] was employed, known for its high precision in replicating the liquid-vapor equilibrium state of these molecules. These TraPPE models have proven reliability and accuracy, making them well-suited for capturing the adsorption behavior of these molecules in the GCMC study. Overall, the TraPPE force field's robustness and versatility make it a rational and reliable choice for simulating adsorption phenomena in this study.

4.8.3 LAMMPS

LAMMPS, an acronym for Large-scale Atomic/Molecular Massively Parallel Simulator, was introduced in 2004 and is extensively documented by Thompson *et al.* [12]. This influential open-source software has established itself as a cornerstone in the realm of molecular dynamics simulations. Its significance lies in its broad utility, offering a versatile and comprehensive tool for modeling particle systems across diverse scales, ranging from the atomistic to continuum levels.

In the context of our work, LAMMPS assumes a central and pivotal role as the primary simulation tool. Its ability to handle massive parallelization enables efficient computations, making it particularly well-suited for large-scale simulations.

4.8.4 Grand Canonical Monte Carlo

To characterize the adsorption of a gas in this system, it's crucial to possess a function enabling the computation of the gas molecule quantity within the structure at a specific pressure. This function is executed through the "fix GCMC" command in LAMMPS, employing the Monte Carlo method, where the "fix" word is used in LAMMPS commands which remain active until otherwise stated. Furthermore, following LAMMPS manual guidelines, a "fix NVT" is combined with "fix GCMC". This integration allows the two functions to collaborate, creating the Grand Canonical ensemble through alternating operations. In practical terms, for every one hundred GCMC steps, where molecules are added and deleted, a single NVT step is implemented for system equilibration. This alternation ensures that the system remains in close proximity to equilibrium, emphasizing the careful balance maintained between the two simulation techniques.

The Grand Canonical ensemble, chosen for molecular dynamics simulations, accommodates a varying number of particles, contrasting with the more conventional microcanonical ensemble. While simulating adsorption under the microcanonical ensemble aligns more closely with experimental conditions, it might be impractical for intricate systems due to extended equilibration times, ranging from minutes to hours, contingent on gas molecule types. Additionally, each minute of experimentation corresponds to approximately 10^9 seconds of simulation time, rendering this ensemble less reasonable for complex systems [97]. Addressing this challenge involves judiciously opting for an ensemble such as the Grand Canonical, ensuring constancy in chemical potential μ , volume V, and temperature T. Notably, these constants refer to the values in the ideal gas reservoir interacting with the simulation box.

Within the Grand Canonical ensemble, equilibrium requires the alignment of gas temperature and chemical potential with their counterparts in the reservoir. LAMMPS employs Monte Carlo simulations to iteratively adjust the chemical potential μ until it converges to the specified value μ^{id} in Equation 4.5.

$$\mu = \mu^{id} + \mu^{ex}$$

$$\mu^{id}$$
: Chemical potential of the ideal gas reservoir. (4.5)
$$\mu^{ex}$$
: Non-ideal contribution caused by interactions between gas molecules.

To input the ideal chemical potential (μ^{id}) into the LAMMPS software, one can employ Equation 4.6. This enables the insertion of reservoir pressure and temperature as input, producing the desired chemical potential as the output.

$$\mu^{id} = k_B T \ln\left(\frac{\Phi P \Lambda^3}{k_B T}\right)$$

$$\Lambda = \sqrt{\left(\frac{h^2}{2\pi m k_B T}\right)} : \text{De Broglie's wavelength.}$$

$$\Phi : \text{Fugacity coefficient of the non-ideal gas.}$$
(4.6)

- P : Pressure of the ideal gas reservoir.
- h : Planck's constant.
- m: Molecular mass of the gas.

Take note that, while Equation 4.6 simplifies the definition of the system of interest by allowing the use of more tangible variables as inputs, it introduces a new component to our system: the fugacity coefficient (Φ). In thermodynamics, the fugacity (f) of an ideal gas represents an effective partial pressure, linked to the total pressure (P) through the fugacity coefficient: $f = \Phi P$. The explicit form of f is evident in Equation 4.6.

Determining the fugacity coefficient involves employing the Equation 4.7 and coefficients derived by Nicolas F. Spycher and M. H. Reed [109] in 1988 for gases such as H_2 , CO_2 , CH_4 , H_2O , and their combinations, spanning multiple pressure and temperature values.

$$\ln \Phi = \left(\frac{a}{T^2} + \frac{b}{T} + c\right)P + \left(\frac{d}{T^2} + \frac{e}{T} + f\right)\frac{P^2}{2}$$
(4.7)

When the LAMMPS manual refers to the Monte Carlo method, it specifically denotes the Metropolis method [110]. This computational technique relies on random sampling to derive numerical outcomes. The crux of the method lies in leveraging multiple different samples to approximate the behavior of intricate systems. In the Metropolis method, random samples are drawn from a probability distribution, serving to simulate the behavior of thermodynamic systems in equilibrium. The aim is to generate particle configurations aligning with a specific thermodynamic state, utilizing acceptance/rejection criteria to ensure the sample distribution aligns with the desired probability distribution.

The Metropolis method, functioning as a stochastic sampling algorithm, iteratively explores the configuration space of the system. At each iteration, a new configuration is proposed through slight adjustments to the current configuration. The probability of adopting the new configuration is then calculated, employing a simple acceptance/rejection criterion based on the energy difference between the new and old configurations. If the energy of the new configuration is lower, acceptance is automatic; otherwise, acceptance probability is determined proportionally to the energy difference.

In this system, the criterion for evaluating configurations is the chemical potential. If a new configuration brings the chemical potential closer to the desired input, it is deemed favorable and accepted. Conversely, if the difference exceeds that of the previous configuration, acceptance occurs with a probability contingent on the disparity.

Unlike the Grand Canonical ensemble, the NVT ensemble (canonical) maintains a constant number of particles. Within the scope of this work, the "fix NVT" command acts as

an intermediary step after each Monte Carlo analysis. Post-Monte Carlo, involving additions, removals, translations, or rotations of molecules and assessment of the system's chemical potential, the system undergoes thermalization. This ensures a constant number of molecules during this phase, crucial because the Monte Carlo method is applicable solely to equilibrium systems.

It's essential to underscore that the GCMC method employed for simulating the adsorption system doesn't replicate the actual dynamics of the process. This method operates through particle creation, translation, rotation, and removal, simulating a different aspect than the experimental transport of molecules within the structure to the storage site. Consequently, assessing the adsorption and desorption times using this method is not viable. Nevertheless, it enables the determination of the total adsorption capacity of the system at specific pressure and temperature values.

4.9 DATA PROCESSING

In addition to LAMMPS, which served as the primary simulation tool, other software applications played crucial roles in different facets of the simulation workflow. These auxiliary tools contributed to tasks such as structural visualization, input generation, and result analysis, enhancing the overall efficiency and comprehensiveness of the study.

4.9.1 VESTA

One significant contributor to the crafting of structures used in the simulation was VESTA ("Visualization for Electronic and Structural Analysis") [111]. VESTA played a pivotal role by enabling the creation of files containing the coordinates of Schwarzites. Functioning as a visualization and structural analysis tool, VESTA facilitates the generation of crystalline structures based on input parameters like lattice parameters, space groups, and fractional coordinates. The specific properties essential for constructing the Schwarzites in this study were derived from tabulated data provided by H. Terrones and M. Terrones [13], emphasizing the collaborative nature of utilizing various resources in computational studies.

4.9.2 VMD

Another indispensable tool in the entire simulation process is Visual Molecular Dynamics (VMD) [112]. Similar to LAMMPS, VMD exhibits high versatility and functionality. Its capabilities include adjusting data files, inspecting preliminary results, and converting files generated by VESTA into formats compatible with LAMMPS, facilitated by the TopoTools tool [113]. The integration of VMD into the workflow underscores the significance of employing a diverse set of software tools to streamline different aspects of the simulation pipeline, from initial structure creation to the final analysis of simulation results.

5 RESULTS AND ANALYSIS

Given the outlined concepts and methodologies, the adsorption of CO_2 within three distinct structures, namely P8-1, P8-3, and P8-7, of the P family of schwarzites were investigated. Employing the "fix GCMC" and "fix NVT" commands as described earlier, the Grand Canonical ensemble was established, alternating between the stochastic Monte Carlo and conventional MD calculations to ascertain the total CO_2 molecules each structure could capture, for each temperature and pressure observed. That is, each point, representing a pressure and temperature value is considered an independent system, and it's total adsorption capacity was calculated accordingly, this is illustrated in figure 5.1. Examples of the convergence of such systems can be seen in figure 5.2. In figure 5.2 it is also possible to notice that, for each value of temperature and pressure three separate samples exist, that is, to enhance statistical robustness, each system was converged three times independently, mitigating potential biases arising from statistically rare events.

Analysis of figure 5.2 reveals significant observations. Firstly, as pressure increases under constant temperature and structure, the influence of different samples diminishes, attributed to a higher particle count at elevated pressure enhancing overall statistical reliability. The second observation to be made is that increasing the size of the structure also decreases the variance in the number of CO_2 present before convergence, likely due to the increase in the number of CO_2 molecules.

Now, knowing that each pressure-temperature-structure combination represents a distinct independent system. It is possible to, taking the final convergence values from each sample, create the adsorption isotherms seen in figure 5.3. Here, each point represents the asymptotic value of that sample at that pressure value. Again larger discrepancies between samples can be seen at lower pressure values, while increasing the temperature shows the opposite effect, since as mentioned before, the increase in temperature has a negative effect on the adsorption capacity, reducing the amount of CO_2 molecules present and increasing the chances of rare events.

Taking the mean asymptotic values of the three samples for each pressure-temperature scenario, it becomes possible to create the isotherms seen in figure 5.4. Take note that from now on, each point symbolizes the mean asymptotic value of three different samples of the same system at that pressure. Figure 5.5 showcases snapshots of a sample of the P8-3 schwarzite at different pressures.

Each image in figure 5.4 displays the adsorption isotherm of a structure at different temperature values, with each pair of structures presenting identical data observed at different pressure ranges to highlight diverse potential applications. Just as expected, the increase in temperature has a negative effect on the adsorption, necessitating higher pressures for saturation. Also, notice that the effect of temperature is so significant that for all structures at 200K the first pressure of 0.01 bars already presents significant adsorption, unlike the systems at 300K and 400K. The effect of temperature on adsorption can be used for the desorption process, necessary for the storage of any adsorbed gas.

For a more meaningful structural comparison, adsorption capacity (y-axis) is expressed in $mmol \ g^{-1}$, representing the number of CO_2 molecules per molar mass of the adsorbing structure. This enables comparisons between structures of varying sizes, such as the considerably larger P8-7 schwarzite. Such comparison can be seen in figure 5.6, where the dots represent the measured values and the dashed lines now represent the curve fitted using the Langmuir equation 2.10,



(C)

Figure 5.1: Snapshots of the P8-3 converging at 10 bars and 300K, in grey is the carbon structure while the small molecules of grey and red atoms are the CO_2 molecules, showcasing steps (a) 30000, (b) 60000 and (c) 90000. From step 30000 to step 90000 there's been a total of 825 atoms added to the system. Here the blue outlines represent the simulation box.



Figure 5.2: Convergence curves for all three samples of each schwarzite at 300K, in the y-axis the amount of adsorbate per molar mass of the adsorbent is displayed in mmol g^{-1} , the x-axis shows the simulations steps, the figures show the (a) P8-1 at 0.8 bars, (b) P8-1 at 30 bars, (c) P8-3 at 0.8 bars, (d) P8-3 at 30 bars, (e) P8-7 at 0.8 bars and (f) P8-7 at 30 bars.



Figure 5.3: Adsorption isotherms of all three samples of all structures, this time the y-axis remains as the amount of adsorbate per molar mass of adsorbent in mmol g^{-1} while the x-axis displays the pressure of the gas reservoir in bars, the figures show the (a) P8-1 at 200K, (b) P8-1 at 300K, (c) P8-1 at 400K,(d) P8-3 at 200K, (e) P8-3 at 300K, (f) P8-3 at 400K,(g) P8-7 at 200K, (h) P8-7 at 300K and (i) P8-7 at 400K.



Figure 5.4: Adsorption isotherms for the schwarzites at different temperatures, each pair of figures shows the same data within different pressure ranges, here the y-axis remains as the amount of adsorbate per molar mass of adsorbent in mmol g^{-1} while the x-axis displays the pressure of the gas reservoir in bars, (a) shows the P8-1 at pressures ranging from 0.01 bars to 50 bars, (b) shows The P8-1 at pressures ranging from 0.01 bars to 1.0 bar, (c) shows the P8-3 at pressures ranging from 0.01 bars to 50 bars, (d) shows The P8-3 at pressures ranging from 0.01 bars to 1.0 bar, (e) shows the P8-7 at pressures ranging from 0.01 bars to 50 bars, and (f) shows The P8-7 at pressures ranging from 0.01 bars to 1.0 bar.



Figure 5.5: Snapshots of the P8-3 at 300K and (a) 0.1 bars, (b) 1.0 bars and (c) 10 bars. Here the blue outlines represent the simulation box.



Figure 5.6: Adsorption isotherms for all three schwarzites compared at different temperatures, where dots represent the simulated values while the dashed lines represent the fitted curves. Figure (a) shows 200K with pressures ranging from 0.01 bars to 50 bars, (b) shows 200K with pressures ranging from 0.01 bars to 1.0 bars, (c) shows 300K with pressures ranging from 0.01 bars to 50 bars, (d) shows 300K with pressures ranging from 0.01 bars to 1.0 bars, (e) shows 400K with pressures ranging from 0.01 bars to 50 bars, (d) shows 300K with pressures ranging from 0.01 bars to 1.0 bars, (e) shows 400K with pressures ranging from 0.01 bars to 50 bars and (f) shows 400K with pressures ranging from 0.01 bars to 1.0 bars.

where the asymptotic value of each curve was used for K', the K values are seen on the legends of each figure.

Examining the fitted curves reveals that, although Langmuir may not precisely capture the intricacies of our system, it still proves to be a suitable fit for the resulting isotherms. Despite its limitations, Langmuir provides a practical approximation that aligns well with the observed data.

Looking at figure 5.6 the relationship between structures becomes evident, with the P8-1 schwarzite saturating rapidly, at less than 1.0 bar for all temperatures. Thanks to the small size of the P8-1 it becomes clear the effect of temperature, as it does not reduce the total capacity of adsorption, but simply makes the process of achieving such saturation much harder, as expected from an exothermic process. When looking at the P8-3 structure exhibits temperature-dependent saturation, such that for 400K, at the pressure range observed here, saturation is not achieved. Despite this, P8-3 presents competitive adsorption at 300K and 200K, even surpassing the P8-7 at 300K 1.0 bar. This effect highlights the need to observe adsorption at different pressure ranges, as the P8-3 has either more or less adsorption capacity when compared to the P8-7 depending on the pressure observed. For the P8-7, only at 200K does it saturate, presenting an amazing adsorption capacity, though at very specific conditions.

6 CONCLUSIONS

In conclusion, this study employed a combination of the UFF and TraPPE force fields, robust and versatile tools known for its applicability across diverse chemical systems, to investigate the adsorption behavior of CO_2 within three distinct structures (P8-1, P8-3, and P8-7) of the P family of schwarzites. Leveraging the LAMMPS simulation software, the investigation provided valuable insights into the adsorption dynamics of CO_2 .

The simulations, combining the "fix GCMC" and "fix NVT" commands, successfully created the Grand Canonical ensemble by alternating between stochastic Monte Carlo and conventional MD calculations. This approach allows the exploration of the total adsorption capacity of each structure under different temperature and pressure conditions, by considering each pressure-temperature-structure combination as an independent system.

The convergence analysis revealed intriguing trends, with the influence of different samples diminishing at higher pressures and larger structures. This underscores the importance of statistical robustness when working with molecular dynamics and simulations in general.

The generated adsorption isotherms provided a comprehensive overview of the system's response to varying temperature and pressure conditions. The temperature-dependent effects on saturation and adsorption capacity were clearly delineated, emphasizing the behavior of different structures under distinct pressure ranges.

Structural comparisons, depicted in Figure 5.4 and Figure 5.6, showcase the unique characteristics of each schwarzite. P8-1 exhibited rapid saturation, showcasing the influence of temperature on the adsorption process. P8-3, while not achieving saturation at 400K, demonstrated competitive adsorption at 300K and 200K, even outperforming P8-7 under certain conditions. The larger P8-7 structure, saturated only at 200K, revealed remarkable adsorption capacity under specific temperature and pressure conditions. It's important to note that selecting one structure as superior to the others is not straightforward, as the optimal choice depends on the specific application requirements, influencing the operating pressures and temperatures needed. That being said, when directly comparing with other structures currently being used in adsorption of CO_2 , specifically the MOF-74 [114, 115, 116] presents adsorption capacities similar to that of P8-1, as seen in figure 6.1, ranging from 8 to 12 $mmol g^{-1}$, making the schwarzites studied here very competitive.

This comprehensive exploration sheds light on the intricate interplay of temperature, pressure, and structure size in the adsorption of CO_2 within the P family of schwarzites. The findings not only contribute to our fundamental understanding of adsorption phenomena but also hold implications for potential applications, including gas storage and separation. Continued exploration in this direction holds the potential to unveil further insights for optimizing these structures in practical applications within materials science and environmental engineering. This, in turn, could enhance interest and investment in the synthesis of schwarzites.



Figure 6.1: Figure presents the adsorption capacity of the P-Family of Schwarzites at 300K, the y-axis presents the adsorption capacity as the number of adsorbate molecules per molar mass of each adsorbent, while the x-axis presents the pressure of the gas reservoir. The region highlighted in red shows the range of the adsorption capacity of MOF-74 [114, 115, 116].

REFERENCES

- [1] C. P. Morice, J. J. Kennedy, N. A. Rayner, J. P. Winn, E. Hogan, R. E. Killick, R. J. H. Dunn, T. J. Osborn, P. D. Jones, and I. R. Simpson. An updated assessment of near-surface temperature change from 1850: The hadcrut5 data set. *Journal of Geophysical Research: Atmospheres*, 126(3), 2021.
- [2] A Park Williams, Edward R Cook, Jason E Smerdon, Benjamin I Cook, John T Abatzoglou, Kasey Bolles, Seung H Baek, Andrew M Badger, and Ben Livneh. Large contribution from anthropogenic warming to an emerging north american megadrought. *Science*, 368(6488):314–318, April 2020.
- [3] Geert Jan van Oldenborgh, Karin van der Wiel, Antonia Sebastian, Roop Singh, Julie Arrighi, Friederike Otto, Karsten Haustein, Sihan Li, Gabriel Vecchi, and Heidi Cullen. Attribution of extreme rainfall from hurricane harvey august 2017. *Environmental Research Letters*, 12(12):124009, dec 2017.
- [4] Mark D. Risser and Michael F. Wehner. Attributable human-induced changes in the likelihood and magnitude of the observed extreme precipitation during hurricane harvey. *Geophysical Research Letters*, 44(24):12,457–12,464, 2017.
- [5] A.G. Olabi and Mohammad Ali Abdelkareem. Renewable energy and climate change. *Renewable and Sustainable Energy Reviews*, 158:112111, 2022.
- [6] Stefano E. Zanco, José-Francisco Pérez-Calvo, Antonio Gasós, Beatrice Cordiano, Viola Becattini, and Marco Mazzotti. Postcombustion co₂ capture: A comparative techno-economic assessment of three technologies using a solvent, an adsorbent, and a membrane. ACS Engineering Au, 1(1):50–72, 2021.
- [7] Y. Artioli. Adsorption. In Sven Erik Jørgensen and Brian D. Fath, editors, *Encyclopedia of Ecology*, pages 60–65. Academic Press, Oxford, 2008.
- [8] Qanytah, Khaswar Syamsu, Farah Fahma, Gustan Pari, and Indrie Ambarsari. Activated carbon paper as ethylene adsorber. *Nordic Pulp Paper Research Journal*, 38(1):121–130, 2023.
- [9] Hong-Cai Zhou, Jeffrey R. Long, and Omar M. Yaghi. Introduction to metal–organic frameworks. *Chemical Reviews*, 112(2):673–674, 2012.
- [10] Martin Oliver Steinhauser. *Computer Simulation in Physics and Engineering*. De Gruyter, Berlin, Boston, 2013.
- [11] Adrian Colaso, Pablo Prieto, Jose-Angel Herrero, Pablo Abad, Valentin Puente, and Jose-Angel Gregorio. Accuracy vs. computational cost tradeoff in distributed computer system simulation, 2019. Submitted on arXiv.
- [12] Aidan P. Thompson, H. Metin Aktulga, Richard Berger, Dan S. Bolintineanu, W. Michael Brown, Paul S. Crozier, Pieter J. in 't Veld, Axel Kohlmeyer, Stan G. Moore, Trung Dac Nguyen, Ray Shan, Mark J. Stevens, Julien Tranchida, Christian Trott, and Steven J. Plimpton. Lammps - a flexible simulation tool for particle-based materials modeling at the atomic, meso, and continuum scales. *Computer Physics Communications*, 271, 2 2022.

- [13] Humberto Terrones and Mauricio Terrones. Curved nanostructured materials. *New Journal* of *Physics*, 5:126, 10 2003.
- [14] A. L. MACKAY and H. TERRONES. Diamond from graphite. Nature, 352:762–762, August 1991.
- [15] K. S. W. Sing. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity (recommendations 1984). *Pure and Applied Chemistry*, 57(4):603–619, 1985.
- [16] Matthias Thommes, Katsumi Kaneko, Alexander V. Neimark, James P. Olivier, Francisco Rodriguez-Reinoso, Jean Rouquerol, and Kenneth S.W. Sing. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (iupac technical report). *Pure and Applied Chemistry*, 87(9-10):1051–1069, 2015.
- [17] P. Brohan, R. Allan, E. Freeman, D. Wheeler, C. Wilkinson, and F. Williamson. Constraining the temperature history of the past millennium using early instrumental observations. *Climate of the Past*, 8(5):1551–1563, 2012.
- [18] J. R. Petit, J. Jouzel, D. Raynaud, N. I. Barkov, J.-M. Barnola, I. Basile, M. Bender, J. Chappellaz, M. Davis, G. Delaygue, M. Delmotte, V. M. Kotlyakov, M. Legrand, V. Y. Lipenkov, C. Lorius, L. PÉpin, C. Ritz, E. Saltzman, and M. Stievenard. Climate and atmospheric history of the past 420,000 years from the vostok ice core, antarctica. *Nature*, 399(6735):429– 436, Jun 1999.
- [19] L. Pépin, D. Raynaud, J.-M. Barnola, and M. F. Loutre. Hemispheric roles of climate forcings during glacial-interglacial transitions as deduced from the vostok record and Iln-2d model experiments. *Journal of Geophysical Research: Atmospheres*, 106(D23):31885–31892, 2001.
- [20] J. Jouzel, V. Masson-Delmotte, O. Cattani, G. Dreyfus, S. Falourd, G. Hoffmann, B. Minster, J. Nouet, J. M. Barnola, J. Chappellaz, H. Fischer, J. C. Gallet, S. Johnsen, M. Leuenberger, L. Loulergue, D. Luethi, H. Oerter, F. Parrenin, G. Raisbeck, D. Raynaud, A. Schilt, J. Schwander, E. Selmo, R. Souchez, R. Spahni, B. Stauffer, J. P. Steffensen, B. Stenni, T. F. Stocker, J. L. Tison, M. Werner, and E. W. Wolff. Orbital and millennial antarctic climate variability over the past 800,000 years. *Science*, 317(5839):793–796, 2007.
- [21] J.-R. Petit, J. Jouzel, D. Raynaud, N.I. Barkov, J.-M. Barnola, I. Basile, M.L. Bender, J.A. Chappellaz, M.D. Davis, G. Delaygue, M. Delmotte, V.M. Kotlyakov, M. Legrand, V.Y. Lipenkov, C. Lorius, L. Pépin, C. Ritz, E.S. Saltzman, and M. Stievenard. Noaa/wds paleoclimatology - vostok - isotope and gas data and temperature reconstruction. https: //doi.org/10.25921/kcry-ae86, 11 2001. Accessed 2024-01-05.
- [22] J. B. Pedro, T. D. van Ommen, S. O. Rasmussen, V. I. Morgan, J. Chappellaz, A. D. Moy, V. Masson-Delmotte, and M. Delmotte. The last deglaciation: timing the bipolar seesaw. *Climate of the Past*, 7(2):671–683, 2011.
- [23] E Monnin, A Indermühle, A Dällenbach, J Flückiger, B Stauffer, T F Stocker, D Raynaud, and J M Barnola. Atmospheric CO2 concentrations over the last glacial termination. *Science*, 291(5501):112–114, January 2001.

- [24] Bénédicte Lemieux-Dudon, Eric Blayo, Jean-Robert Petit, Claire Waelbroeck, Anders Svensson, Catherine Ritz, Jean-Marc Barnola, Bianca Maria Narcisi, and Frédéric Parrenin. Consistent dating for antarctic and greenland ice cores. *Quaternary Science Reviews*, 29(1):8–20, 2010.
- [25] Jeremy D Shakun, Peter U Clark, Feng He, Shaun A Marcott, Alan C Mix, Zhengyu Liu, Bette Otto-Bliesner, Andreas Schmittner, and Edouard Bard. Global warming preceded by increasing carbon dioxide concentrations during the last deglaciation. *Nature*, 484(7392):49– 54, April 2012.
- [26] Jorg Lippold, Yiming Luo, Roger Francois, Susan Allen, Jeanne Gherardi, Sylvain Pichat, Ben Hickey, and Hartmut Schulz. Strength and geometry of the glacial atlantic meridional overturning circulation. *Nature Geosci*, 5:813–816, 10 2012.
- [27] Feng He, Jeremy D Shakun, Peter U Clark, Anders E Carlson, Zhengyu Liu, Bette L Otto-Bliesner, and John E Kutzbach. Northern hemisphere forcing of southern hemisphere climate during the last deglaciation. *Nature*, 494(7435):81–85, February 2013.
- [28] Georg Feulner, Stefan Rahmstorf, Anders Levermann, and Silvia Volkwardt. On the origin of the surface air temperature difference between the hemispheres in earth's present-day climate. *Journal of Climate*, 26(18):7136 – 7150, 2013.
- [29] Stephen R. Meyers and Alberto Malinverno. Proterozoic milankovitch cycles and the history of the solar system. *Proceedings of the National Academy of Sciences*, 115(25):6363–6368, 2018.
- [30] Russell Deitrick, Rory Barnes, Thomas R. Quinn, John Armstrong, Benjamin Charnay, and Caitlyn Wilhelm. Exo-milankovitch cycles. i. orbits and rotation states. *The Astronomical Journal*, 155, 1 2018.
- [31] A. Buis. Milankovitch (orbital) cycles and their role in earth's climate. Global climate change, vital signs of the planet, NASA's Jet Propulsion Laboratory, 2020. Online, https://climate.nasa.gov/news/2948/milankovitch-orbitalcycles-and-their-role-in-earths-climate/.
- [32] Richard A. Kerr. Climate control: How large a role for orbital variations? *Science*, 201(4351):144–146, 1978.
- [33] NASA Global Climate Change. Global climate change: Climate resources, 2020. Accessed: 14 Jan. 2024. Online, https://climate.nasa.gov/climate_resources/ 189/graphic-temperature-vs-solar-activity/.
- [34] X. Lan, P. Tans, and K. W. Thoning. Trends in globally-averaged co₂ determined from noaa global monitoring laboratory measurements. Version 2024-01, 2024. https: //doi.org/10.15138/9N0H-ZH07.
- [35] Evan J. Gowan, Xu Zhang, Sara Khosravi, Alessio Rovere, Paolo Stocchi, Anna L. C. Hughes, Richard Gyllencreutz, Jan Mangerud, John-Inge Svendsen, and Gerrit Lohmann. A new global ice sheet reconstruction for the past 80 000 years. *Nature Communications*, 12(1):1199, Feb 2021.

- [36] Christine L. Batchelor, Martin Margold, Mario Krapp, Della K. Murton, April S. Dalton, Philip L. Gibbard, Chris R. Stokes, Julian B. Murton, and Andrea Manica. The configuration of northern hemisphere ice sheets through the quaternary. *Nature Communications*, 10(1):3713, Aug 2019.
- [37] Kristian Vasskog, Petra M. Langebroek, John T. Andrews, Jan Even Ø. Nilsen, and Atle Nesje. The greenland ice sheet during the last glacial cycle: Current ice loss and contribution to sea-level rise from a palaeoclimatic perspective. *Earth-Science Reviews*, 150:45–67, 2015.
- [38] R. J. Francey, C. E. Allison, D. M. Etheridge, C. M. Trudinger, I. G. Enting, M. Leuenberger, R. L. Langenfelds, E. Michel, and L. P. Steele. A 1000-year high precision record of ¹³c in atmospheric co₂. *Tellus B: Chemical and Physical Meteorology*, 51(2):170–193, 1999.
- [39] P. D. Quay, B. Tilbrook, and C. S. Wong. Oceanic uptake of fossil fuel co₂: Carbon-13 evidence. *Science*, 256(5053):74–79, 1992.
- [40] A. Buis. Why milankovitch (orbital) cycles can't explain earth's current warming. Global climate change, vital signs of the planet, NASA's Jet Propulsion Laboratory, 2020. Online, https://https://climate.nasa.gov/explore/ask-nasaclimate/2949/why-milankovitch-orbital-cycles-cant-explainearths-current-warming/.
- [41] Cong Chao, Yimin Deng, Raf Dewil, Jan Baeyens, and Xianfeng Fan. Post-combustion carbon capture. *Renewable and Sustainable Energy Reviews*, 138:110490, 2021.
- [42] Paul Breeze. Chapter 7 carbon capture and storage. In Paul Breeze, editor, *Coal-Fired Generation*, pages 73–86. Academic Press, Boston, 2015.
- [43] A. Basile, A. Gugliuzza, A. Iulianelli, and P. Morrone. 5 membrane technology for carbon dioxide (co2) capture in power plants. In Angelo Basile and Suzana Pereira Nunes, editors, Advanced Membrane Science and Technology for Sustainable Energy and Environmental Applications, Woodhead Publishing Series in Energy, pages 113–159. Woodhead Publishing, 2011.
- [44] Miguel A. Zamarripa, John C. Eslick, Michael S. Matuszewski, and David C. Miller. Multiobjective optimization of membrane-based co₂ capture. In Mario R. Eden, Marianthi G. Ierapetritou, and Gavin P. Towler, editors, 13th International Symposium on Process Systems Engineering (PSE 2018), volume 44 of Computer Aided Chemical Engineering, pages 1117–1122. Elsevier, 2018.
- [45] Dina G. Boer, Jort Langerak, and Paolo P. Pescarmona. Zeolites as selective adsorbents for co₂ separation. ACS Applied Energy Materials, 6(5):2634–2656, 2023.
- [46] Renata Avena Maia, Benoît Louis, Wanlin Gao, and Qiang Wang. Co2 adsorption mechanisms on mofs: a case study of open metal sites, ultra-microporosity and flexible framework. *React. Chem. Eng.*, 6:1118–1133, 2021.
- [47] Yang Han and W.S. Winston Ho. Polymeric membranes for co₂ separation and capture. *Journal of Membrane Science*, 628:119244, 2021.
- [48] Douglas M. Ruthven. Principles of Adsorption and Adsorption Processes. John Wiley & Sons, University of New Brunswick, Fredericton, Canada, 1984.

- [49] A Dąbrowski. Adsorption from theory to practice. Advances in Colloid and Interface Science, 93(1):135–224, 2001.
- [50] B. S. Bahl, Arun Bahl, and G. D. Tuli. Essentials of Physical Chemistry: 2nd edition, chapter 23, pages 843–849. RSC, UK, Gurdaspur, India, 2009.
- [51] Houston Frost, Tina Düren, and Randall Q. Snurr. Effects of surface area, free volume, and heat of adsorption on hydrogen uptake in metalorganic frameworks. *The Journal of Physical Chemistry B*, 110(19):9565–9570, 2006.
- [52] Mahdieh Mozaffari Majd, Vahid Kordzadeh-Kermani, Vahab Ghalandari, Anis Askari, and Mika Sillanpää. Adsorption isotherm models: A comprehensive and systematic review (20102020). Science of The Total Environment, 812:151334, 2022.
- [53] Can Erkey and Michael Türk. Chapter 6 thermodynamics and kinetics of adsorption of metal complexes on surfaces from supercritical solutions. In Can Erkey and Michael Türk, editors, Synthesis of Nanostructured Materials in Near and/or Supercritical Fluids, volume 8 of Supercritical Fluid Science and Technology, pages 73–127. Elsevier, 2021.
- [54] Stephen. Brunauer, Lola S. Deming, William Edwards Deming, and Edward Teller. On a theory of the van der waals adsorption of gases. *Journal of the American Chemical Society*, 62:1723–1732, 1940.
- [55] Zeid Alothman. A review: Fundamental aspects of silicate mesoporous materials. *Materials*, 5:2874–2902, 12 2012.
- [56] H. Freundlich. Of the adsorption of gases. section ii. kinetics and energetics of gas adsorption. introductory paper to section ii. *Trans. Faraday Soc.*, 28:195–201, 1932.
- [57] Irving Langmuir. The constitution and fundamental properties of solids and liquids. part i. solids. *Journal of the American Chemical Society*, 38(11):2221–2295, 1916.
- [58] Irving Langmuir. The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical Society*, 40(9):1361–1403, 1918.
- [59] Stephen Brunauer, P. H. Emmett, and Edward Teller. Adsorption of gases in multimolecular layers. *Journal of the American Chemical Society*, 60(2):309–319, 1938.
- [60] Hailian Li, Mohamed Eddaoudi, M. O'Keeffe, and O. M. Yaghi. Design and synthesis of an exceptionally stable and highly porous metal-organic framework. *Nature*, 402(6759):276– 279, Nov 1999.
- [61] Meicheng Wen, Guiying Li, Hongli Liu, Jiangyao Chen, Taicheng An, and Hiromi Yamashita. Metal–organic framework-based nanomaterials for adsorption and photocatalytic degradation of gaseous pollutants: recent progress and challenges. *Environ. Sci.: Nano*, 6:1006–1025, 2019.
- [62] Imteaz Ahmed and Sung Hwa Jhung. Composites of metal–organic frameworks: Preparation and application in adsorption. *Materials Today*, 17(3):136–146, 2014.
- [63] Chao-Yang Wang, Lingshan Ma, Chong-Chen Wang, Peng Wang, Leonardo Gutierrez, and Weiwei Zheng. Light-response adsorption and desorption behaviors of metal–organic frameworks. *Environmental Functional Materials*, 1(1):49–66, 2022.

- [64] Yu Liang, Xiaoxin Yang, Xiaoyu Wang, Zong-Jie Guan, Hang Xing, and Yu Fang. A cage-onmof strategy to coordinatively functionalize mesoporous mofs for manipulating selectivity in adsorption and catalysis. *Nature Communications*, 14(1):5223, Aug 2023.
- [65] Hongjuan Liu, Tianyu Fu, and Yuanbing Mao. Metal–organic framework-based materials for adsorption and detection of uranium(vi) from aqueous solution. ACS Omega, 7(17):14430– 14456, 2022.
- [66] Haiqing Lin and Yifu Ding. Polymeric membranes: chemistry, physics, and applications. *Journal of Polymer Science*, 58(18):2433–2434, 2020.
- [67] C. Martínez and A. Corma. 5.05 zeolites. In Jan Reedijk and Kenneth Poeppelmeier, editors, *Comprehensive Inorganic Chemistry II (Second Edition)*, pages 103–131. Elsevier, Amsterdam, second edition edition, 2013.
- [68] Stuart L. James. Metal-organic frameworks. Chem. Soc. Rev., 32:276–288, 2003.
- [69] Ines M Hönicke, Irena Senkovska, Volodymyr Bon, Igor A Baburin, Nadine Bönisch, Silvia Raschke, Jack D Evans, and Stefan Kaskel. Balancing mechanical stability and ultrahigh porosity in crystalline framework materials. *Angew Chem Int Ed Engl*, 57(42):13780–13783, September 2018.
- [70] Hao Li, Libo Li, Rui-Biao Lin, Wei Zhou, Zhangjing Zhang, Shengchang Xiang, and Banglin Chen. Porous metal-organic frameworks for gas storage and separation: Status and challenges. *EnergyChem*, 1(1):100006, 2019.
- [71] Dalal Alezi, Youssef Belmabkhout, Mikhail Suyetin, Prashant M. Bhatt, Łukasz J. Weseliński, Vera Solovyeva, Karim Adil, Ioannis Spanopoulos, Pantelis N. Trikalitis, Abdul-Hamid Emwas, and Mohamed Eddaoudi. Mof crystal chemistry paving the way to gas storage needs: Aluminum-based soc-mof for ch₄, o₂, and co₂ storage. *Journal of the American Chemical Society*, 137(41):13308–13318, 2015. PMID: 26364990.
- [72] Mohammed Kadhom and Baolin Deng. Metal-organic frameworks (mofs) in water filtration membranes for desalination and other applications. *Applied Materials Today*, 11:219–230, 2018.
- [73] Yutian Duan, Lei Li, Zhiqiang Shen, Jian Cheng, and Kewu He. Engineering metal-organicframework (mof)-based membranes for gas and liquid separation. *Membranes*, 13(5), 2023.
- [74] Claudio Pettinari and Alessia Tombesi. Mofs for electrochemical energy conversion and storage. *Inorganics*, 11(2), 2023.
- [75] Mosaed S. Alhumaimess. Metal–organic frameworks and their catalytic applications. *Journal of Saudi Chemical Society*, 24(6):461–473, 2020.
- [76] Hessamaddin Sohrabi, Shahin Ghasemzadeh, Zahra Ghoreishi, Mir Reza Majidi, Yeojoon Yoon, Nadir Dizge, and Alireza Khataee. Metal-organic frameworks (mof)-based sensors for detection of toxic gases: A review of current status and future prospects. *Materials Chemistry and Physics*, 299:127512, 2023.
- [77] Mao-Lin Hu, Mohammad Yaser Masoomi, and Ali Morsali. Template strategies with mofs. *Coordination Chemistry Reviews*, 387:415–435, 2019.

- [78] Siddharth Gautam and David Cole. CO(2) adsorption in Metal-Organic framework Mg-MOF-74: Effects of Inter-Crystalline space. *Nanomaterials (Basel)*, 10(11), November 2020.
- [79] Da-Ae Yang, Hye-Young Cho, Jun Kim, Seung-Tae Yang, and Wha-Seung Ahn. Co2 capture and conversion using mg-mof-74 prepared by a sonochemical method. *Energy Environ. Sci.*, 5:6465–6473, 2012.
- [80] Ziyu Gao, Lin Liang, Xiao Zhang, Ping Xu, and Jianmin Sun. Facile one-pot synthesis of zn/mg-mof-74 with unsaturated coordination metal centers for efficient co₂ adsorption and conversion to cyclic carbonates. ACS Applied Materials & Interfaces, 13(51):61334–61345, 2021.
- [81] Benny D. Freeman and Ingo Pinnau. Gas and Liquid Separations Using Membranes: An Overview, chapter 1, pages 1–23. 2004.
- [82] Vahid Vatanpour, Mehmet Emin Pasaoglu, Hossein Barzegar, Oğuz Orhun Teber, Recep Kaya, Muhammed Bastug, Alireza Khataee, and Ismail Koyuncu. Cellulose acetate in fabrication of polymeric membranes: A review. *Chemosphere*, 295:133914, 2022.
- [83] O.S. Serbanescu, S.I. Voicu, and V.K. Thakur. Polysulfone functionalized membranes: Properties and challenges. *Materials Today Chemistry*, 17:100302, 2020.
- [84] Yuanhui Tang, Yakai Lin, Wenzhong Ma, and Xiaolin Wang. A review on microporous polyvinylidene fluoride membranes fabricated via thermally induced phase separation for mf/uf application. *Journal of Membrane Science*, 639:119759, 2021.
- [85] Xuemei Tan and Denis Rodrigue. A review on porous polymeric membrane preparation. part i: Production techniques with polysulfone and poly (vinylidene fluoride). *Polymers* (*Basel*), 11(7), July 2019.
- [86] Ranjani V. Siriwardane, Ming-Shing Shen, Edward P. Fisher, and James A. Poston. Adsorption of co₂ on molecular sieves and activated carbon. *Energy & Fuels*, 15(2):279–284, 2001.
- [87] Carmine Colella and Alessandro Gualtieri. Cronstedt's zeolite. Microporous and Mesoporous Materials - MICROPOROUS MESOPOROUS MAT, 105:213–221, October 2007.
- [88] Rolando Roque-Malherbe. Chapter 12 applications of natural zeolites in pollution abatement and industry. In Hari Singh Nalwa, editor, *Handbook of Surfaces and Interfaces of Materials*, pages 495–522. Academic Press, Burlington, 2001.
- [89] Abdul Khaleque, Md Masruck Alam, Mozammel Hoque, Shuvodip Mondal, Jahid Bin Haider, Bentuo Xu, M.A.H. Johir, Aneek Krishna Karmakar, J.L. Zhou, Mohammad Boshir Ahmed, and Mohammad Ali Moni. Zeolite synthesis from low-cost materials and environmental applications: A review. *Environmental Advances*, 2:100019, 2020.
- [90] Matthias Thommes. Chapter 15 textural characterization of zeolites and ordered mesoporous materials by physical adsorption. In Jiří Čejka, Herman van Bekkum, Avelino Corma, and Ferdi Schüth, editors, *Introduction to Zeolite Science and Practice*, volume 168 of *Studies in Surface Science and Catalysis*, pages 495–XIII. Elsevier, 2007.

- [91] Oraib Alketan, Dong-Wook Lee, Reza Rowshan, and Rashid Abu Al-Rub. Functionally graded and multi-morphology sheet tpms lattices: Design, manufacturing, and mechanical properties. *Journal of the Mechanical Behavior of Biomedical Materials*, 102:103520, 11 2019.
- [92] H. A. Schwarz. *Gesammelte Mathematische Abhandlungen*. Springer Berlin Heidelberg, 1890.
- [93] David Hilbert and Stefan Cohn-Vossen. Geometry and the imagination, 1952.
- [94] Efrem Braun, Yongjin Lee, Seyed Mohamad Moosavi, Senja Barthel, Rocio Mercado, Igor A Baburin, Davide M Proserpio, and Berend Smit. Generating carbon schwarzites via zeolite-templating. *Proc Natl Acad Sci U S A*, 115(35):E8116–E8124, August 2018.
- [95] Pawan Boonyoung, Takatoshi Kasukabe, Yasuto Hoshikawa, Ángel Berenguer-Murcia, Diego Cazorla-Amorós, Bundet Boekfa, Hirotomo Nishihara, Takashi Kyotani, and Khanin Nueangnoraj. A simple "nano-templating" method using zeolite y toward the formation of carbon schwarzites. *Frontiers in Materials*, 6, 2019.
- [96] Ming-Wei Wang, Zuoyu Li, Yujian Liu, Wei Jiang, and Zhaohui Wang. Precise synthesis of schwarzite carbon: hypothesis or reality? Org. Chem. Front., 10:2808–2812, 2023.
- [97] Daan Frenkel and Berend Smit. Understanding Molecular Simulation: From Algorithms to Applications. Academic Press, Inc., 1st edition, 1996.
- [98] P.W. Atkins and J. de Paula. *Atkins' Physical Chemistry*. OUP Oxford, 2014. pages 111-112.
- [99] Yanxiang Zhao. Brief introduction to the thermostats. https://home.gwu.edu/ yxzhao/ResearchNotes/ResearchNote007Thermostat.pdf, Accessed January 2024.
- [100] A. K. Rappé, C. J. Casewit, K. S. Colwell, W. A. Goddard III, and W. M. Skiff. Uff, a full periodic table force field for molecular mechanics and molecular dynamics simulations. *J. Phys. Chem*, 1992.
- [101] F.W. Sears and G.L. Salinger. *Thermodynamics, Kinetic Theory, and Statistical Thermody-namics*. Addison-Wesley principles of physics series. Addison-Wesley Publishing Company, 1975. pages 206-210.
- [102] R.K. Pathria. Statistical Mechanics. Elsevier Science, 2016. pages 98-110.
- [103] Weinan E and Dong Li. The andersen thermostat in molecular dynamics. Communications on Pure and Applied Mathematics, 61(1):96–136, 2008.
- [104] H. J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren, A. DiNola, and J. R. Haak. Molecular dynamics with coupling to an external bath. *The Journal of Chemical Physics*, 81(8):3684–3690, 10 1984.
- [105] R. W. Pastor. Techniques and Applications of Langevin Dynamics Simulations, pages 85–138. Springer Netherlands, Dordrecht, 1994.
- [106] Becky L. Eggimann, Amara J. Sunnarborg, Hudson D. Stern, Andrew P. Bliss, and J. Ilja Siepmann. An online parameter and property database for the trappe force field. *Molecular Simulation*, 40:101–105, January 2014.

- [107] Jeffrey J Potoff and J Ilja Siepmann. Vapor–liquid equilibria of mixtures containing alkanes, carbon dioxide, and nitrogen. *AIChE Journal*, 47:1676–1682, 2001.
- [108] Becky L. Eggimann, Yangzesheng Sun, Robert F. DeJaco, Ramanish Singh, Muhammad Ahsan, Tyler R. Josephson, and J. Ilja Siepmann. Assessing the quality of molecular simulations for vapor-liquid equilibria: An analysis of the trappe database. *Journal of Chemical Engineering Data*, 65:1330–1344, March 2020.
- [109] Nicolas F Spycher and Mark H Reed. Fugacity coefficients of h2, co2, ch4, h2o and of h2oco2-ch4 mixtures: A virial equation treatment for moderate pressures and temperatures applicable to calculations of hydrothermal boiling. *Geochimica et Cosmochimica Acta*, 52:739–749, 1988.
- [110] Nicholas Metropolis, Arianna W. Rosenbluth, Marshall N. Rosenbluth, Augusta H. Teller, and Edward Teller. Equation of state calculations by fast computing machines. *The Journal* of Chemical Physics, 21:1087–1092, 6 1953.
- [111] Koichi Momma and Fujio Izumi. Vesta3 for three-dimensional visualization of crystal, volumetric and morphology data. *Journal of Applied Crystallography*, 44:1272–1276, 2011.
- [112] William Humphrey, Andrew Dalke, and Klaus Schulten. Vmd visual molecular dynamics. *Journal of Molecular Graphics*, 14:33–38, 1996.
- [113] Axel Kohlmeyer, Josh Vermaas, and Efrem Braun. akohlmey/topotools: Release 1.8, May 2020.
- [114] Lei Lei, Yan Cheng, Changwei Chen, Mohammadreza Kosari, Zeyu Jiang, and Chi He. Taming structure and modulating carbon dioxide (co2) adsorption isosteric heat of nickelbased metal organic framework (mof-74(ni)) for remarkable co₂ capture. *Journal of Colloid and Interface Science*, 612:132–145, 2022.
- [115] Changwei Chen, Mohammadreza Kosari, Meizan Jing, and Chi He. Microwave-assisted synthesis of bimetallic nico-mof-74 with enhanced open metal site for efficient co₂ capture. *Environmental Functional Materials*, 1(3):253–266, 2022.
- [116] Abhijit Krishna Adhikari and Kuen-Song Lin. Improving co₂ adsorption capacities and co2/n2 separation efficiencies of mof-74(ni, co) by doping palladium-containing activated carbon. *Chemical Engineering Journal*, 284:1348–1360, 2016.