

**COMPARATIVE MOLECULAR DYNAMICS STUDY OF
EQUILIBRIUM AND NON-EQUILIBRIUM APPROACHES IN
COF AND MOF MEMBRANES FOR GAS SEPARATION**



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by
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To my beloved family and husband.



DECLARATION OF ORIGINALITY

I hereby declare that I am the sole author of this thesis and that this is the true copy of my thesis, including the final revisions, approved by my thesis committee. All data and information have been obtained, produced, and presented in accordance with the rules of research ethics and principles of academic honesty. As required by these rules, to the best of my knowledge I have acknowledged ideas, thoughts, and any copyrighted material in accordance with the standard referencing rules. I certify that any part of this thesis has not been submitted for a degree or diploma in another educational institution.

Parivash Jamshidi Ghaleh

ABSTRACT

This thesis study presents a comprehensive investigation of covalent organic frameworks (COFs) and metal organic frameworks (MOFs) as gas separation membranes, using a non-equilibrium approach called concentration gradient-driven molecular dynamics (CGD-MD). First, hydrogen (H_2) and methane (CH_4) flux was simulated through two distinct COF membranes, COF-300 and COF-320, for which experimental data are available in the literature. The results were in strong agreement with the experimental permeability and selectivity values. Leveraging the same methodology, thirteen COFs were screened, revealing promising candidates such as NPN-1 and PCOF-2 for H_2/CH_4 separation. We then compared our findings with simulations utilizing the well-known approach that merges grand canonical Monte Carlo (GCMC) and equilibrium molecular dynamics (EMD) to predict gas adsorption and diffusion parameters in COF membranes. Our results showed that when the pore sizes of COF membranes are below 10 Å, the two methods can give different results. The GCMC+EMD approach predicts CH_4 selectivity, whereas the CGD-MD method indicates H_2 selectivity. It shows that the choice of method is important for evaluating gas transport performance of COF membranes.

In the second part, the pressure-induced amorphization of zeolitic imidazolate framework-8 (ZIF-8) was studied. Simulations showed that the atomic charge assignment models and the presence of guest CH_4 molecules inside the pores, strongly affect the onset and pathway of structural collapse. Different simulation runs with random initial velocities produced different results, highlighting the stochastic nature of the amorphization process. We performed pair distribution function (PDF) $g(r)$ analysis to capture the loss of long-range order during the pressure-induced amorphization of ZIF-8. The crystallinity of ZIF-8 is preserved up to 0.8 GPa, but further pressure increases result in the loss of PDF peaks from approximately 7 to 30 Å, indicating the degradation of long-range order and

the transition to an amorphous state. Incorporating a moderate number of adsorbed CH₄ molecules (≤ 54) into ZIF-8 does not affect the initial amorphization pressure. However, when the number of adsorbed CH₄ molecules increases to a saturated loading (400), the amorphization onset shifts to approximately 1.0 GPa. The CGD-MD method was finally applied to crystalline and created amorphized ZIF-8 membranes for CO₂/CH₄ separation. The crystalline form showed higher permeability for both gases, with 23,380 Barrer for CO₂ and 1,746 Barrer for CH₄. In contrast, the structure obtained at 0.4 GPa (aZIF-8@0.4 GPa) had lower permeabilities of 11,617 Barrer for CO₂ and 591 Barrer for CH₄. Despite this reduction, aZIF-8@0.4 GPa exhibited higher CO₂/CH₄ ideal selectivity (19.65) compared to the crystalline form (13.39). Mean residence time analysis confirmed that CO₂ interacts more strongly and remains longer in the frameworks than CH₄.

In conclusion, this study compares GCMC+EMD and CGD-MD methods for gas transport in porous membranes and shows how amorphization can be used to improve their gas separation performance. These results help to understand the gas transport in porous materials and highlight the value of non-equilibrium simulations for designing future COF and MOF membranes.

Keywords: Concentration gradient-driven molecular dynamics, membranes, gas separation, amorphization, covalent organic framework

ÖZET

Bu tez çalışması, gaz ayrımı amacıyla membran olarak kullanılan kovalent organik yapılar (COF) ve metal organik yapılar (MOF) üzerinde kapsamlı bir moleküler dinamik incelemesini sunmaktadır. Çalışmada, konsantrasyon gradyanına dayalı moleküler dinamik (CGD-MD) yöntemi kullanılmıştır. İlk olarak, literatürde deneysel verileri mevcut olan iki farklı COF membranı, COF-300 ve COF-320 üzerinden hidrojen (H_2) ve metan (CH_4) akışı simüle edilmiştir. Elde edilen sonuçlar, deneysel geçirgenlik ve seçicilik değerleriyle güçlü bir uyum göstermiştir. Aynı yöntem kullanılarak on üç farklı COF daha incelenmiş ve H_2/CH_4 ayrımı için NPN-1 ve PCOF-2 gibi umut verici adaylar belirlenmiştir. Ardından, sonuçlarımız gaz adsorpsiyonu ve difüzyon parametrelerini tahmin etmek için grand kanonik Monte Carlo (GCMC) ve denge moleküler dinamik (EMD) yöntemlerini birleştiren yaklaşım ile karşılaştırılmıştır. Bulgular, COF membranlarının gözenek boyutları 10 Å'nın altına indiğinde iki yöntemin farklı sonuçlar verebildiğini göstermiştir. GCMC+EMD yöntemi CH_4 seçiciliği öngörürken, CGD-MD yöntemi H_2 seçiciliği göstermektedir. Bu durum, COF membranlarının gaz taşınım performansını değerlendirirken seçilen yöntemin önemini ortaya koymaktadır.

Tezin ikinci bölümünde, zeolitik imidazolat yapı-8 (ZIF-8)'in basınca bağlı amorflaşma süreci ayrıntılı olarak incelenmiştir. Simülasyonlar, atomik yük atama modellerinin ve gözeneklerdeki CH_4 misafir moleküllerinin varlığının, yapısal çöküşün başlangıcı ve ilerleyişi üzerinde güçlü bir etkiye sahip olduğunu göstermiştir. Rastgele başlangıç hızlarıyla yapılan farklı simülasyonlar, amorflaşma sürecinin rastlantısal doğasını ortaya koymuştur. ZIF-8'in basınca bağlı amorflaşma sürecinde uzun menzilli düzenin kaybını izlemek için $g(r)$ çift dağılım fonksiyonu (PDF) analizi yapılmıştır. ZIF-8'in kristallliği 0.8 GPa'ya kadar korunmakta, ancak daha yüksek basınçlarda yaklaşık 7–30 Å aralığındaki PDF piklerinin kaybolmasıyla uzun menzilli düzen bozulmakta ve

yapı amorf hale gelmektedir. Orta miktarda adsorbe olmuş CH_4 molekülü (≤ 54) kristalden amorf yapıya geçiş basıncını deęiřtirmezen, yüksek yükleme (400 molekül) durumunda amorflařma bařlangıcının yaklaşık 1.0 GPa'ya kaydığını gözlenmiřtir.

Amorflařma ile elde edilen yapılar kullanılarak CGD-MD yöntemi, kristal ve amorf ZIF-8 membranlarında CO_2/CH_4 ayrımı için uygulanmıřtır. Kristal form, CO_2 için 23.380 Barrer ve CH_4 için 1.746 Barrer olmak üzere daha yüksek geçirgenlik göstermiřtir. Buna karřılık, 0.4 GPa'da elde edilen yapı (aZIF-8@0.4 GPa) CO_2 için 11.617 Barrer ve CH_4 için 591 Barrer geçirgenlik sergilemiřtir. Bu düşüře raęmen, aZIF-8@0.4 GPa'nın CO_2/CH_4 ideal seçicilięi (19.65) kristal forma (13.39) göre daha yüksek bulunmuřtur. Ortalama kalma süresi (MRT) analizi, CO_2 moleküllerinin yapı içinde CH_4 'e kıyasla daha uzun süre kaldığını ve daha güçlü etkileřimler gösterdiğini doęrulamıřtır.

Sonuç olarak, bu çalıřma, gözenekli membranlarda gaz tařınımını incelemek için GCMC+EMD ve CGD-MD yöntemlerini karřılařtırmakta ve amorflařmanın gaz ayırma performansını iyileřtirmek için nasıl kullanılabileceğini göstermektedir. Bu bulgular, gözenekli malzemelerde gaz tařınımının anlaşılmasına katkı saęlamakta ve gelecekteki COF ve MOF membranlarının tasarımı için denge dıřı simülasyonların önemini vurgulamaktadır.

Anahtar Kelimeler: Konsantrasyon gradyanına dayalı moleküler dinamik, membran, gaz ayrımı, amorflařma, kovalent organik yapı

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LIST OF ACRONYMS AND ABBREVIATIONS

MD	Molecular Dynamics
EMD	Equilibrium Molecular Dynamics
NEMD	Non-Equilibrium Molecular Dynamics
CGD-MD	Concentration Gradient-Driven Molecular Dynamics
GCMC	Grand Canonical Monte Carlo
LAMMPS	Large-scale Atomic/Molecular Massively Parallel Simulator
NVT	Canonical Ensemble
NPT	Isothermal–Isobaric Ensemble
μVT	Grand Canonical Ensemble
PLUMED	PLUgin for MolEcular Dynamics
IFR	Inlet Force Region
ICR	Inlet Control Region
ITR	Inlet Transition Region
OFR	Outlet Force Region
OCR	Outlet Control Region
OTR	Outlet Transition Region
ASA	Accessible Surface Area
LCD	Largest Cavity Diameter
PLD	Pore Limiting Diameter
PDF	Pair Distribution Function

MRT	Mean Residence Time
ZIF	Zeolitic Imidazolate Framework
MOF	Metal Organic Framework
COF	Covalent Organic Framework
H₂	Hydrogen
CH₄	Methane
CO₂	Carbon Dioxide
OVITO	Open Visualization Tool
N	Number of Particles
P	Pressure
T	Temperature
V	Volume
LJ	Lennard–Jones
k_B	Boltzmann Constant

1. INTRODUCTION

Membranes have become an essential technology in modern separation processes because of their versatile applications in energy, environmental, and industrial fields. They are widely used in water desalination, wastewater treatment, gas separation, pervaporation, and biomedical applications [4]. Compared to conventional separation techniques, membranes offer several advantages such as compact design, lower energy consumption, modular operation, and reduced environmental impact [5]. Membranes operate without the need for a thermal driving force, making them highly attractive for reducing the substantial energy costs, approximately 90%, associated with separation processes [6]. In recent decades, membrane-based gas separation has gained increasing attention as a sustainable solution for addressing challenges in clean energy production, natural gas upgrading, and carbon capture [7]. Two particularly important industrial applications are hydrogen recovery and natural gas purification, which are discussed in the following section.

1.1 Some industrial gas separation applications

1.1.1 *Hydrogen recovery*

Hydrogen (H_2) is widely recognized as a crucial energy storage medium in fuel cell systems and as an environmentally friendly substitute for fossil fuels in next generation energy applications. It plays a vital role in achieving carbon neutrality and the sustainable development goals of future societies, as it enables electricity generation with only water as a byproduct when utilized in fuel cells [8].

Among various H_2 production methods, approximately 96% of global H_2 is derived from fossil fuels, with steam methane reforming (SMR) being the most prevalent technique [9, 10]. The SMR process, however, produces a mixture that contains not only H_2 but also significant amounts of unreacted methane (CH_4). This highlights the urgent

need for efficient large-scale separation of H_2 and CH_4 . The separation of H_2 from CH_4 remains a considerable challenge due to the close chemical and physical similarities of these molecules. Consequently, the industry continues to invest heavily in the search for new materials and technologies that can achieve efficient and cost-effective H_2/CH_4 separation. This demand is further intensified by the increasing importance of H_2 in meeting the high energy transition and carbon neutrality targets set for the upcoming decades [9, 10].

Membrane-based H_2/CH_4 separation is widely recognized as a practical technology and offers a promising solution with both economic and environmental benefits, including convenient fabrication in compact designs, low energy consumption, ease of operation, and reduced levels of waste products [11, 5]. The development of such systems, however, requires careful material selection. Membrane materials must remain stable under operating conditions, which requires considerable mechanical strength [12].

1.1.2 Natural gas purification

Natural gas is one of the most important energy resources worldwide, but raw natural gas streams often contain a significant fraction of carbon dioxide (CO_2) in addition to CH_4 . The presence of CO_2 reduces the calorific value of natural gas, increases transportation costs, and, when combined with water, causes pipeline corrosion [13, 14]. To ensure safety and quality, natural gas must be treated before entering transmission pipelines. According to U.S. pipeline specifications, the CO_2 concentration must be reduced to less than 2%, with limits of 4 ppm for H_2S and 120 ppm for water [13]. These strict requirements highlight the necessity of efficient CO_2 removal from CH_4 in natural gas processing and upgrading.

Conventional separation methods, such as chemical absorption using amine solutions, are widely applied but are energy-intensive, costly, and environmentally

harmful [15]. Membrane-based separation offers a promising alternative because of its low energy consumption, simple operation, and scalability. For effective CO₂/CH₄ separation, membrane materials must exhibit high separation performance, while maintaining stability under high pressure and acidic conditions. These requirements have motivated the search for novel porous materials that can overcome the limitations of conventional methods [16, 17].

1.2 Performance metrics for membrane-based gas separation

The efficiency of a membrane in gas separation processes is often determined by key properties such as permeability and selectivity. Permeability quantifies the ability of a gas to pass through a membrane material and is typically expressed in Barrer units. High permeability indicates that a membrane can achieve a large gas flux, which is desirable to minimize the required membrane area and reduce total costs [4]. However, high permeability alone is not sufficient, an efficient separation process also requires a membrane to effectively separate different gas species. This is captured by selectivity, which is defined as the ratio of the permeabilities of two gases. Selectivity provides a measure of how well a membrane can separate a target gas (e.g., H₂ or CO₂) from a mixture [11, 7].

A well-known challenge in membrane development is the trade-off between permeability and selectivity (Figure 1.1), often referred to as the Robeson upper bound [3]. This empirical relationship, originally proposed for polymeric membranes, indicates that an increase in permeability is generally accompanied by a decrease in selectivity, and vice versa. The Robeson upper bound has been a central benchmark in the evaluation of new membrane materials, as it highlights the inherent performance limitations of conventional polymers such as polysulfones and polyimides [11, 18]. Inorganic membranes, such as zeolites, have demonstrated the ability to surpass the polymeric performance, offering

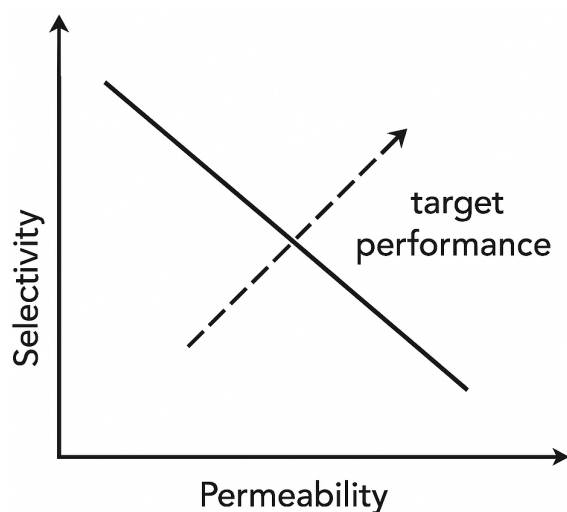


Figure 1.1: Schematic illustration of the trade-off relationship between permeability and selectivity in membrane materials.

higher selectivities and superior thermal and chemical stability. However, their application remains restricted by high synthesis costs and complex fabrication procedures [19]. In recent years, research has increasingly turned toward the crystalline porous materials such as covalent organic frameworks (COFs) and metal organic frameworks (MOFs). These materials offer large surface areas, tunable pores, and chemical versatility, making them attractive candidates to surpass the permeability selectivity trade-off [17, 20]. For instance, several COFs have shown outstanding H_2/CH_4 and CO_2/CH_4 separation performance in both experimental and computational studies, while MOFs such as zeolitic imidazolate frameworks (ZIFs) have been extensively investigated for their stability and selective transport properties [21, 22, 23]. In general, the choice of membrane material plays a decisive role in determining gas separation performance. By optimizing permeability and selectivity, while addressing the constraints posed by the Robeson upper bound, next-generation materials such as COFs and MOFs present promising pathways toward more efficient and scalable membrane-based separation technologies [16].

On the other hand, crystalline MOF structures can lose their ordered structure and

become amorphous when exposed to external stimuli such as pressure, heat, electrical discharge, radiation, or ball milling [24, 25]. During this process, the chemical composition and connectivity of the framework remain intact, but the long-range order and intermolecular interactions are altered [26]. As a result, amorphous MOFs (aMOFs) not only preserve the basic properties of crystalline MOFs but also show additional features such as isotropy, transparency, accessible active sites, and improved flexibility [27].

ZIFs as a subclass of MOFs, are more popular because they combine the tunable porosity of MOFs with the high chemical and thermal stability of zeolites [28]. These features expand their potential in gas storage, separation, and energy-related applications. Among them, ZIF-8 has become a prototypical structure due to its stability and well-characterized framework, making it an excellent model for investigating pressure-induced amorphization [29]. Understanding this process with the help of computational tools is essential, as the presence of confined molecules can significantly influence the mechanical response and phase transition behavior. Therefore, this thesis also provides computational insights into the amorphization of ZIF-8 and complements experimental efforts and contributed to the design of MOFs with improved performance.

In addition to understanding the structural evolution of ZIF-8 under pressure, it is also important to examine how amorphization influences its functional performance in gas separation. Experimental and computational studies have shown that the degree of amorphization can strongly affect pore size distribution, surface area, and framework flexibility, all of which are critical parameters in molecular transport and selectivity [2, 30, 31]. In particular, partially amorphized structures may retain sufficient porosity while introducing structural disorder that modifies diffusion pathways and optimizes separation processes.

1.3 Thesis overview

This thesis consists of three main studies, each addressing different aspects of membrane-based gas separation. The rest of this thesis is organized as follows: In Chapter 2, a comprehensive literature review is provided, covering H_2/CH_4 separation in COF membranes, the pressure-induced amorphization of ZIF membranes, and CO_2/CH_4 separation in amorphous ZIF membranes. Chapter 3 describes the computational methodology, including equilibrium molecular dynamics (EMD) and non-equilibrium molecular dynamics (NEMD) simulations, as well as the structural characterization tools used to analyze porous materials. The first study is reported in Chapter 4, where the H_2/CH_4 separation performance of 13 COF membranes was investigated. In Chapter 5, pressure-induced amorphization of ZIF-8 is explored through atomistic simulations. Chapter 6 extends the NEMD method to investigate CO_2/CH_4 separation in both crystalline and amorphized ZIF-8 structures. Lastly, Chapter 7 summarizes the main conclusions drawn from this thesis and outlines possible future research directions.

2. LITERATURE REVIEW

2.1 H₂/CH₄ separation in COF membranes

COFs are a class of porous crystalline materials composed of light elements such as boron, silicon, carbon, nitrogen, and oxygen linked by strong covalent bonds [32, 33, 34, 35]. They have attracted significant attention as promising membrane candidates for their exceptional structural stability, tunable chemical compositions, large surface areas, and high porosities [36, 37, 38, 39]. For gas separation, the inherently low density of COFs provides several advantages, including enhanced surface area, storage capacity, permeability, and energy efficiency. In addition, their high permeabilities reduce the required membrane area, thereby lowering the overall capital cost, making COFs attractive materials for practical membrane applications [20]. For example, COF-300 was shown to have a high H₂ permeability of 1.1×10^5 Barrer and an ideal H₂/CH₄ selectivity of 3.25 [40]. The COF-320 membrane on porous α -Al₂O₃ exhibited an H₂ permeability of 6.77×10^3 Barrer and an ideal H₂/CH₄ selectivity of 2.83 [41]. Fan et al. [42] synthesized a bilayer COF membrane with a cross-linked pore network, COF-LZU1-ACOF-1, achieving a very high H₂/CH₄ selectivity of 105, outperforming many ZIF membranes. The same group [43] later proposed a MOF-in-COF strategy to control COF pore size by inserting MOF structures inside the COF matrix. On an α -Al₂O₃ substrate, they fabricated a ZIF-67-in-TPPA-1 membrane, consisting of TPPA-1, 1,3,5-triformylbenzene, and *p*-phenylene diamine. This MOF-in-COF membrane exhibited an H₂/CH₄ selectivity of 33.3 and an H₂ permeability of up to 3.9×10^3 Barrer, ranking it among the best membrane materials for H₂ purification. More recently, they developed an LA- α -CD-in-TpPa-1 membrane that enables the passage of H₂ molecules while restricting CH₄ diffusion, thus achieving an H₂ permeability of 4615.95 Barrer and an H₂/CH₄ selectivity of 39.4, outperforming many zeolite, MOF, and graphene

membranes [44]. In another study, composite membranes of COF (TpPa-a) and MXene ($\text{Ti}_3\text{C}_2\text{T}_x$) were fabricated, yielding an H_2 permeability of 136.64 Barrer and an ideal H_2/CH_4 selectivity of 7.34 [45]. Furthermore, Qi et al. [46] employed a “MOF-in/on-COF” pore modification strategy to create a ZIF-67-in-Schiff base-based COF membrane (named the PBD membrane), which exhibited an H_2/CH_4 selectivity of 33.48. Collectively, these experimental efforts have demonstrated that COF membranes hold strong potential for enhancing H_2/CH_4 separation technologies, making them promising candidates for future large-scale gas separation applications.

Given the impracticality of evaluating the performance of a large number of COFs through experimental methods, computational studies are crucial for identifying promising membrane materials. In recent years, such studies have significantly expanded the literature on the potential of COFs as membrane materials. For example, Tong et al. [47] computationally demonstrated that COFs, particularly nitroso polymer networks (NPNs) and COF-1, outperform commonly used zeolites and MOFs in terms of CH_4/H_2 adsorption selectivity. Yang et al. [20] reported that COF-102, COF-103, COF-105, and COF-108 exhibited superior selectivities of 11.7, 14, 28.8, and 33.2, respectively, in membrane-based H_2/CH_4 separation at 10 bar and 298 K, surpassing well-studied MOFs such as IRMOF-1 and Cu-BTC.

Keskin’s group [48] also showed the potential of COFs for H_2/CH_4 separation. By analyzing 572 COFs, they revealed that several highly porous structures displayed a good balance of H_2 permeability ($> 10^5$ Barrer) and H_2/CH_4 selectivities up to 4.6 at 1 bar and 298 K. [49] In another study, the same group examined 589 experimentally synthesized COFs and 120 hypothetical (computer-generated) COFs to assess their potential for He/CH_4 , He/N_2 , H_2/CH_4 , and H_2/N_2 separations [50]. They showed that COFs with large pore limiting diameters (PLDs) ranging from 18 to 45 Å were the most promising for H_2/CH_4 separation, achieving a maximum selectivity of 6.3.

In all these studies, gas permeability data were obtained by combining EMD simulations with grand canonical monte carlo (GCMC) simulations. However, recent findings indicate that using self-diffusion coefficients derived from EMD simulations to calculate gas transport properties can lead to inaccuracies in permselectivity [51], due to the inherent assumptions in this approach. When gas molecules interact weakly, as at low pressures, the GCMC+EMD method, based on the solution–diffusion model, is generally considered more reliable [51]. However, this method neglects possible mass transfer resistance at the membrane surface, as it relies on periodic boundary conditions (PBC) applied to crystalline structures.

Several NEMD strategies have been used for gas transport in MOF and polymer membranes. A classical approach is a pressure-driven scheme that employs an impermeable, movable wall on one side of the membrane to create a pressure gradient and drive flow [52]. This method is not ideal for steady-state membrane studies or mixtures because the feed becomes depleted and the feed composition cannot be controlled during the run [53]. To address these issues, a dual-force-zone NEMD (DFZ-NEMD) technique was introduced, where gentle body forces are applied in two zones to sustain a gradient without depleting the feed [54]. For membrane separations, two methods are widely used. The first is dual control volume grand canonical MD (DCV-GCMD), which couples MD dynamics in the central region to GCMC control cells at the boundaries to fix chemical potentials (or densities), thereby sustaining a concentration gradient across the membrane [55]. The second uses deterministic bias forces (or constant-chemical-potential reservoirs) to keep target concentrations in inlet and outlet control regions, producing a stable gradient without particle insertions/deletions; recent developments include CGD-MD [53]. These approaches have been applied to fluid transport through porous MOF and polymer membranes and provide molecular-level insight into steady-state permeation under experimentally relevant gradients. Motivated by this work, we performed CGD-MD

simulations to analyze gas transport through COF membranes for the first time in the literature, providing realistic insight into their gas transport behavior.

2.2 Pressure-induced amorphization of ZIF membranes

Crystalline ZIFs, can be transformed into amorphous phases through pressure, heat, electrical discharge, radiation, or mechanical ball milling [56, 57, 24]. This process modifies the intermolecular forces and results in new structural features [30, 25]. As a result, amorphous ZIFs show isotropy, transparency, and enhanced flexibility compared to their crystalline counterparts, expanding their applications in gas storage [58, 59], energy storage [60], selective gas separation [61, 2], toxin capture [57], and drug delivery [62, 63]. These applications often rely on reversible, irreversible, or semi-crystalline to amorphous phase transitions.

ZIFs, constructed from tetrahedrally coordinated metal centers and imidazolate-based linkers, are particularly attractive because they can amorphize under experimentally accessible conditions. For example, ZIF-4 amorphizes under low pressures (~ 0.35 GPa) in the absence of solvent, while the introduction of guest molecules such as DMF increases the critical pressure for amorphization [64, 57]. ZIF-8 has become the most studied system due to its high thermal stability in both aqueous and nonaqueous environments [65, 29]. Experimental studies have shown that amorphization of ZIF-8 can either be delayed or accelerated by the presence of guest molecules, highlighting the importance of host–guest interactions [66, 67]. On the computational side, Coudert and co-workers [68] demonstrated that the shear modulus of crystalline zeolitic imidazolate framework-8 (cryZIF-8) decreases progressively during amorphization, with confined CH_4 molecules delaying the onset pressure. Quantum mechanical calculations further revealed a link between shear instability and asymmetric “gate-opening” motions of imidazolate linkers [69]. Ab initio MD simulations have suggested that the compressive

strength of cryZIF-8 is about 50% lower than its tensile strength, while the electronic properties remain unaltered due to the insulating nature of the linkers [70].

2.3 CO₂/CH₄ separation in ZIF membranes

ZIFs are attractive porous frameworks for membrane based CO₂/CH₄ separation [65, 71]. To overcome the limits of crystalline ZIFs, recent research has focused on amorphous and glassy ZIFs [72]. These materials retain many properties of crystalline ZIFs while adding features of glasses, such as isotropy and higher flexibility [72]. Ma et al. [2] showed that ZIF-8 becomes amorphous under 0.75 GPa pressure and reported a CO₂/CH₄ ideal selectivity of 16.23 and a CO₂ permability of 625.45 Barrer. Bennett et al.[73] studied glasses ZIF-62 and their gas transport properties, showing that disordered frameworks can maintain favorable diffusion paths. These findings show that amorphization can be an effective way to tune molecular transport in ZIF membranes and support further studies on their separation performance. Motivated by this work, Mahdavi et al. [74] developed a self-supporting amorphous ZIF-62 membrane with a CO₂/CH₄ selectivity of 64.1, and permeabilities of 146 and 2.28 Barrer for CO₂ and CH₄, respectively, placing it on the Robeson upper bound 2015 [75]. These findings show that amorphization can be an effective way to tune molecular transport in ZIF membranes and support further studies on their separation performance.

In addition to pure ZIF membranes, efforts have been made to surpass Robeson's upper-bound limit by incorporating ZIFs into polymer matrices, forming mixed matrix membranes (MMMs) [76]. ZIF-based MMMs combine the selectivity of ZIF frameworks with the processability of polymers, resulting in hybrid membranes that outperform both components individually [77, 78]. For instance, a ZIF-8/PIM-1 MMM containing 67.2% ZIF-8 achieved a CO₂ permeability of 6338 Barrer and a CO₂/CH₄ selectivity of 18.8 at 35 °C and 3.5 bar, significantly exceeding the performance of the corresponding pure

PIM-1, which exhibited 3874 Barrer permeability and 17.6 selectivity [79]. Feng et al. [80] further improved this concept by developing an amorphous ZIF-62/PIM-1 membrane through in-situ thermal treatment. The resulting amorphous ZIF-62/PIM-30% membrane displayed a remarkable CO₂/CH₄ selectivity of 67 and CO₂ permeability of 5914 Barrer, highlighting the potential of structural disorder to enhance gas separation in MMMs.

Computational studies have also contributed to understanding the separation performance of ZIF-based membranes. Atci and Keskin [81] performed GCMC+EMD simulations on ten ZIF structures at room temperature and 10 bar, reporting CO₂/CH₄ permeation selectivities ranging from 0.5 to 22.3. Their findings revealed that CO₂ molecules exhibit strong preferential adsorption over CH₄, primarily due to electrostatic interactions between CO₂ and the framework atoms. These computational insights complement experimental results and provide a molecular-level understanding of how framework chemistry and topology govern gas transport in both crystalline and amorphous ZIF membranes. Demir et al.[82] provided a broader perspective on MOF and MOF-composite membranes for CO₂ capture, highlighting strategies for integrating MOFs into polymer matrices to enhance selectivity and stability. In their review, they report that many MOF-polymer membranes achieve CO₂/CH₄ selectivities in the 20–50 range, while CO₂ permeabilities mainly fall between 100 and 1000 Barrer depending on MOF type and loading. They also discussed cases where functionalizing MOFs or improving polymer–MOF interface adhesion led to selectivity increases of 10 to 30 % over unmodified composites. These computational insights complement the experimental results and provide a molecular-level understanding of how framework chemistry and topology govern gas transport in both crystalline and amorphous ZIF membranes.

3. COMPUTATIONAL METHODOLOGY

3.1 Software and packages

All simulations in this thesis were conducted using a combination of well established open-source software packages. Molecular dynamics (MD) simulations were performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [83], which is widely used for classical atomistic simulations of materials under both equilibrium and non-equilibrium conditions. For the adsorption studies and the initialization of gas molecules within porous frameworks, the RASPA2 simulation package [84] was used. RASPA provides adsorption isotherms, and loading estimations for gases in porous materials. To calculate geometry-based structural descriptors of porous materials, such as the pore limiting diameter (PLD), the largest cavity diameter (LCD), the accessible surface area (ASA), and accessible pore volume, zeo++ software (version 0.3) [85] was used. The Packmol package (version 20.14.2) [86] was used to generate non-overlapping initial positions of gas molecules. Finally, to implement bias forces required in NEMD simulations, particularly in the CGD-MD approach, the plugin for molecular dynamics (PLUMED) plugin (version 2.9.0) [87] was combined with LAMMPS. For visualization of simulation trajectories and structural changes, Open Visualization Tool (OVITO) [88] and Crystal Maker software [89] were employed. Post-processing analysis, including density analysis, mean residence time (MRT) calculations, pair distribution function (PDF) evaluations, and additional data processing, were performed using Python Programming Language [90]. These software tools form a robust computational framework for modeling, analyzing, and visualizing the structural, thermodynamic, and transport properties of materials.

3.2 Molecular simulations

Molecular simulations provide a framework to bridge the microscopic behavior of atoms and molecules with the macroscopic thermodynamic properties observed in experiments. This connection is established through statistical mechanics, which describes a system in terms of *macrostates* and *microstates*. A macrostate is defined by a set of thermodynamic variables, such as the number of particles (N), volume (V), temperature (T), and pressure (P). Each macrostate corresponds to a large number of microstates, where a microstate i is specified by the complete set of positions and momenta of all particles. Every microstate has an associated energy E_i [91, 92, 93, 94].

3.2.1 Statistical ensembles

The choice of a statistical ensemble determines how the system is simulated under specific thermodynamic conditions. In this study, three ensembles were primarily used. The canonical ensemble (NVT) maintains constant N, V, and T. The isothermal–isobaric ensemble (NPT) maintains constant N, P, and T, while allowing V to change, and the grand canonical ensemble (μ VT) considers constant chemical potential (μ), V, and T.

The central quantity in statistical mechanics is *partition function*, which links microscopic states with macroscopic observables. For an NVT ensemble with discrete E_i , the partition function is as follows:

$$Z = \sum_i e^{-E_i/k_B T} \quad (3.1)$$

where k_B is the Boltzmann constant ($1.380\,6452 \times 10^{-23} \text{ J K}^{-1}$) and T is the absolute temperature. For continuous systems, the summation is replaced by an integration over the entire phase space:

$$Z = \frac{1}{N!h^{3N}} \int d^N r d^N p e^{-E(r,p)/k_B T} \quad (3.2)$$

Here, h is Planck's constant, included to ensure the correct normalization of phase space in accordance with quantum mechanics. The $N!$ account for the indistinguishability of the particles, preventing overcounting identical configurations. $d^N r$ and $d^N p$ represent integrations over all possible positions and momenta of the N particles in the system. The variable r denotes the position coordinates of all atoms, while p corresponds to their respective momenta. Together, r and p define the full phase space of the system, which includes all possible microscopic states that the particles can occupy [91].

3.2.2 Interaction potentials

The total energy of a molecular system includes both kinetic and potential contributions. The kinetic energy is associated with particle motion, while the potential energy arises from the intermolecular and intramolecular interactions.

The non-bonded van der Waals forces were modeled using the classical 12–6 Lennard–Jones (LJ) potential [95]:

$$U^{\text{LJ}}(r_{ij}) = 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] \quad (3.3)$$

where ε defines the potential well depth and reflects the strength of the attractive interaction and σ corresponds to the finite distance at which the interparticle potential becomes zero. The variable r_{ij} denotes the distance from the center of one particle i to other j . 12-term and 6-term correspond to repulsive and attractive part of the LJ potential, respectively.

Electrostatic interactions were described using the Coulomb potential [91]:

$$U^{\text{Coulombic}}(r_{ij}) = \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j}{r_{ij}} \quad (3.4)$$

Where q_i and q_j are the charges of the particles i and j , r_{ij} is their separation distance, and ε_0 is the vacuum permittivity.

The mixed interaction parameters between nonsimilar particles were determined using an additional approximation named the Lorentz–Berthelot mixing rules [96, 97]:

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}, \quad \varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \quad (3.5)$$

The interactions between bonded atoms were represented as intramolecular contributions to the total potential energy, in our models we used following terms (Equation 3.6) [91]:

$$U^{\text{bonded}} = \sum_{\text{bonds}} u_b(r) + \sum_{\text{bends}} u_\theta(\theta) + \sum_{\text{torsion}} u_\phi(\phi) + \sum_{\text{improper}} u_\chi(\chi) \quad (3.6)$$

In Equation 3.6, the first term corresponds to the bond stretching energy between two bonded atoms. The second term represents the angle bending energy involving three bonded atoms. The third term accounts for torsional (dihedral) interactions among four bonded atoms, and the final term describes improper torsions, which are used to maintain planarity or chirality in certain molecular groups.

For Equations 3.3, 3.4, and 3.6, pre-defined parameters are required. These parameter sets are commonly referred to as “force fields”. The overall potential energy of a system is expressed as a combination of bonded and non-bonded interactions [91].

$$U^{\text{total}} = U^{\text{bonded}} + U^{\text{LJ}} + U^{\text{Coulombic}} \quad (3.7)$$

At the molecular scale, the most widely applied approaches for materials modelling are Monte Carlo (MC) and MD simulations. The MC technique is based on probabilistic sampling and is mainly employed to evaluate equilibrium properties of materials. In contrast, MD follows a deterministic scheme, where the equations of motion for all

particles are integrated to capture the microscopic system dynamics. Both techniques are rooted in statistical mechanics, yet they differ in philosophy: MC emphasizes sampling of configuration space, whereas MD generates trajectories governed by Newtonian mechanics [92].

3.2.3 *Molecular dynamics (MD) simulations*

In MD, atoms and molecules are treated as classical particles whose motion is governed by Newton's laws [94]. The force between particles i and j is obtained as:

$$f_{ij} = -\frac{\partial u_{ij}}{\partial r_{ij}} \quad (3.8)$$

Where u_{ij} is the pair potential and r_{ij} is the interatomic distance. Once the forces acting on each atom are calculated, Newton's second law is numerically integrated to update the velocities and positions of all atoms.

$$m \frac{d^2 r}{dt^2} = f \quad (3.9)$$

In this work, the Leap-Frog algorithm was employed to integrate the equations of motion. The method updates the velocity and position of each particle as follows:

$$v(t + \frac{1}{2}\Delta t) = v(t - \frac{1}{2}\Delta t) + \Delta t \frac{f(t)}{m} \quad (3.10)$$

$$r(t + \Delta t) = r(t) + \Delta t v(t + \frac{1}{2}\Delta t) \quad (3.11)$$

Where Δt is the time step. The Leap-Frog scheme is an explicit integration method that provides good energy conservation and numerical stability over long simulation times. The integration works as follows: at each step, the velocities are first updated by half a time step using the current forces. Then, these velocities are used to propagate the particle positions over a full timestep. Finally, the new forces are computed from the updated

positions and the cycle repeats. In this way, positions and velocities “leapfrog” over each other in time [98]. By iterating this procedure, MD simulations generate trajectories that describe the temporal evolution of the system. From these trajectories, thermodynamic observables such as temperature and pressure can be computed as time averages [94].

All MD simulations in this thesis were performed using the LAMMPS package [83]. Initial configurations were provided as Cartesian coordinates (x, y, z) , and initial velocities were assigned randomly from a Maxwell–Boltzmann distribution [99] (Eq.(3.12)). These velocities are generated through a pseudorandom-number sequence in LAMMPS, initialized by a user-defined seed value. In this way, the canonical ensemble is sampled correctly, while every trajectory can be reproduced exactly [100].

$$f(v) = \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} 4\pi v^2 e^{-\frac{mv^2}{2k_B T}} \quad (3.12)$$

During simulations, LAMMPS computes thermodynamic quantities such as pressure, temperature, and energy [94]. Pressure is obtained from the virial equation:

$$P = \frac{Nk_B T}{V} + \frac{1}{dV} \sum_{i=1}^N \mathbf{r}_i \cdot \mathbf{f}_i \quad (3.13)$$

The temperature follows from the equipartition theorem:

$$T = \frac{2E_K}{N_{\text{DOF}} k_B} \quad (3.14)$$

Where the kinetic energy is

$$E_K = \sum_{i=1}^N \frac{1}{2} m_i v_i^2 \quad (3.15)$$

and the active degree of freedom (N_{DOF}) is

$$N_{\text{DOF}} = dN - d - N_{\text{fix DOF}} \quad (3.16)$$

Here, d is the dimensionality, dN is the total number of degrees of freedom for N particles, and $N_{\text{fix DOF}}$ accounts for atoms whose motion is constrained (e.g., frozen atoms, rigid bonds, or center-of-mass motion removed by thermostats). The subtraction of d reflects the fact that the system's overall translational motion in d dimensions does not contribute to thermal fluctuations. In practice, this correction ensures that temperature reflects only the internal motions of the system rather than including collective drift. The total energy of the system is finally expressed as the sum of kinetic and potential contributions.

3.2.4 Monte carlo (MC) simulations

The MC method is a stochastic, time independent approach that is widely employed to evaluate the equilibrium properties of materials [93]. The definition of the partition function was introduced in Eq. 3.1. In classical statistical mechanics, the ensemble average of an observable A can be written as

$$\langle A \rangle = \frac{\sum_i A_i e^{-E_i/k_B T}}{\sum_i e^{-E_i/k_B T}} \quad (3.17)$$

for a system with discrete levels E_i .

When the system possesses a continuous energy spectrum, the summations in Eq. 3.17 are replaced by integrals, and the energy is described by the Hamiltonian. Since the Hamiltonian depends on both positions and momenta, the integration must be carried out over all coordinates $\mathbf{r}$ and momenta $\mathbf{p}$. The momentum integration can be performed analytically because of the quadratic dependence of the kinetic energy on momentum. However, the integration over positional coordinates is far more challenging due to the complex functional form of the potential energy. If the observable A depends only on particle positions, Eq. 3.17 reduces to:

$$\langle A \rangle = \frac{\int d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N e^{-U(\mathbf{r}_1, \dots, \mathbf{r}_N)/k_B T} A(\mathbf{r}_1, \dots, \mathbf{r}_N)}{\int d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N e^{-U(\mathbf{r}_1, \dots, \mathbf{r}_N)/k_B T}} \quad (3.18)$$

For systems with many particles ($N > 100$) and complicated potential energy

functions, the direct computation of the partition function becomes intractable [92]. The MC method offers an efficient alternative by approximating these integrals through statistical sampling. The algorithm explores phase space by applying random moves to the system configuration. At each step, the energy difference between the trial configuration and the current one, ΔU , is evaluated, and the associated Boltzmann factor $e^{-\Delta U/(k_B T)}$ is computed. This factor is then used to decide whether the new configuration is accepted or rejected. The type of statistical ensemble determines the set of possible random trial moves, which may include particle insertion, deletion, translation, or rotation. Each of these moves alters the system configuration and can lead to fluctuations in total energy. At the end of each trial, the move is either accepted or rejected according to the chosen acceptance criterion [93].

3.2.4.1 Grand canonical monte carlo (GCMC) simulations

To estimate the number of adsorbed gas molecules, GCMC simulations were employed under the $(\mu V, T)$ ensemble, where the volume (V), temperature (T), and chemical potential (μ) are fixed. In this ensemble, the total energy of the system and the number of adsorbed molecules (N) fluctuate. At equilibrium, the chemical potential and temperature of the adsorbate inside the porous framework are equal to those of the external reservoir. Although pressure is not explicitly controlled in this formulation, it can be related to the chemical potential or fugacity via an appropriate equation of state. The equilibrium loading is then obtained by averaging over the ensemble configurations generated in the simulation, which can be directly compared to experimental adsorption data such as gravimetric or volumetric measurements [101].

Within the grand canonical ensemble, trial moves include molecular translations, rotations, insertions, and deletions for single-component systems. The acceptance probability for a translational or rotational displacement is expressed as:

$$P = \min [1, e^{-\Delta U/(k_B T)}] \quad (3.19)$$

Where ΔU represents the change in potential energy. A move is accepted if $\Delta U < 0$ or if the Boltzmann factor $e^{-\Delta U/(k_B T)}$ exceeds a random number uniformly chosen between 0 and 1.

For insertion moves, a particle is randomly placed in the system, and the acceptance probability is given by:

$$P = \min \left[1, \frac{fV}{(N+1)k_B T} e^{-\Delta U/(k_B T)} \right] \quad (3.20)$$

where f denotes the fugacity of the adsorbate.

In the case of deletion moves, where a randomly selected particle is removed from the system, the acceptance probability becomes:

$$P = \min \left[1, \frac{Nk_B T}{fV} e^{-\Delta U/(k_B T)} \right] \quad (3.21)$$

For multicomponent systems, an additional identity-exchange move is introduced, where a particle of type i is converted into type j . The acceptance probability for this trial is:

$$P = \min \left[1, \frac{f_j N_i}{f_i (N_j + 1)} e^{-\Delta U/(k_B T)} \right] \quad (3.22)$$

where N_i and N_j represent the number of molecules of components i and j , respectively.

In practice, the overall acceptance rate of MC moves is maintained between 0.4 and 0.5 to ensure efficient sampling [101]. Each GCMC calculation is performed in three distinct phases: initialization, equilibration, and production. In this work, 5×10^4 cycles were used for initialization, another 5×10^4 cycles for equilibration, and 1×10^5 cycles for collecting ensemble averages. Because framework flexibility has a much greater impact

on transport and diffusion properties than on adsorption, atomic structures was treated as rigid during the GCMC simulations in order to reduce computational cost [102, 103].

3.3 Non-Equilibrium MD simulations

Transport of fluids through membranes is inherently a non-equilibrium process, because a flux arises only when intensive variables (concentration, pressure, temperature) differ across the membrane [104, 105]. In NEMD, such driving forces are imposed explicitly, and the system is evolved to a steady state where time-averaged fluxes and gradients can be related by transport laws [106]. A key advantage of NEMD over equilibrium MD is that permeabilities are obtained *directly* from the simulated flux and applied gradient, while naturally accounting for mass transfer resistance in the bulk and pore entrance effects that are often missed by equilibrium MD methods [104, 105].

3.3.1 Concentration Gradient-Driven Molecular Dynamics (CGD-MD)

In the CGD-MD framework [53], the membrane was placed in the center of a simulation box, with dimensions that corresponded to the size of the membrane in the x and y directions, while extending the vacuum (100 Å) in the z direction from each side. Two control regions are defined: the Inlet Control Region (ICR), placed on the feed side, and the Outlet Control Region (OCR), located on the permeate side of the membrane (see Figure 3.1). These control regions are separated from the membrane by two transition zones, Inlet Transition Region (ITR) and the Outlet Transition Region (OTR).

The concentrations within ICR and OCR are regulated by external biasing forces acting on fluid molecules. These forces are located in two narrow regions called the Inlet Force Region (IFR) and the Outlet Force Region (OFR). The bias acts perpendicular to the membrane plane, controlling molecular flux through IFR and OFR, thereby enforcing the desired concentrations in ICR and OCR.

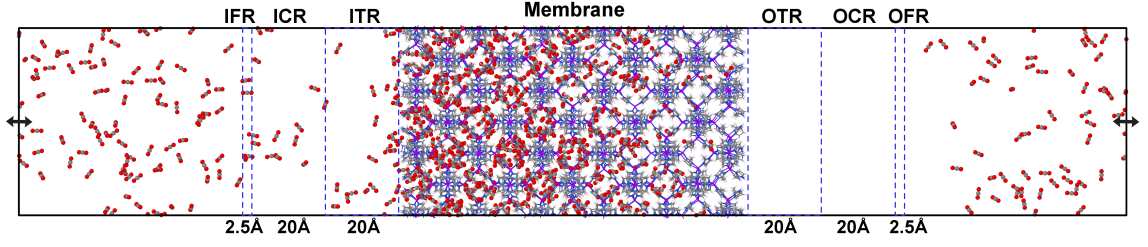


Figure 3.1: Representation of the simulation setup in the CGD-MD method. The black rectangular shows the boundaries of the simulation box. Due to PBC, gas molecules exhibit unrestricted movement between opposing sides of the membrane (showed with two-way arrows). Carbon, nitrogen, zinc, oxygen, and hydrogen atoms are shown in gray, blue, purple, red and white, respectively.

The biased forces were applied using a modified version of the PLUMED 2.9.0 plugin [87]. The applied forces on a particle i are expressed as:

$$F_i^I = k_i^I (n_{i,T,I} - n_{i,ICR}) G_I(z - Z_F^I, w) \quad (3.23)$$

$$F_i^O = k_i^O (n_{i,T,O} - n_{i,OCR}) G_O(z - Z_F^O, w) \quad (3.24)$$

where the superscripts I and O denote the inlet and outlet, respectively. The parameters k_i^I and k_i^O are force constants that determine the strength of the applied bias. $n_{i,T,I}$ and $n_{i,T,O}$ correspond to the target concentrations for the feed and permeate sides, while $n_{i,ICR}$ and $n_{i,OCR}$ represent the instantaneous concentrations within the control regions. G_I and G_O are bell-shaped functions characterized by a width w , centered at Z_F^I and Z_F^O , which define the z -coordinates of IFR and OFR, respectively [53]. In all simulations, the target concentration in the OCR was set to zero to create a vacuum effect on the permeate side. It should be noted that creating a vacuum in membrane MD simulations is not easy. To achieve this effect, the k_i^O was set higher than the k_i^I . The widths of the ICR, the OCR, the ITR, and the OTR were maintained at 20 Å, while the widths of the IFR and OFR were set at 2.5 Å.

The instantaneous concentration of species i in a control region (CR) is computed as:

$$n_i^{CR} = \frac{1}{V_{CR}} \sum_{j=1}^{N_i} \theta(z_j) \quad (3.25)$$

Where V_{CR} denotes the volume of the control region, N_i is the number of molecules of species i in the system, and $\theta(z_j)$ is a selection function defined as:

$$\theta(z_j) = \begin{cases} 1 & \text{if } z_j \in CR \\ 0 & \text{otherwise} \end{cases} \quad (3.26)$$

Here, z_j is the z -coordinate of the j -th molecule. The bias force F_i adapts dynamically depending on the deviation from the target density. If the instantaneous concentration exceeds the target, molecules are repelled toward the bulk; if it falls below, molecules are attracted from the bulk into the control region.

Finally, to establish a steady concentration gradient, periodic boundary conditions are applied along the transport (z) direction. This ensures that molecules permeating through the membrane re-enter from the opposite side, sustaining a continuous flux and allowing the system to reach steady state. CGD-MD simulations were performed using LAMMPS [83] software with the NVT ensemble framework. The temperature was adjusted using the Nosé–Hoover thermostat to hold constant, and separate thermostats were used for each gas in the mixture simulations and for structure to prevent asymmetric thermalization due to hot solute–cold solvent effect [107]. The initial determination of the number of gas molecules required for the simulation setup was carried out using an estimation process based on the GCMC ensemble applied to the Membranes. To apply this procedure, we performed GCMC simulations at room temperature and a pressure equivalent to the average of the target pressures within the ICR and OCR, using the RASPA2 [84] simulation package. The number of gas molecules was incrementally

adjusted to achieve the desired pressure within the specified control regions.

3.3.2 Gas flux, permeability, and selectivity calculations

The measurement of gas flux through a membrane was determined by counting the net number of gas molecules that cross a xy -plane within the membrane. This plane is aligned orthogonally to the z -direction and located at the center of the membrane. By dividing this net molecule count by the product of the cross-sectional area (A_{xy}) and the time interval (t), we obtain the gas flux (J_z):

$$J_z = \frac{N_z^+ - N_z^-}{tA_{xy}} \quad (3.27)$$

Where N_z^+ and N_z^- represent the number of molecules crossing the xy -plane in the positive and negative z -direction, respectively.

The permeability (Π) of the gas was calculated by the equation [108]

$$\Pi = \frac{J_z}{\Delta P/l_m} \quad (3.28)$$

Where ΔP is the fluid's pressure difference between ICR and OCR regions, which was estimated through the pressure/density data from the NIST database [109], corresponding to the concentration difference of these two regions, and l_m denotes membrane thickness in the z -direction.

Selectivity of one gas over another was calculated according to the following formula:

$$S_{i/j} = \frac{\Pi_i}{\Pi_j} \quad (3.29)$$

This formula was applied to both single and mixture component separations to determine the ideal selectivity and the mixture selectivity.

3.4 Structural characterization

3.4.1 Materials

In this thesis, two types of materials were studied: COF and ZIF structures. In Chapter 4, a total of 13 COF structures were selected to investigate H₂/CH₄ separation. The COF structures used in this study were obtained from the CURATED-COF database [110], and the following COFs were considered:

COF-300, an imine-linked tetraphenyl methane and phenyl polymer network [111]; COF-320, an imine-linked tetraphenyl methane and biphenyl polymer network [112]; COF-303, an imine-linked tetraphenyl methane and phenyl polymer network [113]; COF-921, an abenzo[1,2-d:4,5-d']bis(thiazole) linked 1,3,6,8-tetraphenyl pyrene polymer network [114]; 3D-Por-COF, a tetraphenyl methane and tetrakis(4-methyl benzene)-porphyrin polymer network [115]; NPN-1, an azodioxy-linked tetraphenyl methane polymer network [116]; NPN-2, an azodioxy-linked tetraphenyl silane polymer network [116]; NPN-3, an azodioxy-linked tetraphenyl adamantane polymer network [116]; TPE-COF-I, an imine-linked tetraphenyl ethene polymer network [117]; COF-IMAA, a 2,5-dimethoxy benzene linked 3,5-bis(4-(imidazol-1-yl)quinolin-6-yl)-1,1'-biphenyl polymer network [118]; DMTA-TPB2, a tetraphenyl methane and 1,4-dimethoxy-2,5-dimethyl benzene polymer network [119]; TfpBDH, a pyromellitic diimide-linked 1,3,5-tris(4-methyl phenyl) benzene polymer network [120]; and PCOF-2, a 3,3',5,5'-tetrakis(4-methyl phenyl) bimesityl linked 5,10,15,20-tetra (4-aminobiphenyl) porphyrin polymer network [121]. These COFs provide a diverse set of pore sizes, linkages, and functionalities.

In Chapter 5, an atomistic model of a ZIF named ZIF-8 was employed, obtained from the Cambridge Structural Database (CSD) under the OFERUN reference code (CSD entry number: 652032) [122]. ZIF-8 is a zinc(II) 2-methylimidazolate framework composed of tetrahedrally coordinated Zn²⁺ centers linked by 2-methylimidazolate (Im)

ligands, forming a sodalite-type porous network. ZIF-8 was subjected to pressure-induced amorphization, as described in Chapter 5. The amorphous models were generated through MD simulations in which the crystalline framework was compressed until long-range order was lost, while preserving the primary metal–ligand units. We obtained several structures from each pressure steps applied, with altered pore size distributions and framework flexibilities. Subsequently, these models were used in Chapter 6 to provide information on how structural disorder impacts CO₂/CH₄ separation performance.

3.4.2 *Geometry-based characterization*

The structural characterization of COFs and MOFs was performed using the Zeo++ software package (version 0.3) [85]. Zeo++ is a geometry-based analysis tool that employs Voronoi decomposition and MC sampling to evaluate the pore structure and accessible surface area of crystalline porous materials. In this method, the framework is represented as a set of hard spheres, with atom-specific radii defined by the van der Waals parameters. By rolling a spherical probe of a given radius through the framework, Zeo++ identifies the accessible regions and determines several key structural properties.

The pore limiting diameter (PLD) is defined as the diameter of the largest spherical probe that can percolate continuously through the framework, providing an estimate of the size-selectivity limit of the material. The largest cavity diameter (LCD) corresponds to the diameter of the largest sphere that can fit within the pores, indicating the maximum cavity size. The accessible surface area (ASA) is calculated by rolling the probe along the framework surface and averaging over multiple random insertions using MC sampling, while the accessible pore volume or porosity is obtained as the fraction of the total unit cell volume that is accessible to the probe. The choice of probe radius is particularly important for determining the accessible volume and surface area. In this study, a probe radius equivalent to the kinetic diameter of nitrogen (1.86 Å) was employed, consistent with

standard practice for surface area analysis. MC sampling with up to 5×10^4 trial insertions was used to ensure convergence of ASA and porosity calculations. These descriptors provide a quantitative measure of porous structure and connectivity, which are essential for correlating framework topology with adsorption and diffusion behavior.

3.4.3 *Pair distribution function (PDF)*

In MD simulations, the pair distribution function (PDF) $g(r)$ is calculated by counting the number of atom pairs whose separations lie within specified distance bins. The resulting histogram is normalized with the average number density of the system and yields the average atomic density distribution as a function of radial distance. The general mathematical formula is given by:

$$g(r) = \frac{dN}{4\pi r^2 \rho dr} \quad (3.30)$$

Where dN is the average number of atoms located in a spherical shell of thickness dr at a distance r from the reference atom, and ρ is the average number density of the system. In crystalline solids, the PDF curve typically displays sharp peaks corresponding to characteristic interatomic distances repeated throughout the lattice. We computed the partial PDF using a bin size of $0.05 \text{ \AA}$, based on the atomistic coordinates of the structures, as processed in CrystalMaker software [89]. The $g(r)$ analysis provides insights into the local structure by describing how atoms are distributed around a reference atom [123]. Mathematically, it is defined as the ratio of the local particle density at a distance r from a reference atom, $\rho(r)$, to the average particle density, ρ_0 , in the system:

$$g(r) = \frac{\rho(r)}{\rho_0} \quad (3.31)$$

4. COMPREHENSIVE STUDY OF H₂/CH₄ SEPARATION IN COF MEMBRANES

The results given in this chapter were published with the following reference:¹

4.1 Motivation

In this chapter, we investigated COF membranes for H₂/CH₄ separation, leveraging advanced molecular simulations to provide predictive insight into their performance. For the first time in the literature, we employed CGD-MD simulations to directly analyze gas transport through COF membranes under non-equilibrium conditions, thereby offering a more realistic description of gas permeation. Our results were compared with experimental data and showed good agreement, confirming the reliability of this approach. We further compared our findings with the widely used equilibrium strategy that combines GCMC and EMD to estimate adsorption and diffusion parameters in COFs. The comparison revealed that when the pore sizes of COF membranes are below 10 Å, the choice of simulation method strongly influences the predicted separation performance: while the GCMC+EMD approach suggests CH₄ selectivity, the CGD-MD simulations reveal a preference for H₂. This demonstrates that the evaluation of membrane performance critically depends on whether equilibrium or non-equilibrium methods are used, highlighting the importance of systematically comparing both approaches in molecular-level studies of gas separation.

4.2 Simulation details

We employed the CGD-MD approach to simulate steady-state transport of H₂ and CH₄ across 13 distinct COF membranes. The overall computational workflow is

¹Jamshidi Ghaleh, P., Haslak, Z. P., Batyrow, M., & Erucar, I. (2025). Harnessing Pore Size in COF Membranes: A Concentration Gradient-Driven Molecular Dynamics Study on Enhanced H₂/CH₄ Separation. *ACS Applied Materials & Interfaces*, 17(10), 15372–15384.

illustrated in Figure 4.1. At first, single-component H_2 and CH_4 flux on COF-300 and COF-320 were computed to validate the method with experimental results. To model the supercells, the unit cells of COF structures were expanded using the LAMMPS-interface package [124]. For example, COF-300 was replicated in a $2 \times 2 \times 5$ configuration in the x, y, and z directions, respectively. This was done to achieve a reasonable size and ensure that enough particles were present to accommodate the guest molecules responsible for creating pressure on the surface of the membrane. Detailed information on the simulation box sizes and the structural properties of the COF membranes investigated in this work is summarized in Table A.1 provided in the appendix.

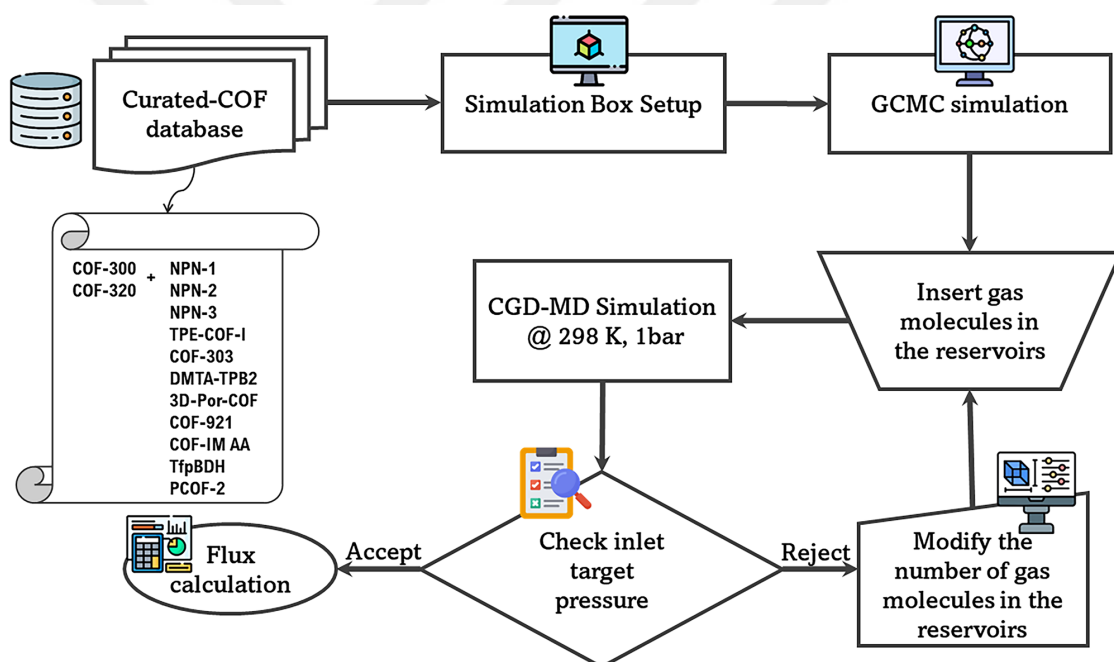


Figure 4.1: Schematic representation of the simulation procedure used in this work.

We used the universal force field (UFF) [125] in our simulations. k_i^I and k_i^O force constants were set to 15,000 and 50,000 $\text{kJ nm}^3 \text{mol}^{-1}$, respectively [51]. The CH_4 and H_2 molecules were modeled using the united atom representation from the LJ potential using the TraPPE force fields with CH_4 ($\varepsilon = 0.294 \text{ kcal/mol}$, $\sigma = 3.73 \text{ \AA}$) [126] and H_2

($\varepsilon = 0.068$ kcal/mol, $\sigma = 2.96$ Å) [127]. In the ICR, we aimed to achieve a concentration corresponding to the total feed pressure of 1 bar, derived from the pressure/density data of the NIST database [109]. For the OCR, we aimed to achieve a concentration of 0 to create a vacuum effect on the permeate side in all our simulations as we mentioned in Chapter 3. A time step of 1 fs was used, and simulations were equilibrated for 2 ns, followed by a production run for a duration of 20 ns. Each simulation was repeated three times to calculate the error bars. Atomistic trajectories were recorded at 1 ps intervals for subsequent analysis of the flux and density profiles.

4.3 Results and discussion

Figure 4.2 illustrates the concentration profiles in both the ICR and the OCR during the production run for pure H₂ and CH₄ across the COF-300 and COF-320 membranes. Moving averages were calculated with a smoothing time of 0.2 ns. The concentrations in both regions remained stable throughout the simulations, fluctuating only around their average values, confirming that steady-state conditions were achieved.

Similarly, the concentration profiles of additional membranes, including NPN-1, NPN-2, NPN-3, TPE-COF-I, COF-303, DMTA-TPB2, 3D-Por-COF, COF-921, COF-IM AA, TfpBDH, and PCOF-2 (Figures B.1–B.3), showed stable behavior, further validating the robustness of the CGD-MD method for studying transport through COFs.

We compared the results from our CGD-MD simulations with the available experimental data for the synthesis of COF-300 [40] and COF-320 [41] at 298 K and 1 bar. Figure 4.3 presents the comparison of (a) ideal selectivities of experimental and simulated COF-300 and COF-320, and (b) the corresponding permeabilities obtained from both CGD-MD and GCMC+EMD.

As shown in Figure 4.3a, the GCMC+EMD results reveal that both COF-300 and COF-320 exhibit CH₄ selectivity over H₂, with ideal selectivity values of 0.78 and 0.29,

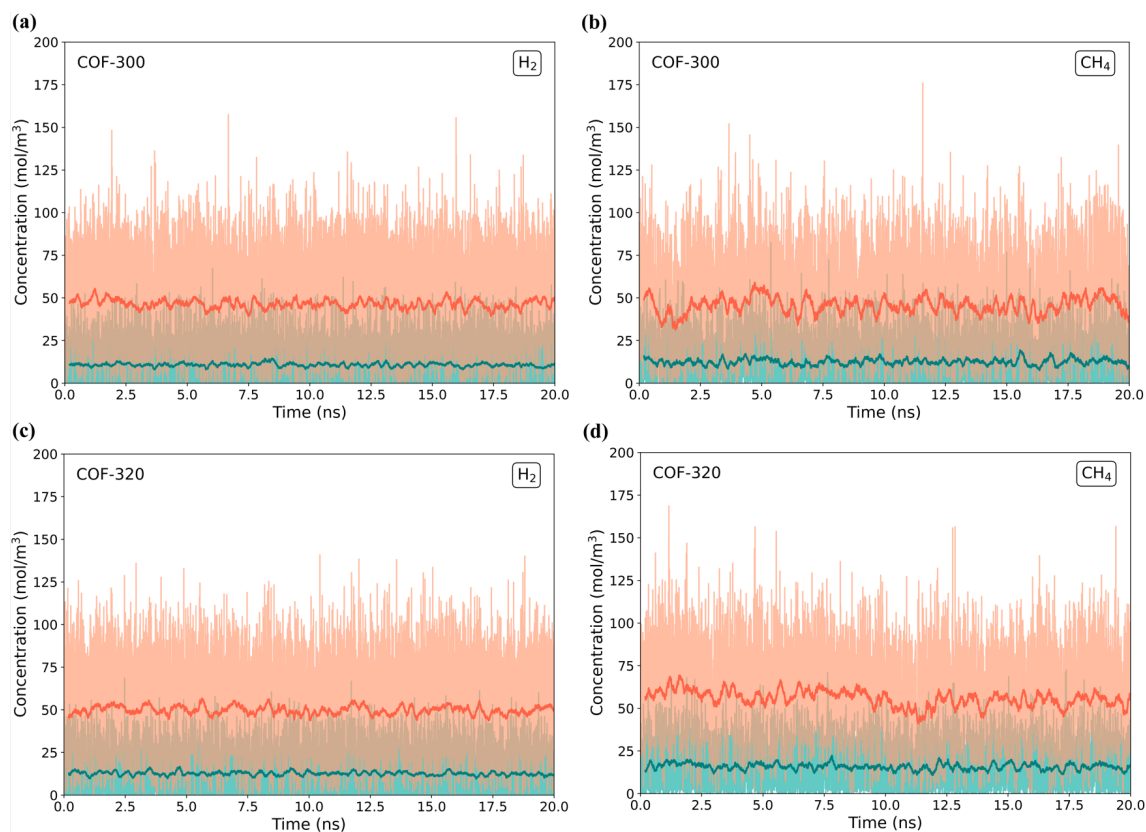


Figure 4.2: Inlet and outlet concentrations for (a) H_2 and (b) CH_4 in COF-300, and also (c) H_2 and (d) CH_4 in COF-320 as a function of simulation time. The ICR and OCR concentration values are shown in light orange and light green, while the moving averages are represented by solid lines.

respectively. Conversely, the H_2/CH_4 ideal permselectivities derived from the CGD-MD simulations were 1.97 ± 0.12 for COF-300 and 2.15 ± 0.28 for COF-320, demonstrating good agreement with the experimental values of 3.25 [40] and 2.52 [41], respectively. These findings underscore the reliability of the CGD-MD method in generating accurate data for qualitative analyses.

Figure 4.3b further clarifies the reverse selectivity for CH_4 over H_2 observed in the GCMC+EMD method. The overprediction of CH_4 permeability in this method may be attributed to the use of the self-diffusion coefficient, which is typically higher than the transport diffusivity [104, 128]. The self-diffusion coefficients of CH_4 have been reported

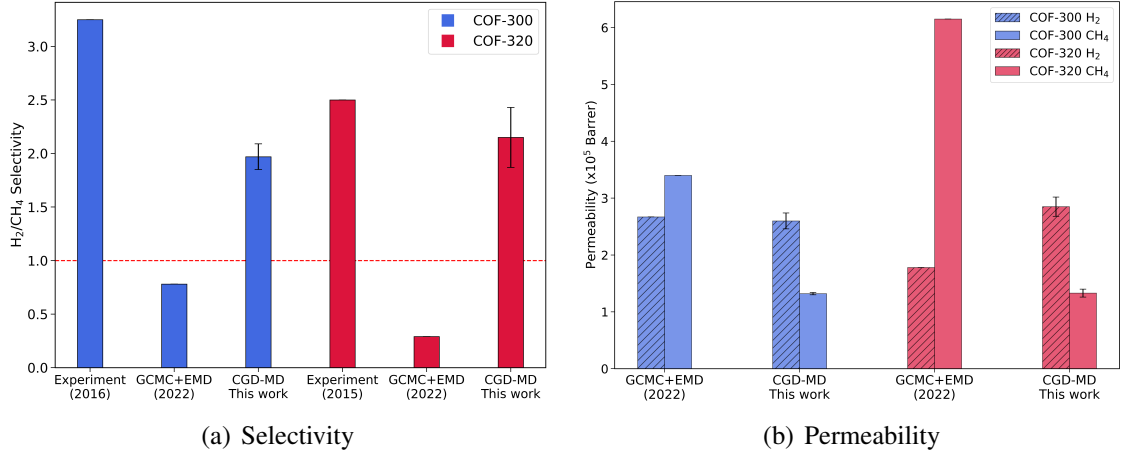


Figure 4.3: Comparison of (a) ideal selectivities of experimental and simulated COF-300 and COF-320, and (b) permeabilities predicted by GCMC+EMD and CGD-MD. Red dashed line marks Selectivity = 1; regions above are H₂-selective, below are CH₄-selective

as 1.5×10^{-4} cm²/s for COF-300 and 1.48×10^{-4} cm²/s for COF-320, while the CH₄ uptake values were 1.51 and 1.37 mol/kg, respectively. Additionally, the GCMC+EMD method does not consider bulk gas-phase transport and surface resistance effects on the feed side of the membrane, which could explain the discrepancy in the selectivity results.

To further investigate the discrepancies observed in the GCMC+EMD method, we examined the potential of 11 additional COF membranes (excluding COF-300 and COF-320) with PLDs ranging from 4 to 26 Å. As shown in Figure 4.4, we applied the CGD-MD method to a total of 13 COF structures to assess their H₂ and CH₄ permeation selectivities at 298 K and 1 bar. The results indicated that all 13 COF structures exhibited H₂ permeation higher than that of CH₄, as expected. The COF structures, arranged by increasing the PLD from left to right in Figure 4.4, reveal a trend of increasing H₂ permeability with larger PLDs. However, the H₂/CH₄ selectivity did not show a corresponding increase with larger pore sizes.

Figure 4.5 provides a comparative analysis of our findings with those of the GCMC+EMD simulations reported by Aydin et al. [50]. Their results suggested that COF structures with PLDs smaller than approximately 10 Å are more likely to favor

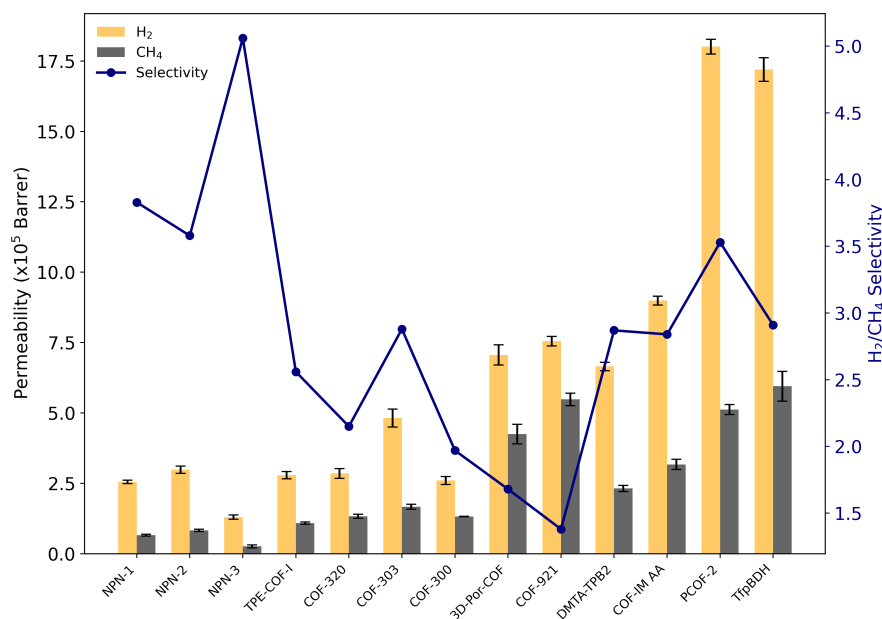


Figure 4.4: CGD-MD simulation results of 13 different COF membranes.

CH₄ selectivity over H₂, in contrast to both our predictions and the experimental findings [40, 41] in the literature. These studies consistently demonstrate higher H₂ selectivity over CH₄ in COF structures, even with smaller pores. This suggests that the GCMC+EMD method may underestimate the performance of COFs for H₂/CH₄ separation, likely due to limitations in accounting for collective transport, surface resistance, and the respective filling of gas molecules inside pores. In contrast, our method implemented in this study appears to offer a more accurate understanding of gas permeation behavior across a wider range of pore sizes.

For comparison, Robeson's 2008 upper bound [3], representing the performance limit of polymeric membranes, is included in Figure 4.6, alongside promising MOF membranes (ZIF-62, ZIF-100, ZIF-8, ZIF-67, JUC-150, UiO-66, MOF-in-COF) [43, 129, 130, 131, 132, 133] and a zeolite named SAPO-34 [134] under the same pressure and temperature conditions. Notably, TPE-COF-I, which was previously found to be below the performance limit using GCMC+EMD, surpassed the upper bound with CGD-MD,

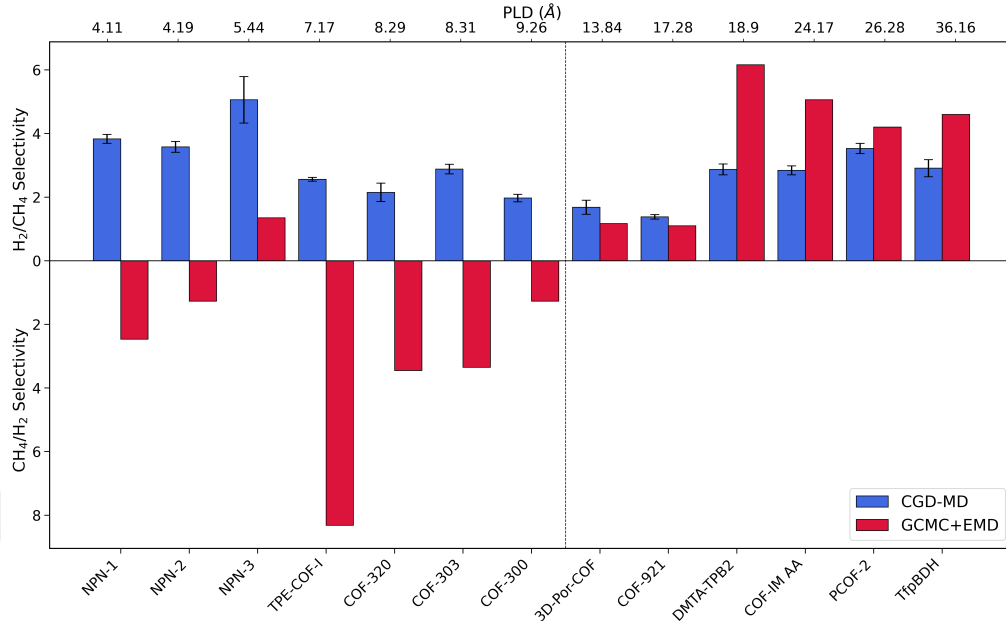


Figure 4.5: Comparison of the CGD-MD and GCMC+EMD methods for structures with different PLD ranges. Values above the x-axis represent the H_2/CH_4 ideal selectivity for simulations with a higher H_2 permeability than CH_4 . Values below the x-axis represent the CH_4/H_2 ideal selectivity for simulations indicating higher CH_4 permeability than H_2 .

achieving a selectivity of 2.56 ± 0.06 and a H_2 permeability of $2.79 \pm 0.13 \times 10^5$ Barrer. Among the examined COFs, NPN-3 emerged as the best performer for H_2/CH_4 separation, with a selectivity of 5.06 ± 0.73 and a H_2 permeability of $1.3 \pm 0.08 \times 10^5$ Barrer.

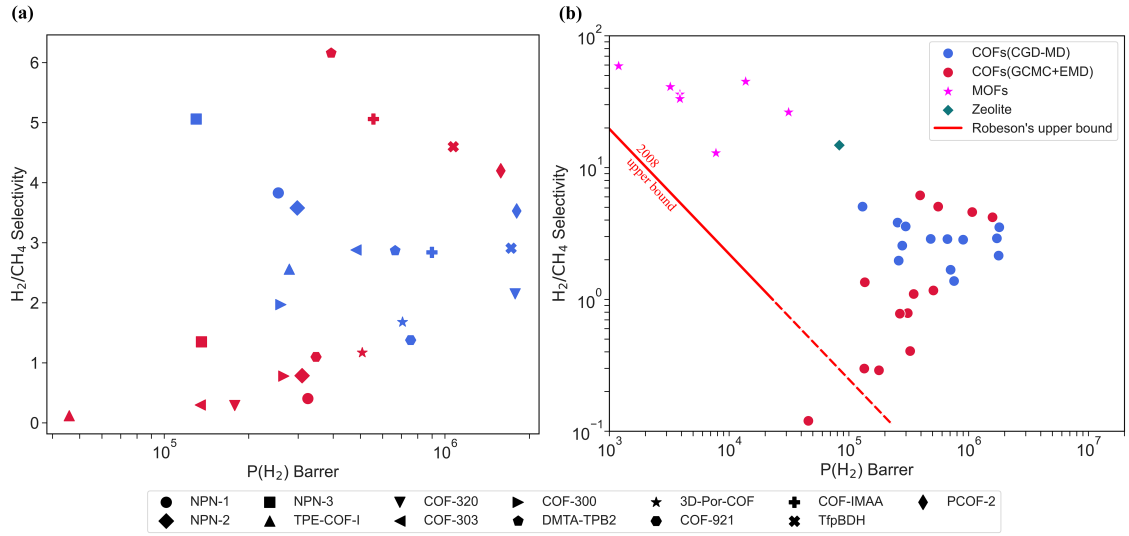


Figure 4.6: H_2 permeabilities and H_2/CH_4 selectivities of 13 COFs, (b) along with experimentally reported promising MOFs and a zeolite, at 1 bar and 298 K, plotted against Robeson's 2008 upper bound [3].

All COFs in this study demonstrated superior performance compared to polymeric membranes, as indicated by their positioning above the Robeson upper limit [3]. The large pore sizes of the COFs enable them to achieve significantly higher H_2 permeabilities. However, H_2/CH_4 selectivities were lower compared to the MOFs, indicating that although COFs exhibit exceptional permeability, their selectivity for H_2 over CH_4 remains limited. This trade-off between permeability and selectivity is particularly evident compared to MOFs, which offer a more balanced performance for H_2/CH_4 separation. Consequently, while COFs show great promise for gas separation applications, further optimization is needed to improve their selectivity to rival the overall separation efficiency of MOFs.

5. PRESSURE-INDUCED AMORPHIZATION OF ZIF-8

The results given in this chapter were published with the following reference:¹

5.1 Motivation

ZIF-8 is a widely studied MOF due to its stability and potential in gas separation [29, 67, 69], yet it undergoes pressure-induced amorphization where long-range order is lost while short-range coordination remains. This transition can significantly alter pore size, framework flexibility, and gas transport properties, making it important to understand for practical applications such as gas separation [61, 62, 63, 31]. Despite these advances, challenges remain in computational simulations for amorphization accurately. Classical force fields such as UFF4MOF [135, 136], Dreiding [137], or Amber [138, 139] do not fully capture bond-breaking processes, while reactive models such as ReaxFF [140, 141] still lack validation for ZIFs [142]. Recently, the flexible and transferable ZIF-FF force field [143, 144] has shown promising accuracy in describing the elasticity and amorphization mechanisms, closely matching experimental findings [145]. However, an additional uncertainty arises from the treatment of electrostatics, as partial charge assignment methods such as the semiempirical charge equilibration (Qeq) [146], density-derived electrostatic and chemical (DDEC) method [147], the partial atomic charges in MOFs (PACMOF) machine learning model, [148], and a partial atomic charge predictor for porous materials based on graph convolutional neural network (PACMAN) model [149] may significantly influence predicted behavior. Both PACMAN and PACMOF are machine learning based packages. PACMOF uses a pre-trained random forest model to estimate charges rapidly for MOFs [148], while PACMAN employs a graph convolutional

¹Jamshidi Ghaleh, P., Haslak, Z. P., Sarbakhshian, O., Öztürk, H., & Erucar, I. (2025). Pressure-Induced Amorphization of ZIF-8: Deciphering the Role of Atomic Charge Assignments and Adsorbed CH₄ Molecules through Atomistic Insights. *The Journal of Physical Chemistry C*.

neural network trained on large datasets to produce charges [149].

In this chapter, we investigated the pressure-induced amorphization of ZIF-8 using MD simulations with the ZIF-FF force field. We systematically evaluate the impact of charge assignment methods and confined CH_4 molecules on the onset pressure, phase transition pathways, and recrystallization behavior. This analysis not only provides atomistic insights into the structural evolution of ZIF-8 under pressure but also builds a foundation for the following chapter, where the functional implications of amorphization on CO_2/CH_4 separation performance are explored.

5.2 Simulation details

The atomic configuration of the cryZIF-8 structure was obtained from the Cambridge Structural Database (CSD) using the OFERUN reference code (CSD upload number: 652032) [122]. A $3 \times 3 \times 3$ supercell of cryZIF-8, as illustrated in Figure 5.1, was constructed. To describe both intra- and intermolecular interactions, the ZIF-FF [143] force field parameters were assigned to cryZIF-8.

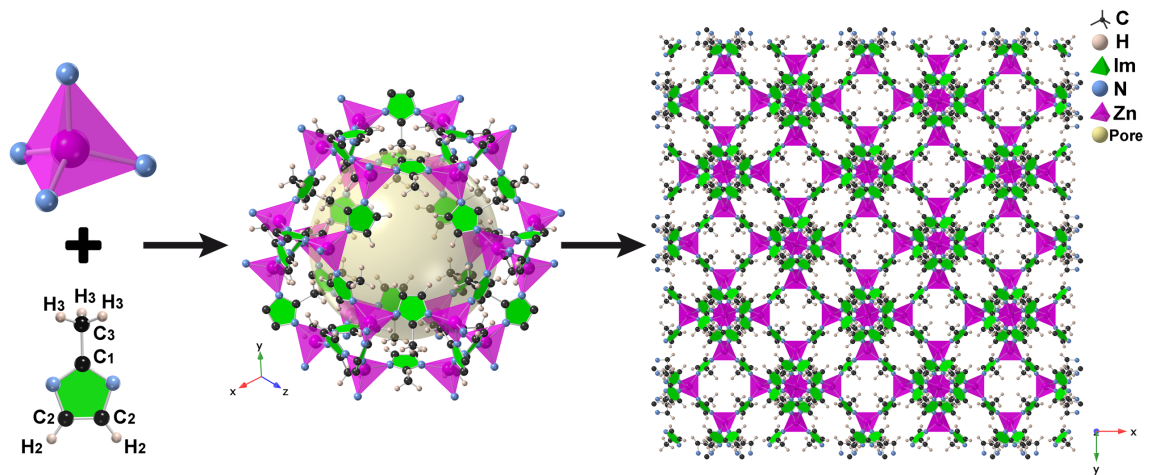


Figure 5.1: Building block, unit cell, and $3 \times 3 \times 3$ supercell representation of cryZIF-8.

MD simulations were performed using the LAMMPS software package [83]. To

allow independent evolution of the simulation cell dimensions during pressure-induced amorphization, the `aniso` keyword was applied, which allows separate control of P_{xx} , P_{yy} , and P_{zz} stress tensor components under external pressure. Consequently, the unit cell lengths evolved independently along the three principal axes. The temperature and pressure were controlled by the Nosé–Hoover thermostat and Nosé–Hoover barostat [150, 151], with damping parameters set to 100 fs and 1000 fs, respectively. To mimic the amorphization process, MD simulations were performed under the NPT ensemble at 300 K, beginning from ambient pressure (1 bar, 1.01325×10^{-4} GPa). The external pressure was increased stepwise up to 1.5 GPa in 15 increments at a rate of 100 Pa/fs. Prior to pressurization, the system was equilibrated for 1 ns at 300 K and 1 bar using the NPT ensemble.

For the reverse amorphization simulations, the pressure was decreased from 1.5 GPa back to ambient conditions in 15 steps at the same rate (100 Pa/fs). During all MD simulations, the system’s total energy and density evolution were monitored. The van der Waals and electrostatic interactions were described using a Lennard-Jones 12–6 potential and Coulomb interactions, with a cutoff distance of 13 Å. Long-range electrostatics were calculated using the particle–particle particle–mesh (PPPM) method with an accuracy of 10^{-6} , ensuring high-precision electrostatic interactions under periodic boundary conditions.

To assess the effect of charge assignment methods, four different charge models were tested: Qeq [146], DDEC [147], PACMOF [148], and PACMAN [149]. The average charges for each scheme are reported in Table C.1. In addition, the role of confined CH₄ molecules was studied by simulating the amorphization of cryZIF-8 with different amounts of adsorbed CH₄. Furthermore, bond-breaking effects are neglected in our classical MD simulations. Chapman et al. [152] demonstrated that ZIF-8 retains its local structure and framework connectivity during amorphization, although its long-range translational

symmetry is disrupted. These findings support our assumption that bond-breaking effects can be neglected under the investigated conditions.

5.3 Results and discussion

The temporal evolution of the lattice parameters (a , b , and c) under compression is shown in Figure 5.2. The initial 1 ns involved equilibration at ambient pressure under the NPT ensemble, followed by a gradual pressure increase from ambient conditions to 1.5 GPa over the subsequent 15 ns. The initial ZIF-8 structure is cubic ($a = b = c \approx 50$ Å). Under increasing external pressure, a smooth reduction in all three cell lengths is observed up to ~ 0.8 GPa (at ~ 9 ns), while maintaining cubic symmetry. At ~ 0.8 GPa, a sudden transition to a tetragonal phase occurs, characterized by $a \approx b < c$. At ~ 1.1 GPa (around 12 ns), a second abrupt transition to an orthorhombic phase is observed ($a \neq b \neq c$), indicating the onset of a shear-related structural instability.

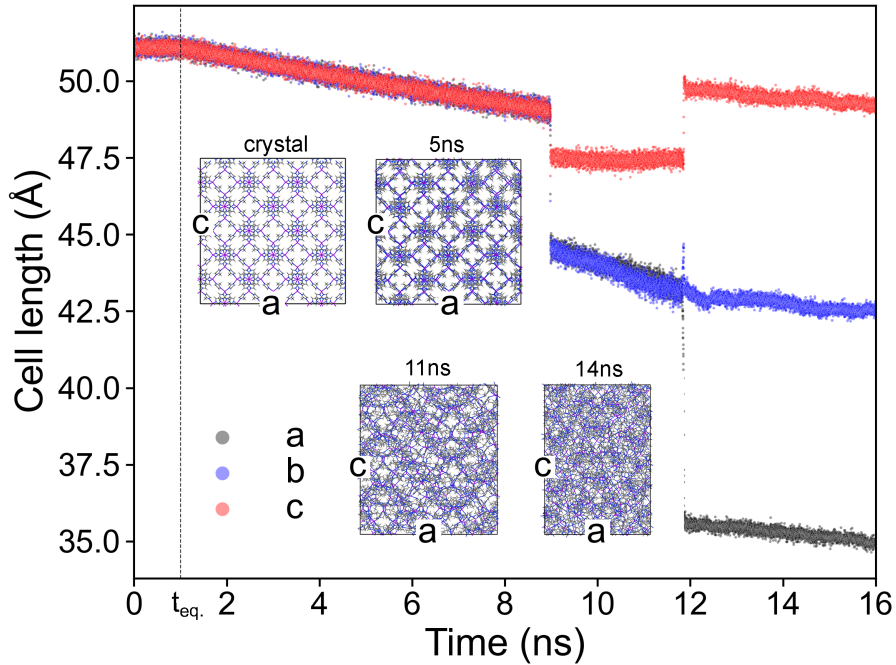


Figure 5.2: The evolution of the unit cell parameters (a , b , and c) during the pressure-induced amorphization of ZIF-8 in MD simulations.

During the amorphization process, the atoms of the crystalline structure undergo spatial rearrangements, losing long-range interactions while short-range interactions become dominant. The amorphous solids tend to exhibit a denser and more compact structure compared to their crystalline counterparts. In this section, we examine the effects of different partial atomic charges, initial velocities, and the presence of adsorbed CH₄ molecules on the amorphization process of cryZIF-8.

5.3.1 *Effect of atomic charges on amorphization of ZIF-8*

Figure 5.3 shows the density profiles of ZIF-8 as a function of pressure obtained from MD simulations using different partial atomic charge models: Qeq, DDEC, PACMOF, and PACMAN. The bold lines show the moving average with a window size of 20 fs. The results indicate that the charge assignment method influences the amorphization pathway, onset pressure, and intermediate phases. For the case without assigned charges (Figure 5.3a), the density sharply increases at ~ 0.8 GPa during the pressure-increase step, with a volume reduction of nearly 30%. Upon decompression, the structure returns to its crystalline state at ~ 0.25 GPa. With Qeq charges (Figure 5.3b), amorphization begins earlier at ~ 0.7 GPa and proceeds through an intermediate crystalline–amorphous phase. The framework loses about 41% of its volume during transition. PACMAN charges (Figure 5.3c) result in a crystalline–amorphous intermediate phase between 0.8–1.0 GPa, followed by full amorphization beyond 1.1 GPa. PACMOF (Figure 5.3d) and DDEC (Figure 5.3e) charges exhibit nearly identical behavior, with amorphization onset at 0.8 GPa and transition to a fully amorphous phase by 1.2 GPa. The computationally determined amorphization pressure aligns well with experimental values (0.35–0.8 GPa) [2, 57, 66]. These findings highlight that while charge models affect the details of the transition, the overall choice of charge assignment method has a minimal impact on the observation of the crystalline–amorphous intermediate phase as well as on the onset of

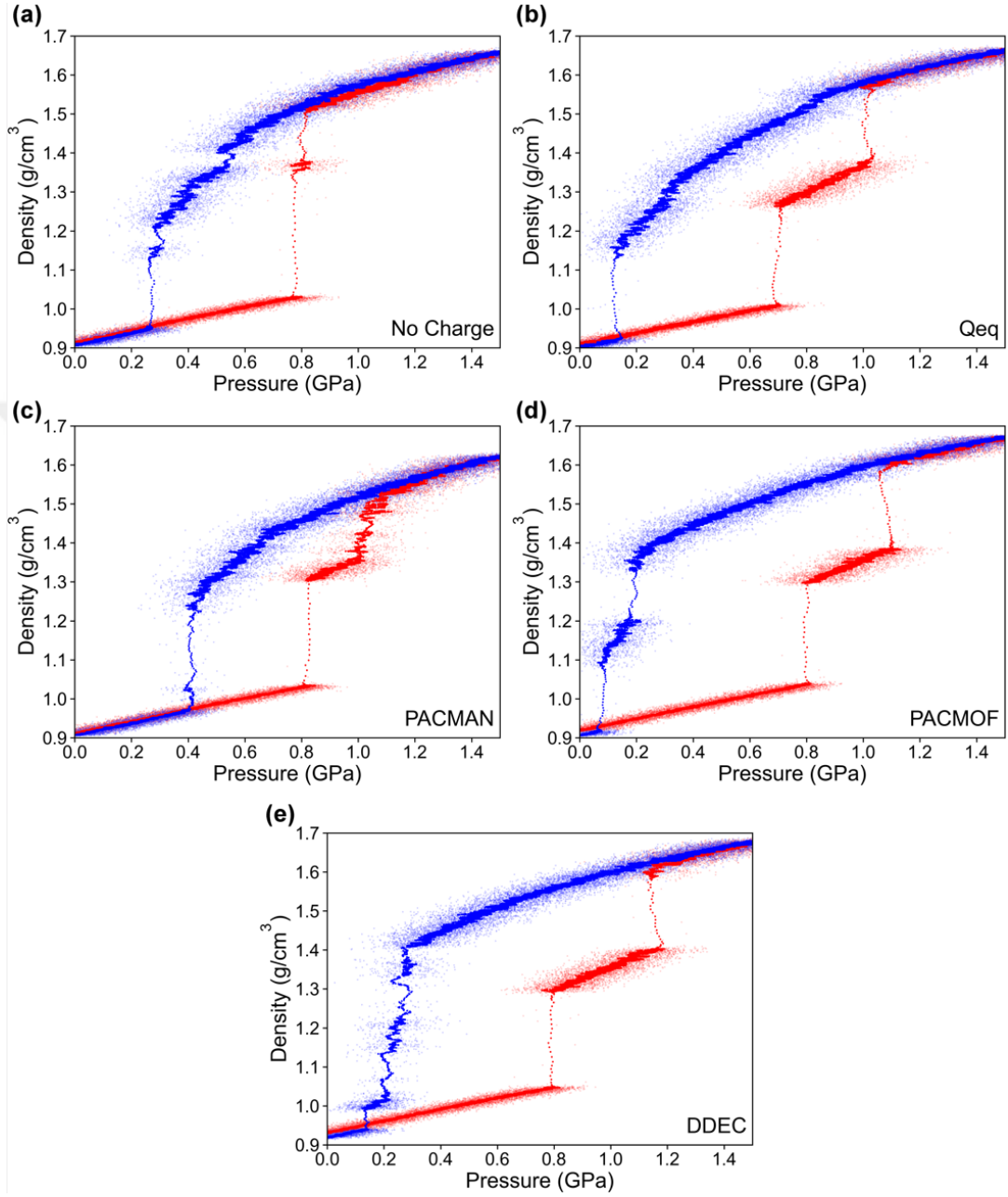


Figure 5.3: Density profiles of ZIF-8 during pressure-induced amorphization with different partial atomic charge models: (a) without charges, (b) Qeq, (c) PACMAN, (d) PACMOF, and (e) DDEC. Pressure increase and decrease steps are represented by red and blue, respectively.

amorphization and crystallization pressures.

5.3.2 *Dependence of phase transition pathways on random initial conditions*

We performed three independent MD simulations for ZIF-8 using ZIF-FF parameters with DDEC charges assigned to ensure reproducibility of our simulation results (Figure 5.4). Simulations were conducted at increasing (Figure 5.4a) and decreasing (Figure 5.4b) pressures using three different random initial velocity seeds (Run-1: black, Run-2: blue, and Run-3: red) to account for variability in the initial conditions. During compression, all three independent MD simulations exhibit a sharp increase in the density at approximately 0.8 GPa. However, the behavior of the intermediate phase varies significantly between runs. In Run-1, the density undergoes an abrupt transition to the final phase, indicating a sudden structural collapse. In contrast, Run-2 exhibits an extended second intermediate phase, followed by another density jump of around 1.2 GPa. Run-3 shows a different pattern, with a shorter second intermediate phase and a second density increase occurring at approximately 0.9 GPa. These variations in phase transition behavior are likely influenced by differences in ligand positioning within the structure prior to the phase change [69]. During decompression, the systems follow distinct pathways depending on the preceding compression steps. Despite these differences, all three simulations converge to the same final density, indicating a common final state.

5.3.3 *Structural changes during amorphization of ZIF-8*

Partial pair distribution function $g(r)$ analysis were performed to monitor the structural changes within ZIF-8 under applied pressures of 0, 0.4, 0.8, 1.0, and 1.2 GPa, as shown in Figure 5.5. The transition from crystalline to amorphous phase is indicated by the broadening and merging of peaks in the $g(r)$ profile, reflecting the breakdown of the periodic arrangement of cryZIF-8. The $g_{\text{Zn-N}}(r)$ peaks at 2.0 and 4.0 Å, corresponding to

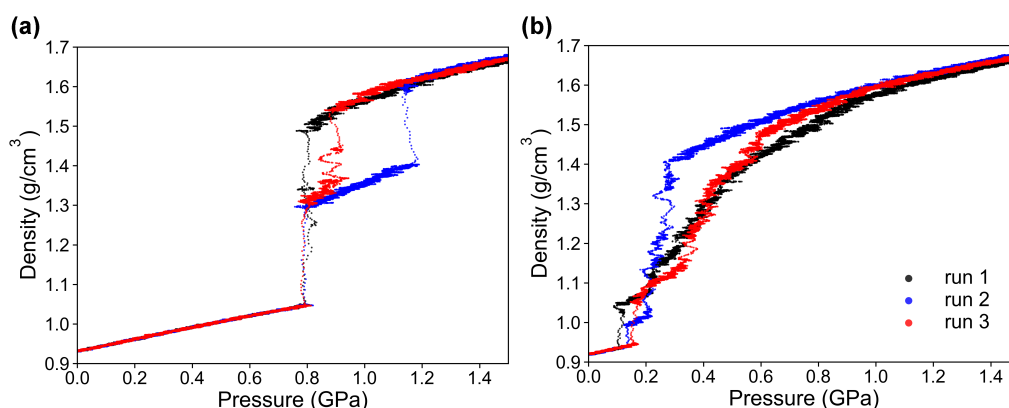


Figure 5.4: Density as a function of increasing pressure (a) and decreasing pressure (b) in ZIF-8 with DDEC charges in amorphization process using 3 different random initial velocity seed numbers

Zn–N coordination in the crystalline framework, remain evident even after amorphization, showing the short-range order. Other characteristic peaks, such as C–C (1.3 and 2.1 Å), C–N (1.3, 2.2, 2.5 Å), N···N (2.2 and 3.2 Å), Zn–Zn (6.0 and 8.5 Å), and Zn–C (3.0, 3.3, 4.2 Å), are also present. During the amorphization process, the C–C, C–N, and C=N bonds of the organic linkers are largely preserved, similar to the Zn–N coordination bonds, whereas the nonbonded N···N interactions weaken due to the loss of long-range order. Overall, the $g(r)$ analysis clearly demonstrates that short-range structural motifs remain while long-range order is lost under pressure, consistent with the amorphization process. These findings are in strong agreement with experimental ball-mill amorphization data for ZIF-8 [28] and previous simulations of pressure-induced amorphization reported in the literature [70].

5.3.4 Effect of adsorbed CH_4 molecules on amorphization of ZIF-8

To examine the influence of confined gas molecules on the pressure-induced amorphization of cryZIF-8, MD simulations were performed in the pressure range of 0–1.5 GPa under both compression and decompression, as shown in Figure 5.6. The simulations included 5, 11, 16, 54, and 400 CH_4 molecules adsorbed within a $3 \times 3 \times 3$

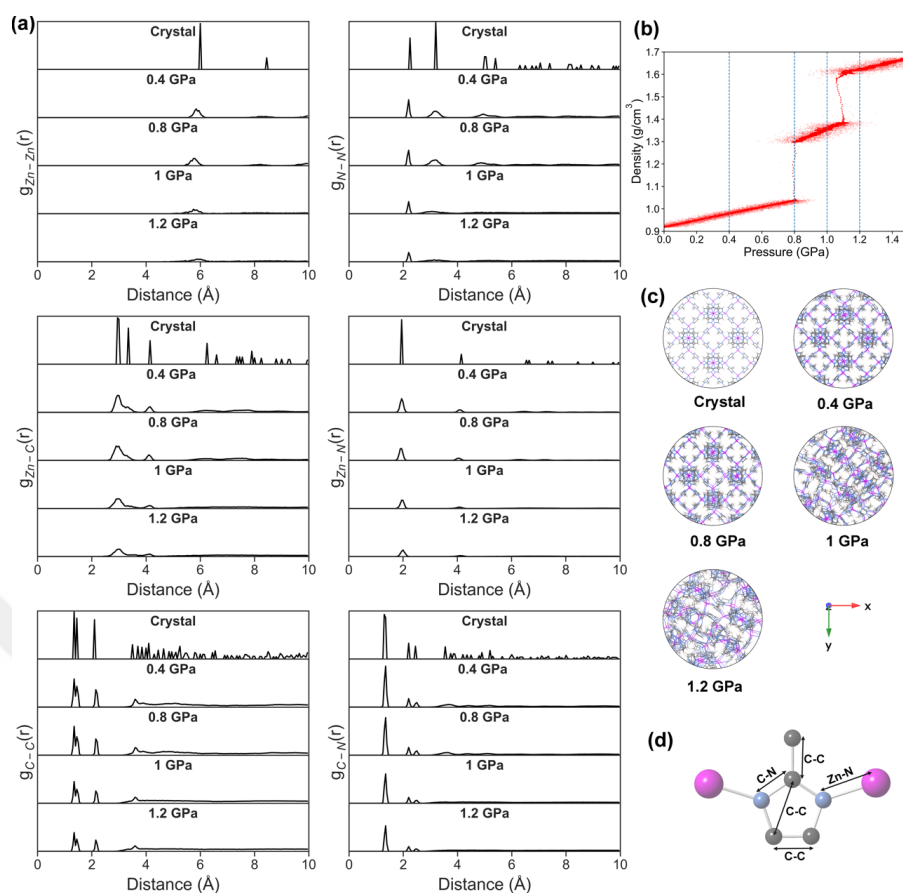


Figure 5.5: Partial PDFs $g(r)$ of cryZIF-8 and aZIF-8 at increasing pressures (0.4, 0.8, 1.0, and 1.2 GPa). The transition to the amorphous state is evident from peak broadening and merging.

supercell of cryZIF-8. Previous studies have indicated that guest molecules can either delay or accelerate amorphization in porous frameworks [64, 67, 68].

As shown in Figure 5.6, moderate loadings of CH₄ molecules (≤ 54) did not alter the onset of amorphization, which remained at 0.8 GPa, consistent with the pristine cryZIF-8 behavior discussed earlier. At a loading of 5 CH₄ molecules (Figure 5.6a), an intermediate phase was observed at 0.8 GPa. However, this intermediate disappeared with higher loadings of 11–54 CH₄ molecules (Figure 5.6b–e), where the framework transitioned directly from crystalline to amorphous at 0.8 GPa. When the number of adsorbed molecules increased to 400, the onset of amorphization shifted to approximately

1.0 GPa, in agreement with Ortiz *et al.* [68], who reported higher critical pressures when cages were highly occupied. At this saturation level, CH₄ molecules provide internal support against collapse, while moderate loadings fill only part of the cavities and do not generate enough internal pressure to modify the mechanical response.

The maximum density at 1.5 GPa decreased from 1.7 g/cm³ (empty framework) to 1.5 g/cm³ with 400 CH₄ molecules, consistent with a stiffer and less compressible host–guest system. With 5 CH₄ molecules, the framework lost 29% of its volume up to 0.8 GPa, followed by an additional 41% volume loss upon amorphization at 1.1 GPa, confirming that small gas loadings do not significantly alter the amorphization process. For 11–54 CH₄ molecules, a sudden structural collapse at 0.8 GPa resulted in an average 35% volume reduction, and further compression densified the material above 1.6 g/cm³. In contrast, at saturated loading (400 CH₄ molecules), the framework lost only 11.5% of its volume until amorphization at ~1.0 GPa.

During decompression, recrystallization of aZIF-8 began below 0.2 GPa for the cases with 5, 16, and 54 CH₄ molecules, consistent with pristine ZIF-8. Systems with 11 CH₄ molecules returned to the crystalline phase at ~0.5 GPa, while the saturated case of 400 CH₄ molecules recrystallized at ~0.65 GPa. These results demonstrate that moderate CH₄ loadings accelerate the crystalline-to-amorphous transition at the same onset pressure, whereas saturated loadings delay amorphization to higher pressures by stabilizing the framework against collapse.

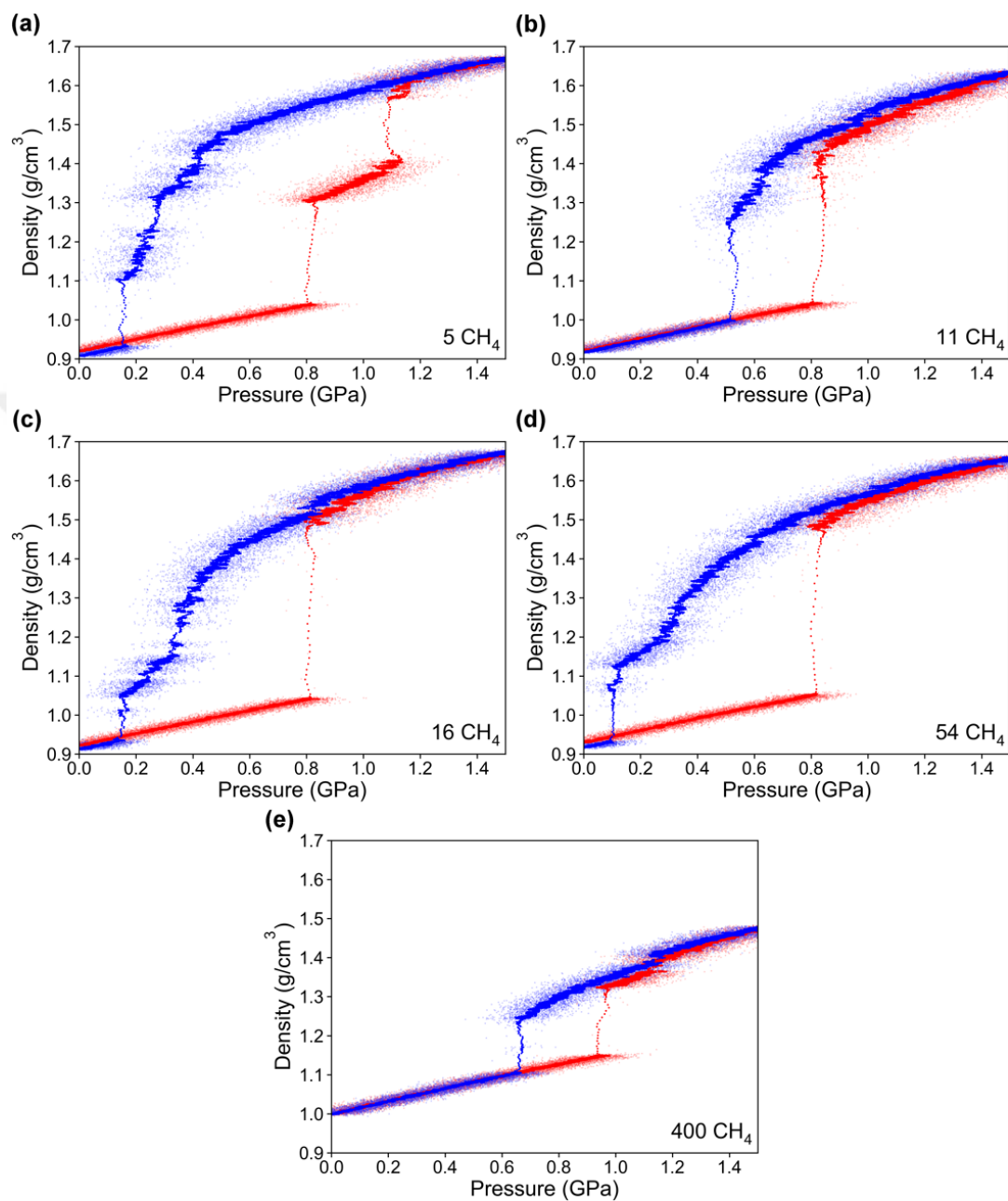


Figure 5.6: Density as a function of pressure during the amorphization of cryZIF-8 with different CH₄ loadings: (a) 5, (b) 11, (c) 16, (d) 54, and (e) 400 CH₄ molecules. Simulations were conducted using ZIF-FF force field parameters and PACMOF charges.

6. EXTENTION OF CGD-MD METHOD TO FLEXIBLE ZIF-8 STRUCTURES FOR CO₂/CH₄ SEPARATION

6.1 Motivation

In the previous chapter, we investigated the pressure-induced amorphization of ZIF-8 and established the structures from each step during the process. Here, three representative structural forms were chosen: the crystalline framework (cryZIF-8), a state obtained at 0.4 GPa (aZIF-8@0.4GPa), and a structure generated at 1.2 GPa (aZIF-8@1.2GPa). These distinct models capture the progressive loss of long-range order in ZIF-8 and provide a valuable platform to examine how structural flexibility influences gas transport. We then performed CGD-MD simulations to evaluate the CO₂/CH₄ separation performance of cryZIF-8 and its compressed counterparts. Although cryZIF-8 is widely recognized for its high crystallinity and well-defined pores, its pressed forms may introduce new structural behavior that may change molecular diffusion pathways and selectivity characteristics. In particular, aZIF-8@0.4GPa is expected to retain partial pore connectivity, whereas the more pressed form (aZIF-8@1.2GPa) exhibits significant densification and loss of porosity. This chapter focuses how partial amorphization affects CO₂/CH₄ separation performance of ZIF-8 under pressure.

6.2 Simulation details

CGD-MD simulations were carried out to study the non-equilibrium transport of CO₂ and CH₄ through different ZIF-8 membranes, including cryZIF-8, aZIF-8@0.4 GPa, and aZIF-8@1.2 GPa at 300 K and 10 bar.

The membrane models were built by extending the ZIF-8 structure along the z -direction and then to remove periodicity in this direction, the outermost zinc atoms were deleted and the exposed nitrogen atoms were terminated with hydrogen atoms. All

atoms were parameterized with the ZIF-FF force field [143] and PACMOF charges [148], as described in Chapter 5. Each membrane structure was then relaxed with a 1 ns NVT run at room temperature using LAMMPS [83].

The NEMD setup followed the same approach described in earlier chapters. While, the inlet concentration region (ICR) was adjusted to represent a total feed pressure of 10 bar, with CO₂ and CH₄ concentrations of 422.16 and 407.76 mol/m³, respectively, based on the NIST pressure–density data [109]. The outlet concentration region (OCR) was set to zero. The applied force constants were $k_i = 8000 \text{ kJ nm}^3 \text{ mol}^{-1}$ at the inlet and $k_o = 500,000 \text{ kJ nm}^3 \text{ mol}^{-1}$ at the outlet. Each simulation consisted of 50 ns equilibration, followed by 40 ns production run. To avoid membrane drifting during NEMD, a weak harmonic spring force (spring constant = $5 \text{ kcal} \cdot \text{mol}^{-1} \cdot \text{\AA}^{-1}$) was applied to zinc atoms, ensuring that the framework remained stable while still allowing natural flexibility.

6.3 Results and discussion

During the CGD-MD simulations, both CO₂ and CH₄ diffused through cryZIF-8 and aZIF-8@0.4GPa, enabling a direct comparison of their separation behavior. In contrast, no gas molecules were able to pass through aZIF-8@1.2GPa during the simulation time (Figure 6.1b), which is consistent with its highly collapsed pore structure. The number of molecules passed from the middle of the (a) cryZIF-8 and (b) aZIF-8@0.4GPa membranes as a function of 40 ns simulation time for single-component CO₂ and CH₄ is provided in Figure 6.2. These numbers were used for calculating the gas flux as described in Chapter 3.

Figure 6.3 shows the concentration profiles in the ICR and OCR regions for single-component CO₂ and CH₄ during the 40 ns production run for (a-b) cryZIF-8 and (c-d) aZIF-8@0.4GPa membranes. In all cases, the concentrations of both regions remained stable around their moving averages (smoothing time of 0.2 ns), confirming that

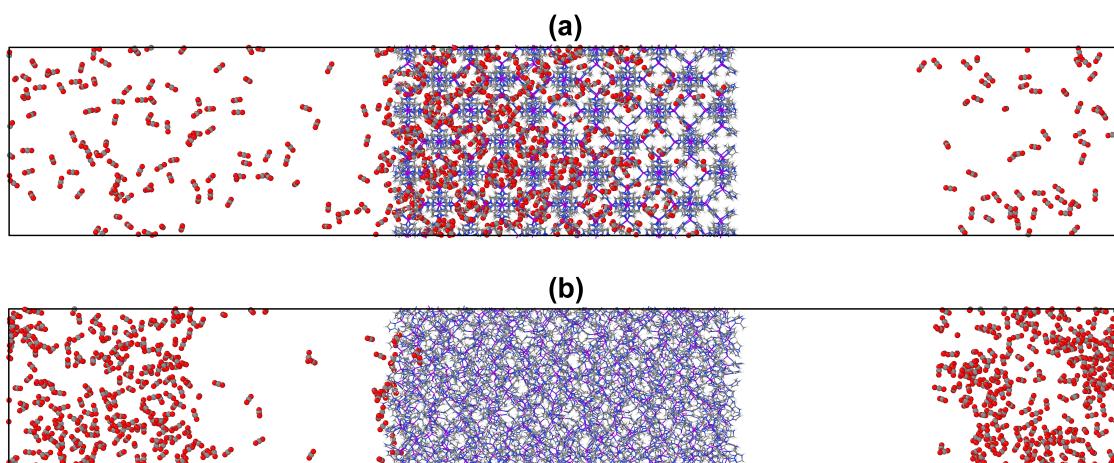


Figure 6.1: (a) cryZIF-8 and (b) aZIF-8@1.2GPa membrane setup.

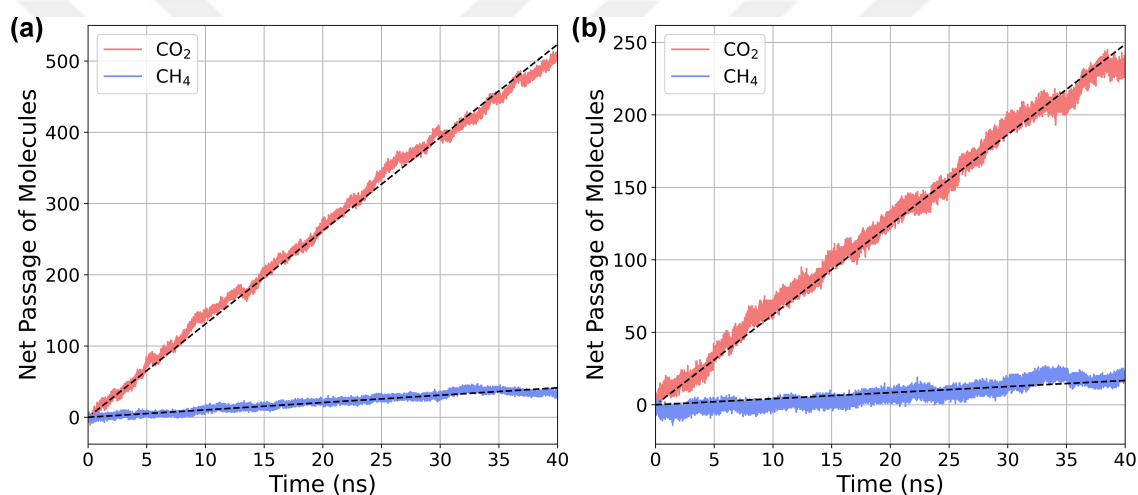


Figure 6.2: The net passage of gas molecules as a function of time during the 40 ns production run from (a) cryZIF-8 and (b) aZIF-8@0.4GPa membranes.

steady-state conditions were reached.

The calculated permeabilities and selectivities are given in Table 6.1. For aZIF-8@0.4GPa, the predicted permeabilities of single-component CO₂ and CH₄ decreased by 50.31% and 88.83%, respectively, compared to cryZIF-8. Since the reduction in CH₄ permeability was more pronounced, the CO₂/CH₄ selectivity increased from 13.39 to 19.65. This improvement can be attributed to a $\sim 7\%$ reduction in ASA (from 2066 to 1920 m²/g), along with decreases in PLD (from 3.42 to 3.27 Å) and LCD (from 11.52 to

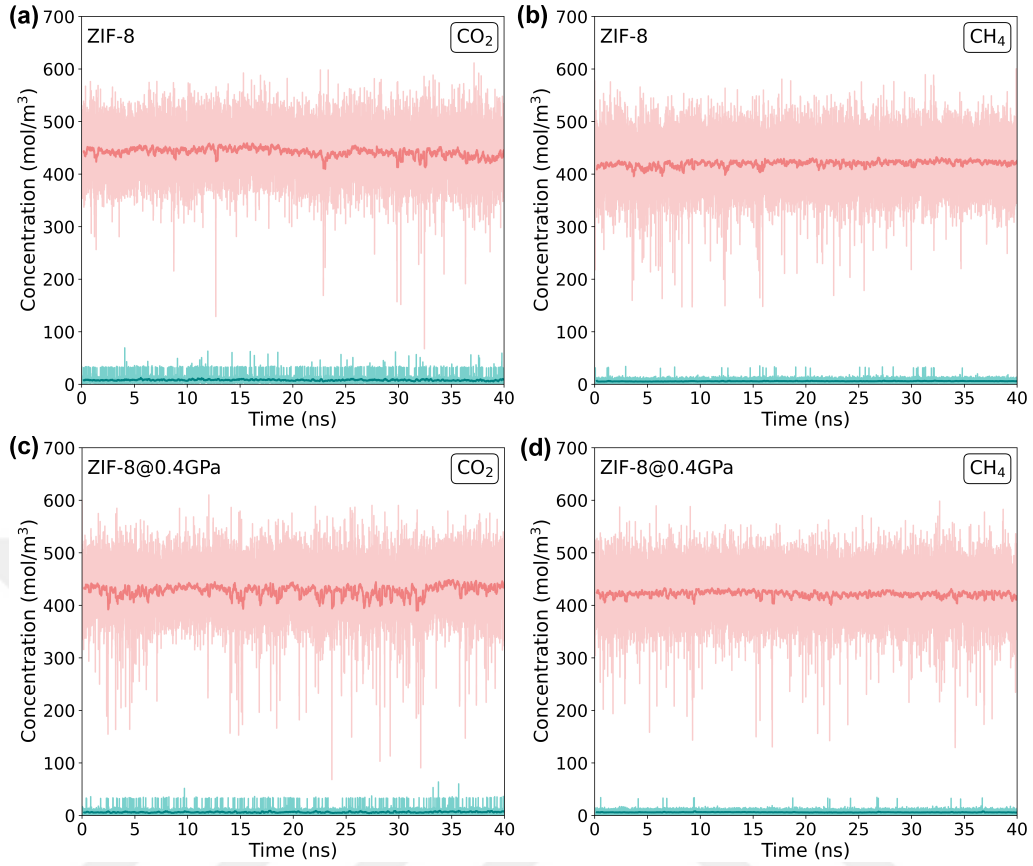


Figure 6.3: Concentration profiles of CO_2 and CH_4 molecules in the ICR and OCR during the production run for (a-b) cryZIF-8 and (c-d) aZIF-8@0.4GPa membranes in CGD-MD simulations. The ICR and OCR concentration values are shown in light pink and light green, while the moving averages are represented by solid lines.

11.04 Å) in aZIF-8@0.4GPa compared to cryZIF-8.

Table 6.1: CGD-MD results and their comparison with experimental results published in literature [1, 2].

Membranes	Permeability (Barrer) $\times 10^3$		Selectivity(CO_2/CH_4)	
	CO_2	CH_4	This work	Experiment
cryZIF-8	23.4 ± 0.05	1.74 ± 0.02	13.39	12.9 [1]
aZIF-8@0.4 GPa	11.6 ± 0.05	0.59 ± 0.03	19.65	16.23 [2]

To better understand gas transport mechanisms, MRT analysis was performed for CO_2 and CH_4 , as shown in Figure 6.4. Error bars were estimated by performing block averaging the 40 ns production run into five segments. Both gases show a sharp increase in

MRT at the entrance of the membranes, followed by a gradual decrease inside the structure. In both cases, CO₂ exhibits higher MRT values than CH₄, reflecting stronger adsorption and longer retention times. The MRT of aZIF-8@0.4GPa (Figure 6.4b) are slightly higher than crystal form and additional peaks appear at the feed-side surface of the membrane. We propose that the applied pressure compressed the structure and increased interfacial resistance, causing the gas molecules to remain longer at the surface before entering the porous network.

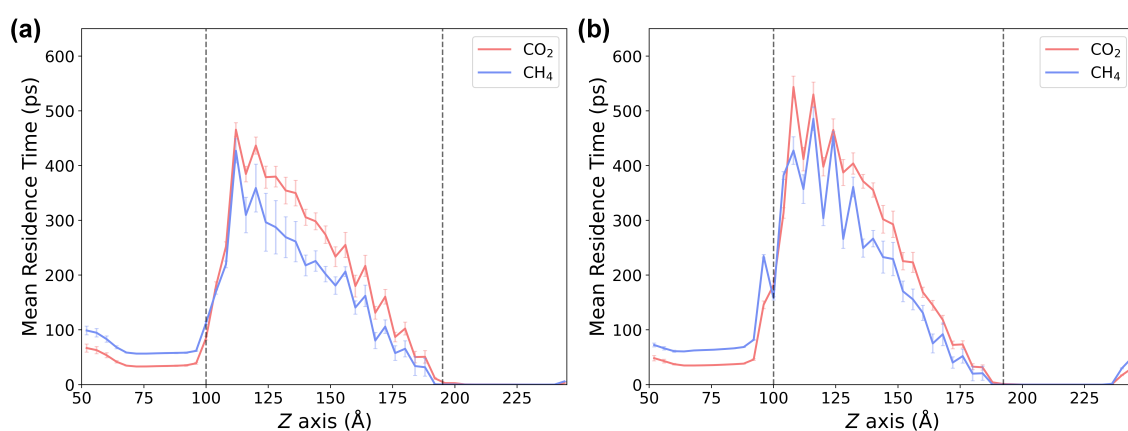


Figure 6.4: MRT profiles for CO₂ and CH₄ during permeation through (a) cryZIF-8 and (b) aZIF-8@0.4GPa membranes in CGD-MD simulations.

Overall, the results show that partial amorphization (aZIF-8@0.4GPa) reduces gas permeability but enhances CO₂/CH₄ selectivity compared to the crystalline framework. This is mainly due to structural densification and reduced pore connectivity, which hinder CH₄ diffusion more effectively than CO₂. These findings demonstrate that amorphization can be a strategy for improving selectivity without completely losing membrane functionality. The results also confirm that the CGD-MD method can effectively capture the effect of framework flexibility on gas transport. This provides a solid foundation for future studies on amorphous or partially disordered porous membranes.

7. CONCLUSIONS

In Chapter 4, the CGD-MD method was applied to evaluate the H₂/CH₄ separation performance of a series of COF membranes and to compare the results with those obtained from the conventional GCMC+EMD approach. By systematically examining COFs with a wide range of PLDs, we identified a distinct threshold behavior at approximately 10 Å. Below this value, the two simulation approaches produced opposite trends in gas selectivity, revealing the sensitivity of gas transport to pore size and confinement effects. Specifically, the GCMC+EMD approach predicted CH₄ selective behavior for COFs with narrow pores (PLD less than 10 Å), whereas the non-equilibrium CGD-MD simulations consistently indicated H₂ selectivity under the same conditions. This difference arises because the CGD-MD method explicitly captures the dynamic transport process and surface resistance effects, which are not accounted for in equilibrium-based methods. The results highlight that when the pore dimensions approach the molecular kinetic diameters of the gases, small variations in confinement strongly influence diffusion pathways and adsorption energetics. These findings demonstrate that the CGD-MD method provides a more realistic representation of molecular transport in nanoporous membranes, particularly for structures with narrow pores. Establishing the 10 Å threshold offers a useful guideline for determining when non-equilibrium simulations are necessary to accurately predict permselectivity in H₂/CH₄ separations. This study showed that the impact of pore size is important in the computational assessment of COF membranes. It validates CGD-MD as a robust framework for guiding the design and screening of COF membranes for advanced gas separation applications.

In Chapter 5, we carried out a comprehensive investigation of the pressure-induced amorphization of cryZIF-8, focusing on the effects of atomic charge assignment methods and the presence of confined methane (CH₄) molecules on the amorphization process. MD simulations using the flexible ZIF-FF force field revealed that the choice of charge

assignment method has only a minimal effect on the crystalline–amorphous phase transition and on the onset pressures for amorphization. The crystallinity of ZIF-8 was preserved up to 0.8 GPa, beyond which the long-range order disappeared, leading to amorphization. These findings were further validated by partial pair distribution function (PDF) analysis.

The results also showed that the incorporation of a moderate number of CH₄ molecules (≤ 54) into cryZIF-8 did not alter the onset pressure of 0.8 GPa, consistent with the pristine structure. However, with a higher loading of 400 CH₄ molecules, the onset of amorphization shifted to approximately 1.0 GPa, delaying the collapse of the framework. Furthermore, moderate gas loadings suppressed the formation of intermediate phases, while higher CH₄ occupancy resulted in a less dense amorphous phase and facilitated an earlier amorphous to crystalline transition upon decompression. These observations confirm that guest molecules play a significant role in the mechanical response of ZIF-8 under compression. In general, the study presented in Chapter 5 improves our understanding of the structural evolution of ZIF-8 under different pressure conditions, providing information on the interplay between atomic charge distributions, confined gas molecules, and phase transitions. The results contribute to the rational design of MOFs with improved mechanical stability for applications in gas storage and separation.

It is important to discuss the limitations of this chapter. Our MD simulations maintain the simulation box in an orthorhombic shape, keeping the angles α , β , and γ constant. However, it is well established that constant-stress simulations require allowing the box to be fully flexible with changing angles [153]. Independent MD simulations with varying initial velocity seeds revealed distinct pathways to amorphization, such as the presence or absence of intermediate phases and variations in the onset pressures for amorphization and crystallization. The dynamic nature of MD simulations enabled the observation of these multiple pathways, highlighting the stochastic behavior of phase

transitions in cryZIF-8 and underscoring the role of atomic-scale fluctuations in governing structural evolution. These findings emphasize the need to expand the conformational space explored by performing a larger number of independent simulations to achieve more robust and generalizable results. Another limitation concerns the choice of charge assignment method. If the charge model employed in the simulations differs from the method used during force field parametrization, the results can deviate from experimental observations. In such cases, reoptimization of the force field becomes essential before performing simulations. In this study, we did not reoptimize the ZIF-FF parameters since the charge assignment methods considered assign physically reasonable and broadly consistent values.

In Chapter 6, the CGD-MD methodology was extended to investigate CO₂/CH₄ separation in crystalline ZIF-8 and its partially amorphized counterpart (aZIF-8@0.4 GPa). The results demonstrated that while amorphization reduces the overall gas permeability compared to the crystalline framework, it significantly enhances CO₂/CH₄ selectivity by restricting CH₄ diffusion more strongly than CO₂. In contrast, aZIF-8@1.2 GPa showed no transport due to severe pore collapse, confirming the strong dependence of gas separation performance on structural integrity. Analysis of concentration profiles and mean residence times further revealed that CO₂ interacts more strongly with the framework than CH₄, leading to longer retention times and improved separation in partially amorphized membranes. These findings highlight the critical balance between pore accessibility and framework densification in determining the transport properties of ZIF-8. Importantly, this chapter demonstrates that moderate amorphization can optimize selectivity without fully compromising permeability, thereby underscoring the potential of structural disorder as a tuning parameter for membrane design. When considered alongside equilibrium approaches, such as GCMC+EMD, the results emphasize the unique advantages of non-equilibrium CGD-MD simulations in capturing realistic steady-state transport

behavior and guiding the development of next-generation MOF-based membranes.

The results of this thesis suggest several directions for future research. The CGD-MD method can be further developed to study multicomponent gas mixtures and to simulate conditions closer to real industrial operations, such as varying temperature and pressure. Future studies should also include more ZIF and COF structures to better understand how pore size, shape, and flexibility affect gas selectivity. Using advanced sampling techniques or machine learning to improve force field optimization could make simulations faster and more accurate. Finally, connecting molecular-level simulations with larger-scale models can help link atomistic transport mechanisms to real membrane performance, supporting the design of more efficient materials for gas separation, storage, and energy applications.

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APPENDICES

APPENDIX A. STRUCTURAL PROPERTIES OF COF MEMBRANES

Table A.1: *Structural characteristics of the COF membranes studied in this work.*

COF Name	System Size	Database	PLD (Å)	LCD (Å)	ASA (m ² /g)	Porosity
COF-300	2×2×5	Original	9.26	9.36	3254.4	0.73
COF-320	2×2×7	Original	8.29	8.45	1804.3	0.63
COF-303	2×2×7	Optimized	8.31	8.60	1827.1	0.61
COF-921	2×2×7	Optimized	17.28	17.77	1797.8	0.70
3D-Por-COF	1×2×2	Optimized	13.84	16.47	6082.4	0.84
NPN-1	4×4×7	Original	4.11	5.37	906.2	0.51
NPN-2	4×4×7	Original	4.19	5.27	1074.6	0.54
NPN-3	3×3×7	Original	5.44	6.14	942.6	0.49
TPE-COF-I	2×3×5	Original	7.17	7.82	1817.2	0.60
COF-IM AA	2×2×6	Original	24.17	24.46	1553.9	0.70
DMTA-TPB2	2×2×7	Optimized	18.90	19.62	1956.5	0.73
TfpBDH	2×2×13	Original	36.16	36.32	2098.4	0.82
PCOF-2	1×2×2	Original	26.28	28.08	6867.5	0.92

APPENDIX B. CONCENTRATION PROFILES OF COF MEMBRANES

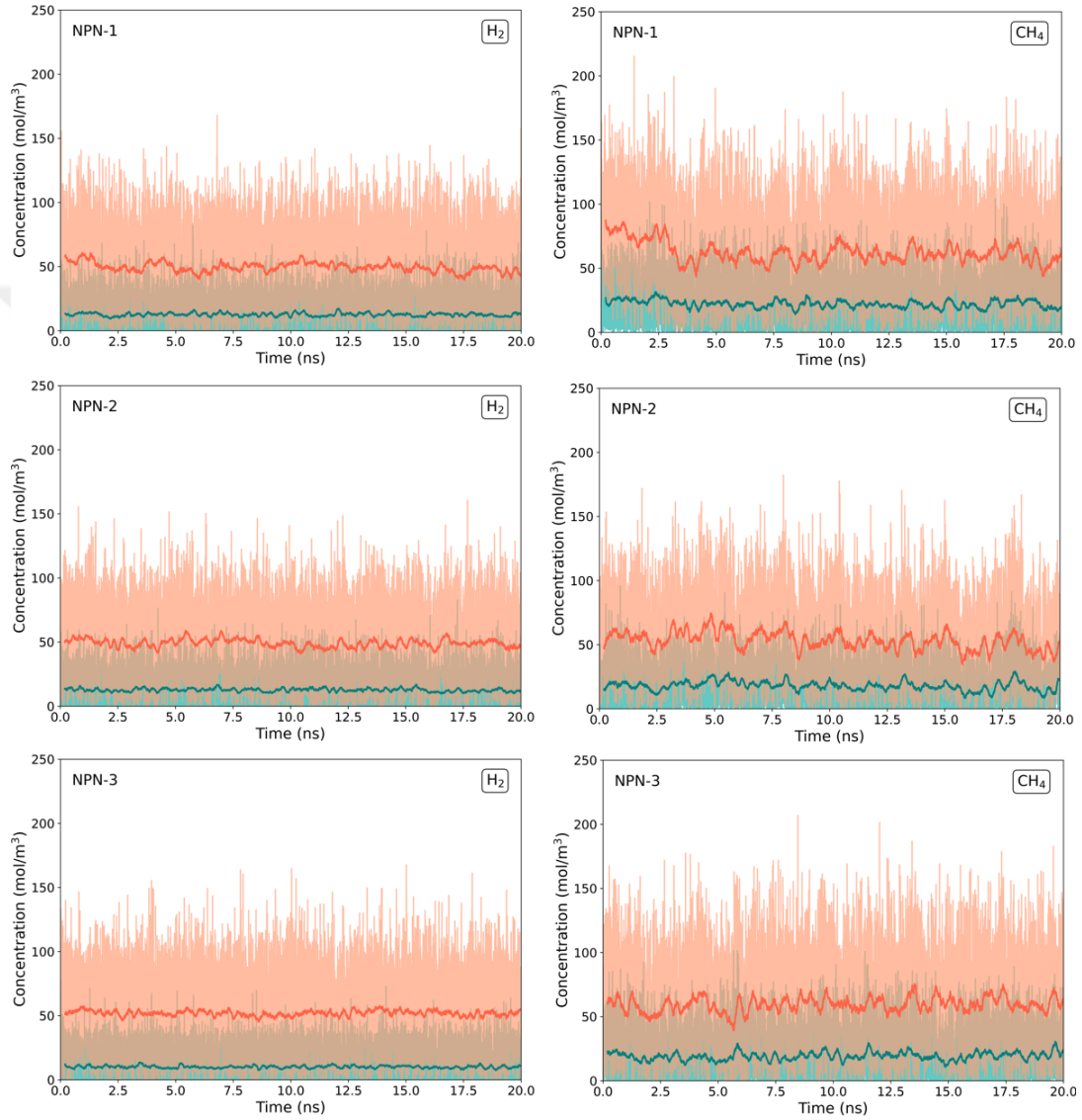


Figure B.1: Inlet and outlet concentrations of H_2 and CH_4 in NPN-1, NPN-2, and NPN-3 as a function of simulation time.

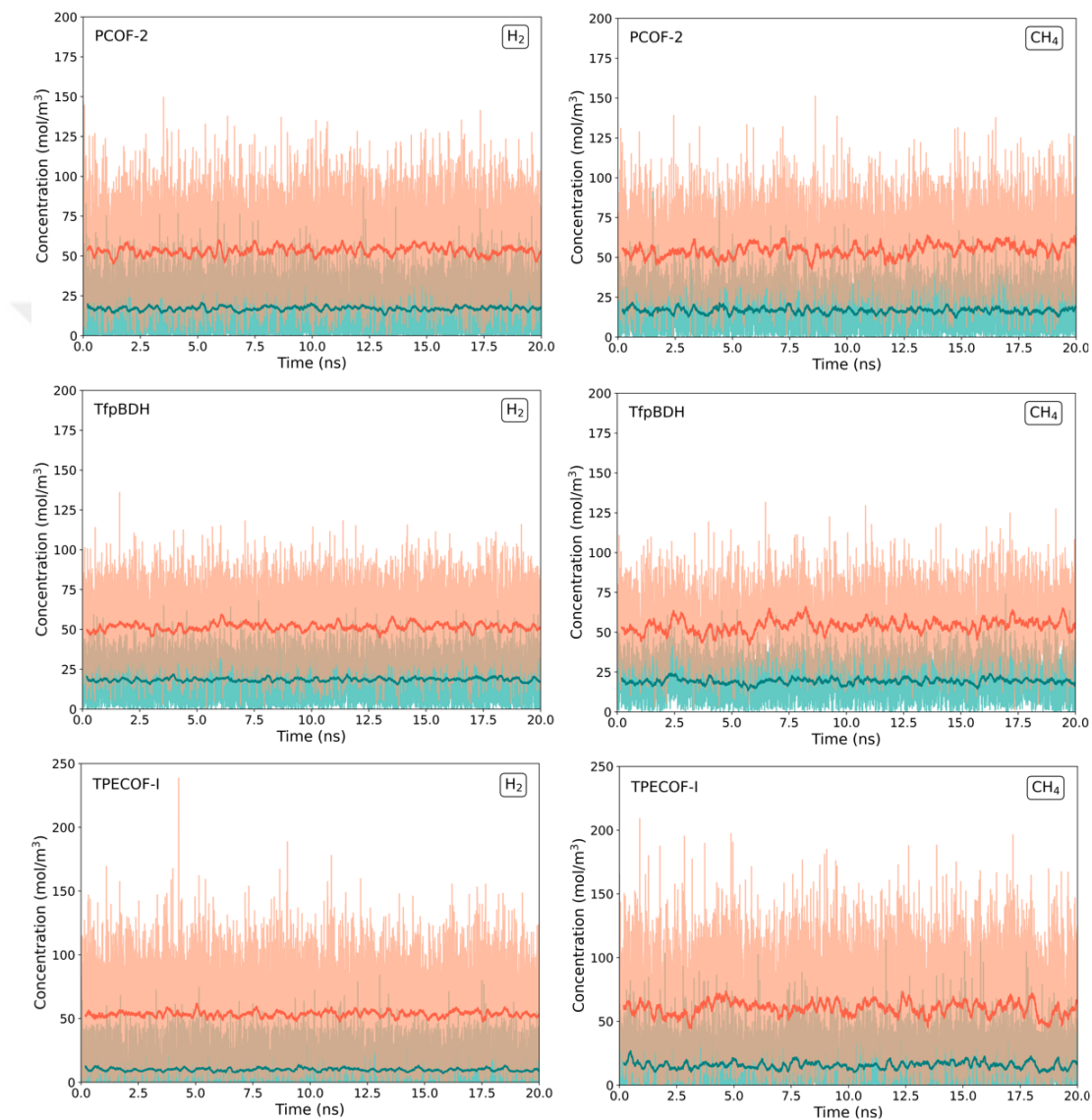


Figure B.2: Inlet and outlet concentrations of H_2 and CH_4 in TPE-COF-I, TfpBDH, and PCOF-2 as a function of simulation time.

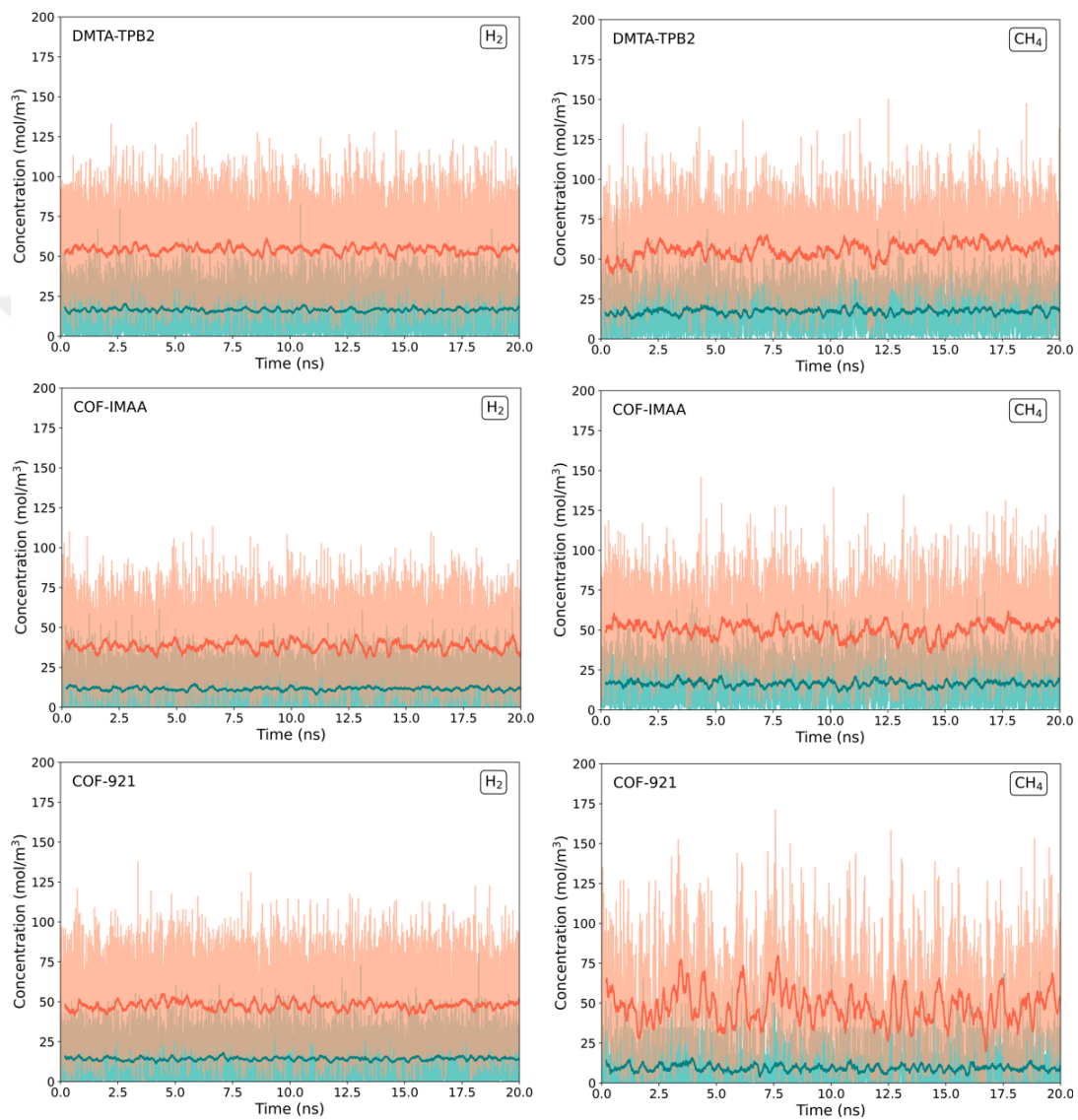


Figure B.3: Inlet and outlet concentrations of H_2 and CH_4 in DMTA-TPB2, COF-IM AA, and COF-921 as a function of simulation time.

APPENDIX C. FORCE FIELD PARAMETERS FOR ZIF-8

The lj parameters for ZIF-8 membrane and different charge models used in this work, are given as follows:

Table C.1: Atomic charges from different assignment models and Lennard–Jones (LJ) parameters for ZIF-8.

Atom Type	DDEC	Qeq	PACMAN	PACMOF	ϵ (kcal/mol)	σ (Å)
C1	+0.437	0.291	0.325	0.392	0.086	3.400
C2	-0.066	0.012	-0.024	-0.075	0.086	3.400
C3	-0.461	-0.324	-0.527	-0.566	0.086	3.400
H2	+0.114	0.090	0.085	0.089	0.015	2.510
H3	+0.138	0.113	0.147	0.165	0.016	2.471
N	-0.420	-0.287	-0.350	-0.344	0.170	3.250
Zn	+0.707	0.117	0.672	0.643	0.012	1.960