Review Paper

An overview of Molecular Simulations Studies in Mixed Matrix Membranes for Gas Separation Processes

Paloma Ortiz-Albo [1], Hiromitsu Takaba [2], Izumi Kumakiri [3,*], João G. Crespo [1], Luísa A. Neves [1,*]

[1] *LAQV/ REQUIMTE, Department of Chemistry, NOVA School of Science and Technology, FCT NOVA, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal*
[2] *School of Advanced Engineering, Environmental Chemistry and Chemical Engineering, Kogakuin University, 2665-1, Nakano, Hachioji, 192-0015, Tokyo, Japan*
[3] *Graduate School of Sciences and Technology for Innovation, Yamaguchi University, 7558611, Ube, Japan*

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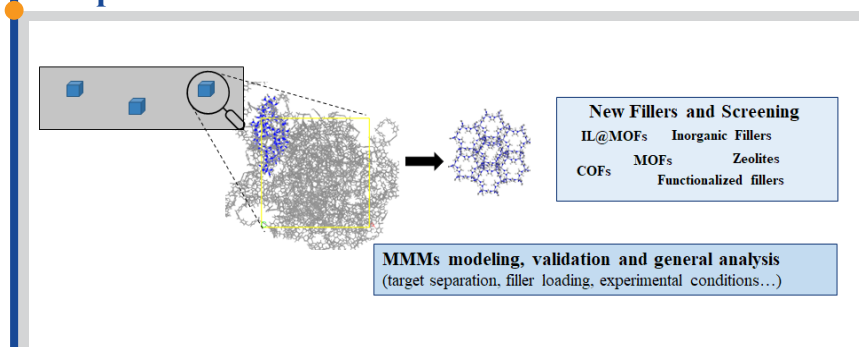
Highlights

• Molecular studies in MMMs relevant to evaluate structural and transport properties
• Different MMM components can be modelled to optimize materials screening
• Novel MMM model design should include interphase analysis
• Model validation supported on experimental data is crucial for emerging materials

Abstract

Industrial gas separation demands and environmental concerns have motivated the development of membrane technology with a large and evolving variety of novel and advanced materials. In particular, Mixed Matrix Membranes (MMMs), where a combination of a polymer and a filler occurs, can be prepared by infinite combinations between them to benefit from the advantageous properties of polymers and fillers. However, not all the pairs lead to obtain an enhanced membrane material. To reduce and optimize the experimental effort, the use of high-throughput screening computational studies has become an important assessment tool to evaluate the introduction of novel fillers inside different polymers and their modifications. Furthermore, the use of molecular simulations adds an attractive source of phenomenological atomical-level understanding of the modeled system and separation, being possible to test multiple potential gas separations with the same simulated membrane. In this review, an analysis of the current state-of-the-art and emerging trends of atomistic studies applied to MMMs for gas separation processes is presented. Simultaneously, it aims to help the reader to understand and distinguish the different alternatives to gather the desired phenomenological information and how to approach atomistic studies from experimental data for MMMs, presenting their advantages and limitations. Future perspectives and methodologies linked to non-ideal MMMs behavior will be also addressed. The most recent and trending advances in this topic can be highlighted as the transition to newer fillers, the incorporation of a third material in the membrane system, and the defect engineering at the interphase.

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* Corresponding author: Luísa A. Neves (lan11892@fct.unl.pt), Izumi Kumakiri (izumi.k@yamaguchi-u.ac.jp)

1. Introduction

Climate change is causing various environmental problems and requires urgent action. The reduction of carbon dioxide (CO_2) and other greenhouse gas emissions is expected to restrict climate change. Membrane separation is considered one of the solutions to address the above challenges [1]. Among various types of membranes, Mixed Matrix Membranes (MMMs), consisting of a polymer and a filler, continue to emerge as a versatile alternative membrane material to be used for gas separation processes. The benefits from polymers and uniformly dispersed fillers to enhance membrane properties and gas separation performance keep motivating the development of new materials and combinations [2,3].

As traditional polymers keep being attractive due to their versatility, low cost, and easy manufacture, more recently developed polymers keep growing as potential alternatives, such as polymers of intrinsic microporosity (PIMs) [2]. On the other hand, numerous fillers and their modifications, with appealing gas separation properties, have been proposed to overcome the trade-off upper bound limit of membrane permeability and selectivity, and improve long-term thermal and mechanical stability of pristine polymers.

A successful preparation of MMMs strongly depends on the compatibility between the selected materials. For example, the poor interactions and affinity between filler and polymer may result in voids formation. The development of non-ideal structures, including voids, pore blockage, polymer rigidification, or particle agglomeration can lead to a decrease in membrane selectivity [4]. Especially for polymers with purely inorganic fillers, such as zeolites, silica-based materials, or carbon-based materials, the preparation of defect-free MMMs is challenging [5,6]. Therefore, fillers with a hybrid organic-inorganic nature, such as metal-organic frameworks (MOFs), and emerging pure porous organic materials, such as covalent organic frameworks (COFs) and porous organic cages (POCs) have attracted interest in the last years [7]. An alternative for improving the interaction of polymer-filler in MMMs can be the modification of the filler external groups or the incorporation of a third component to act as a plasticizer, such as ionic liquids (ILs) [8,9]. Gathering the continuously emerging novel materials and their infinite combinations, it becomes unrealistic to experimentally assess all of them to determine their feasibility for target gas separation processes. The motivation to use computational studies instead of a purely experimental study strongly relies on the associated high cost and time consumption of experimentally testing the potential combinations of materials [10]. There is still a need of extending molecular simulations methods to multicomponent membranes, along with their atomistic description, their microstructure, and the importance of the interphase analysis and its role on gas transport.

In this regard, Keskin and Altinkaya (2019) [11] gathered several simulation works for MOF-based MMMs and described the role of computational studies. They identified the potential of combining experimental work and molecular simulations to provide fundamental knowledge of membrane properties and gas separation at atomic scale. The filler screening through high-throughput molecular simulations unlocks the potential of certain materials for different gas separations. They highlighted the use of molecular simulations (MS) in membranes for gas separation to describe membrane properties and their role in gas separation, causing an increase in the simulation works in the last years.

As guidance for future research efforts, this review provides updated analysis and new trends of the current state-of-the-art of molecular simulations and atomistic computational studies for MMMs in gas separation processes. A condensed description of the simulation works in the literature, highlighting the simulation methodology and the nature of the filler, has been gathered. This review is organized in two sections. First, it discusses how emerging materials,

and their combinations might optimize experimental efforts to later be considered for their atomistic modeling. The strategy followed consisted in gathering the most common experimental techniques to complement/validate MMM simulations in new materials. Secondly, the prospects and future trends of computational studies were theorized considering the current state-of-the-art, where different approaches and methodologies for atomistic modeling of MMMs are considered.

2. State-of-the-art of Simulation Approaches in MMMs

The most typical method to model and predict MMMs behavior has been through the gas performance properties from the individual pristine materials (polymer and filler) and mathematically combining them into the MMM gas permeability results, resulting in the so-called macroscopic permeation models. These models have been developed over the years to include more details about the defects and non-ideality behavior of gas transport. Keskin and Altinkaya [11] also gathered in their review several computational approaches for MOF-based MMMs and described the macroscopic models as resistance-based models, effective medium theory-based models, and simulation-based rigorous models. Regarding the depicted as effective medium theory-based models, MMM permeability is evaluated as a combination of the filler permeability, the filler volumetric loading, and the polymer permeability, where the filler is dispersed. The potential models can be classified as the ones in which only ideal behaviors are assumed, as the traditional Maxwell Model, and the models assuming non-ideal effects. The latter model approaches a more detailed description of the microstructure, non-idealities in the polymer-filler interphase, and effects such as filler shape (ideal or non-ideal morphology), filler packaging, polymer rigidification, and interphase voids (Fig. 1). These macroscopic models along with their assumptions and limitations are summarized in Table 1 [11,12].
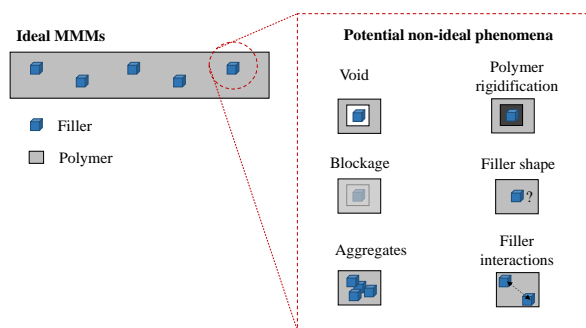
Fig. 1. Scheme of ideal and non-ideal MMM structures.

However, these models, while effective and practical in providing information, are still far from describing fundamental information about the causes of these non-ideal structures and their role in gas separation.

Conversely, molecular simulations (MS) are a powerful tool to model and study materials properties at the molecular level based on intermolecular interactions and have been extensively applied in membrane technology [10]. There are two commonly used methods for the permeation description of gases in MMMs: Grand Canonical Monte Carlo (GCMC) simulations, and Molecular Dynamics (MD) Simulations. The GCMC method involves stochastic

simulations with statistical thermodynamics to construct equilibrium configurations. The chemical potential, volume, and temperature are kept constant in GCMC simulations, while the energy and number of particles from a penetrant reservoir in a system, that is, the membrane, fluctuate to achieve an equilibrium state. The typical application for this type of simulation consists in determining the sorption properties of the system for gases. Sorption isotherms are frequently determined considering a constant composition and a range of gas fugacity. The convergence of the system to a certain number of gas molecules will provide the corresponding gas sorption at a specific fugacity. GCMC simulations, however, will not provide any time evolution of the properties of the simulated membrane, and therefore, cannot be used for the description of the dynamic behavior.

On the other hand, MD is based on classical mechanics, more interestingly applied for diffusion analysis. They have been typically divided into Equilibrium Molecular Dynamics (EMD) and Non-Equilibrium Molecular Dynamics (NEMD) simulations. In these simulations, the evolution of the system and the gas penetrants are followed over time, along with their thermodynamic and dynamic properties as average of their trajectory. The prediction of the membrane properties along time can be performed on a fully flexible or constrained system. A statistical ensemble can also be considered, using macroscopic constraints (number of particles, volume, energy, temperature) to allow the estimation of the thermodynamic properties. However, the EMD simulation does not provide direct information about the transport of molecules under a chemical potential gradient. Still, it is possible to relate the dynamic behavior of gas molecules in the system through the self-diffusion coefficient, which is related to the movement of the molecules in the system.

EMD simulations are typically performed in a three-dimensional periodic cell in which the movement of the penetrant molecules does not suffer an external force. NEMD, on the contrary, describes the membrane as a layer, considering the chemical potential gradient-driven transport of molecules from the designed feed side to the permeate side, and therefore, molecular fluxes can be calculated directly from the simulation. Therefore, external forces will not allow the achievement of the equilibrium of the system, fixing the external gradient in one direction. The advantages of each approach differ in the closeness of the simulation to an actual gas permeating system. While NEMD simulations provide an attractive molecular-level detailed membrane separation process, the high computational effort and time required have strongly limited its application to complex systems, being strongly dependent on the system thickness and structural wideness of the modeled material. Keskin et al. [21] prepared a MOF membrane layer of approximately 4-5 nm, and compared the results from both approaches (EMD and NEMD) requiring several days for NEMD simulation for what it would spend hours in EMD simulations with the same computational resource. Then, Semino et al. [22] compared the use of NEMD simulations with a higher layer thickness in filler (29.8 nm), polymer (40.1 nm), and MMM (93.6 nm), showing the potential of atomical level understanding of NEMD simulations for MMMs with considering void effect correctly, which cannot be obtained by the separated simulation of filler and polymer. Additionally, the thickness considered in this study was closer to the ones found in thin film composite (TFC) membranes [23], in which the selective layer can be a MMM over porous support. The support provides mechanical stability to the membrane, being possible to drastically reduce the thickness of a selective MMM layer. These selective and dense MMM with fillers, such as MOFs, can range from near 200 nm to a few micrometers, and thus, the use of NEMD simulations with these thicknesses can be representative of those types of membranes [22].

Hereinafter, it is presented a comprehensive state-of-the-art summary of the different studies reported in the literature including atomistic computational calculations for MMMs in gas separation processes. The variable selected for the classification has been the number of components considered in the molecular simulation (single, two, or three), and the main discussion is focused on the materials and methodology used in each work. As a guide through the gathered works, details regarding the materials used, target gas separation, approach selected, and objective of the simulation study are summarized in Table 2.

Table 1

MMM permeation models [11,12] along with their main assumptions and limitations. Schematic representation makes reference to Fig. 1 where non-ideal structures are shown.

Model	Schematic representation	Description
Maxwell [13]		• Simplest and most used model • Ideal morphology • Valid for low loadings (≤20wt.%) • Assumes that streamlines around spherical particles are not affected by nearby particles • Does not account for particle size distribution, particle shape and aggregation of particles
Extended Maxwell [14]		• Generally applicable to dilute suspension of spherical particles • Accounts the correction for interactions between particles and introduces the reduced permeation polarization as a factor
Modified Maxwell (two-phase) [15]		• Accounts the effects of polymer chains rigidification at the polymer-filler interphase • Based on two-phase descriptions (polymer and particles-interphase-pseudo-inert phase) • Does not account for particles size distribution, shape and aggregation of particles • For low and moderate values of filler loading (≤20wt.%)
Modified Maxwell (four-phase) [16]		• Considers chain rigidification, pore blockage effect and particle aggregation • Permeation is modeled considering four phases: Phase 1 – polymer matrix, Phase 2 – chain rigidification, Phase 3 – nanoparticles and particle blockage layer, Phase 4 – particle aggregate layer • Low-moderate filler loading (≤20wt.%)
Maxwell-Wagner-Sillars		• Filler is ellipsoid. No interaction between the particles • Low-moderate filler loading (≤20wt.%)
Bruggeman [17]		• No defects in the polymer-particle interface • Similar limitations to the Maxwell approach
Modified Bruggeman (pseudo-two phase) [16]		• Considers the formation of voids in the interphase layer of MMM. Pseudo two-phase region – matrix and filler plus void region
Lewis-Nielsen [18]		• No defects in the polymer-particle interface • Valid for a broader range of filler concentration (up to maximum packing volume fraction = 0.64) • Effect of morphology related to particle size distribution, particle shape, and aggregation of particles. Without this consideration, it is simplified to the Maxwell model.
Pal [19]		• Effect of morphology related to particle size distribution, particle shape, and aggregation of particles. Without this consideration, it is simplified to Bruggeman model.
Modified Pal (pseudo-two phase) [16]		• Polymer matrix and interfacial rigidified matrix chains
Felske [20]		• Dispersed particles as a core • Surrounding interfacial layer (rigidified layer, voids, or particle pore blockage) as shell • Model reduced to Maxwell model if interlayer is absent
Modified Felske [16]		• Particle morphology and packaging factor • Reduced to Felske model or Lewis-Nielson model or Maxwell model depending on simplification

2.1. Single component modeling of porous fillers

Several works, led by Keskin *et al.* [11], have focused on performing hybrid high-throughput filler screening for target gas separations or performing a broad analysis to determine the most feasible separation. These studies emphasized the versatility of atomic-level theoretical modeling of MOFs along with experimental permeation data from polymers.

The protocol followed reflects on the independent modeling of sorption properties from the dynamic gas behavior in the desired filler: GCMC simulations for gas sorption, and EMD simulations for gas transport. Fig. 2 depicts this methodology including the necessary equation previously described. The simulation conditions, such as target gas, temperature, and pressure, are typically selected to represent experimental data. GCMC simulations were performed to determine the pure gas sorption isotherms at a defined temperature. Porous fillers are typically characterized by gas uptake isotherms, being a useful and fast approach to validate the forcefield selection of the filler. Additionally, the GCMC simulations allow to obtain the number of gas molecules at a specific pressure and temperature, which is typically used for the next EMD simulation. Therefore, it is advantageous to sequentially perform these simulations in this sequence. GCMC simulations were used for several key aspects before performing further simulations: fast filler forcefield validation through gas sorption isotherms, the calculation of the number of gas molecules at specific conditions, and the prepared filler framework with the corresponding gas molecules for the dynamic simulation. EMD simulations in this approach consist in performing a NPT ensemble dynamic simulation (constant number of particles, pressure, and temperature) which allows for the calculation of the self-transport diffusivity using Einstein relation of the mean-square displacement of gas molecules [24,25]. The self-diffusivity includes interactions with the filler framework and other gas molecules. To convert the self-diffusivity to transport diffusivity, a relation through the loading-dependent corrected diffusivity and thermodynamic factor was used (Eq. 1 in Fig. 2). The latter can be calculated by analytical differentiation of the fitted gas sorption isotherm from GCMC simulations [26].

Using the calculated transport diffusivity and Fick's Law [27] (Eq. 2 in Fig. 2), a flux was estimated using as a gradient the molar concentrations. The gas permeability was ultimately calculated through the theoretical flux (Eq. 3 in Fig. 2). Then, the estimated filler permeability was used, along with experimentally known polymer permeation data through the macroscopic permeation models from Table 1 to determine the MMM gas permeability at different filler loadings.

Using the crystallography information from Cambridge Data Base (CDB) and rigid framework, Erucar, and Keshin [28] modeled the transport properties of 16 different MOFs to later be combined with experimentally 7 potential polymers for H_2/CH_4 and CO_2/CH_4 separations. They analyzed the loading influence using Maxwell and modified Felske models compared with other potential models such as modified Maxwell, Bruggeman, Lewis-Nielson, Pal, and Felske (Table 1). The selection and validation of the atomic model developed were based on the comparison with existing experimentally prepared and tested MMMs.

Through this approach, they successfully determined the most promising MOF and polymer configurations based on the gas separation performance.

The same authors extended their work [29] to other MOFs, and more specifically, Zeolitic Imidazole Framework (ZIF) materials following a similar methodology for CO_2/N_2 separation. Then, in another study [30], the potential of multiple MOFs for CO_2/CH_4 separation was analyzed. Via atomistic simulations, the performance properties of several MOFs were determined and combined with experimental data of other potential polymers using the Maxwell permeation model. Particularly in this work, the rigid MOF framework was complemented by the analysis of MOF framework flexibility through MD simulations. Due to the high computational time required for the diffusivity analysis in a flexible framework, two structures were compared: narrow pored and large pored frameworks. The latter one suffered a lower impact in its permeability and selectivity than the narrow-pored structure. Similar observations were obtained in a later work [31]. Over five thousand MOFs combined with different polymers were explored for O_2/N_2 separation. Variables such as MOF loading, and mixture were included in the study to later evaluated the effect of MOF framework flexibility. While the flexibility assumption affected the narrowed channels of the MOFs, the simplification of the rigid framework allowed a high-throughput analysis of the potential of these materials for a certain separation.

Other works [24,32] following this methodology, focused on ZIFs use along with several polymers studied for a wider range of potential gas applications, and their performance was modeled for H_2, CO_2, CH_4, and N_2. The authors simulated the ZIFs properties using GCMC+EMD, along with the Maxwell and modified Felske permeation models in theoretical MMMs as previously described (Fig. 2). The validation of the methodology consisted of two parts: pure ZIF-8 and ZIF-90 data, and specific MMMs with selected polymers were evaluated. Most promising combinations were suggested for these new pairs depending on the desired gas separation.

In another single component simulation study, Velioglu and Keskin [21] compared the gas transport properties of MOF-5, Cu-BTC, ZIF-8, and another MOF, called MEFMEQ, for a GCMC+EMD approach over a NEMD simulation for H_2 and CH_4. NEMD-based simulations allow a more realistic determination of gas transport through a certain material. The gas flux was estimated considering a simulated pressure difference between a gas bath of approximately 90 Å delimited by a graphene layer (feed) and a vacuum space of 200 Å (permeate), separated by the MOF layer (40-50 Å). Most recent work from Zhai et. al. [33] applied their previously developed methodology of dual-control plane non-equilibrium molecular dynamics (DCP-NEMD) to determine single and binary gas mixture permeation at different temperatures. They applied this method, especially for CAU-1, an aluminum-based amine-functionalized MOF, with a simulated membrane thickness of 3.55 nm. Each simulation works modeled transport in one direction, while considering periodic boundary conditions in the other two. However, in the first case, a fixed pressure of gas was considered to permeate through the membrane along time, while in the second, the DCP-NEMD considered two plane controls, in the high-pressure compartment (feed) and in the low-pressure compartment (permeate). These plane controls generate and delete gas molecules on each side of the membrane layer, to maintain a constant driving force through the membrane. Therefore, the first case represents a closed permeation system with a varying driving force, while the second represents a continuous open system.
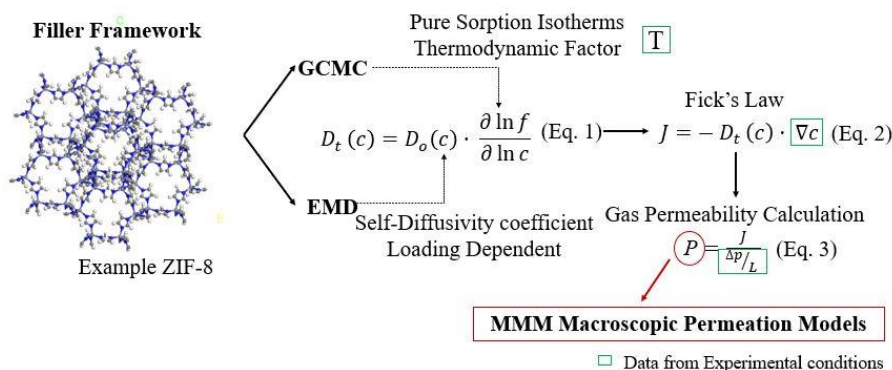
Fig. 2. Schematic representation of GCMC+EMD methodology followed for single-component modeling. Embedded equations refer to transport diffusivity calculation from loading dependence correction (Eq. 1), Fick's Law (Eq. 2), and gas permeability calculation (Eq. 3), where T is the temperature; D_t, the transport diffusivity coefficient; D_o, the corrected diffusivity coefficient; f, gas fugacity; c, gas concentration; J, flux; p, pressure; L, membrane thickness and P, gas permeability.

The use of computational tools for MOF screening considering several applications as MMMs has been the most used approach for single component atomical studies. However, emerging fillers, such as COFs, [34,35] have also started to take interest in gas separation processes, and therefore, in simulation works. In a first instance, Keskin et al. [36] analyzed the potential of 288 COFs from a computation-ready, experimental (CoRE) COF database prepared by Zhong *et. al.* [34,35] for CO_2/H_2 selective sorption processes using GCMC simulations, to complement the study with MD simulations for the best candidates as COF-based membranes. After analyzing two potential forcefields (UFF and Dreiding forcefield), Dreiding forcefield was selected for all the modeled systems. Then, in another work [37], more than five hundred COFs from Clean, Uniform, and Refined with Automatic Tracking from Experimental Database (CURATED) COFs [38] were modeled for CH_4 separation from H_2, N_2 and C_2H_6. In this study, the simulation approach combined GCMC, MD and DFT simulations. While these works did not link their results to potential MMMs, the screening and model definition establish a starting point to effectively analyze the optimal material for a target gas separation in a MMM framework. And thus, COF (and functionalization) and MOF were combined with different polymers in posterior works [39,40] for CH_4/N_2 separation using versatile polymers, such as PDMS, PEBA or SBS. These studies established a successful starting point to analyze the potential of COFs for gas separation as MMMs.

Nevertheless, the potential of combining GCMC and EMD to be extended to modified fillers through an additional component has also been evaluated. More specifically, several molecular simulation studies for the composites comprising ILs supported by MOFs (commonly designed as IL@MOFs). The interest behind this alternative relies on the improvement of sorption selectivity by the incorporation of an IL. In this regard, simulation studies have successfully extended the previously described methodology (Fig. 2) to describe the sorption and dynamic behavior of several appealing IL-MOF combinations for several gases. Polat *et al.* [41] analyzed the most suitable generic forcefields (Universal Force Field (UFF) and Drieding) to model IL@Cu-BTC composites with seven different ILs. The incorporation of IL in the Cu-BTC framework consisted of several steps. Firstly, the IL structure was optimized in terms of cation-anion pair orientation, considering that the structures are rigid as computational simplification. Then, their incorporation into the Cu-BTC framework was accomplished through GCMC simulations divided into three moves: translation, rotation, and random translation, followed by an energy optimization algorithm. They successfully obtained gas uptake data representing the experimental sorption data and estimated the gas self-diffusivity considering an infinite dilution system for the dynamic simulation. In a similar approach [42], the incorporation of one molecule of a modified IL with different group tailoring (CH_3^-, SO_3H^-, and NH_2^-) in ZIF-8 particle was analyzed using GCMC simulations in terms of sorption uptake and ideal sorption selectivity, to later develop experimentally the corresponding MMMs. In this case, the incorporation of modified ILs optimized by density functional theory (DFT) methods in the ZIF-8 cavity was performed through Ab initio molecular dynamics (AIMD) simulations within the canonical ensemble (NVT). Experimentally, the preparation of the composites can be approached through different synthesis routes: ionothermal and post-synthesis modifications [43]. A key factor in these protocols is the effective incorporation at the desired location, e.g. inside the large MOF cavity or at the external surface. In the IL@MOF simulations, the effective incorporation of IL inside the MOF cavity is designed, without considering a partial non-ideal composite.

Posterior works have also used molecular simulations for the evaluation of IL incorporation in the MOF [39,44] and COFs [45] following high-throughput screening analysis. Both studies did not include the combination with different polymers in the computational analysis, being in [44] validated by experimentally prepared IL@MOF composites and MMM. Nevertheless, the reduction of potential candidates for CO_2/N_2 considering thousands of combinations allows future experimental works toward effective CO_2-selective materials and compare to other types of fillers.

The modeling of a single component, in this case, the filler, has allowed to analyze and screen its potential for different applications. The combination of atomistic modeling of the filler with more elaborated permeation models has the potential to also determine and characterize non-ideal configurations in the filler and the resulting membranes in a versatile approach.

The main challenges faced in this approach have been the extension of this methodology to novel materials. The appropriate selection of the forcefields and atomic methods is the key to effectively model the material. Additionally, as requirements to apply this approach to new materials, experimental permeation data from the desired polymer, extensive experimental characterization, and gas performance from the filler are required for model validation. Moreover, key MMMs experimental data will be needed for validation and check of the selection of an adequate permeation model. In this sense, simulated databases have motivated and facilitated the extension of these screening methods to other materials, which are relatively common and updated for the described fillers, but, on the contrary for MMMs, scarce for experimentally combined filler/polymer. Moreover, novel and advanced fillers, such as COFs or IL@MOFs, face the difficulty of not possessing enough MMM studies, while their preliminary potential has been already discussed.

2.2. Two Components – MMMs

Inorganic porous materials have been considered as fillers in MMMs due to their molecular sieve properties. The loading of fillers affects the membrane perm-selectivity as increasing the filler concentration will favor, up to a defined load, the permeability and selectivity of the resulting MMMs. However, high filler concentrations may lead to the occurrence of non-ideal structures, which limits the mechanical properties of these membranes and their long-term performance. Accordingly, there is usually an optimum loading. One way to find this optimum is to fabricate MMMs with different loadings. The use of simulation tools is another way, of combining the modeling of the desired polymer and filler for different loadings. In contrast to the cases from Section 2.1., herein the molecular simulation studies involve the modeling of filler and polymer simultaneously. The research works using the simulation of polymer and filler in a single system are organized depending on the nature of the filler: metal oxides, silica and carbon-based materials, zeolites, metal-organic frameworks, and others.

2.2.1. Metal Oxides, Silica, and Carbon

Amirkhani *et al.* [46] and Riasat Harami *et al.* [47] investigated the influence of loading in MMMs consisting of two metal oxides: zinc oxide (ZnO) and iron oxide III (Fe_2O_3), respectively, along with the thermoplastic elastomer poly (amide-6-b-ethylene oxide) (or PEBA). Both works combined experimental membrane characterization and MS to analyze the metal oxide filler in terms of solubility and diffusivity coefficients through GCMC and EMD, respectively. This combination of GCMC and EMD has been typically used for other simulation works described in this Section 2.2.. On the contrary to the filler cases, in MMM modeling, GCMC simulations are used to determine the modeled membrane solubility coefficient through the determination of sorption isotherms. Then, the gas molecules at a defined pressure and temperature are inserted through GCMC simulation. Then, the sorbed gas molecules are utilized to perform a EMD simulation, which will describe their dynamic behavior in the membrane cell. For both studies, loadings below 2wt.% were simulated and optimal loadings considering CO_2 permeability against CH_4 [46] and N_2 [47], temperature and pressure were obtained for both systems.

Similarly, silica nanoparticles dispersed in poly(1-trimethylsilyl-1-propyne) [PTMSP] [48] were simulated. The dynamic behavior of several gases (H_2, O_2, N_2, CO_2, CH_4, n-C_4H_{10}) was determined at different loadings in the polymer, from 20 to 60wt.%. Additionally, particle size was analyzed by maintaining the silica loading constant but using particles with diverse radii. The highest membrane performance was obtained with the smallest particle size modeled. The authors also determined the thermodynamic data for pure polymer and optimal MMM structures. Analyzing the total system energy, a positive effect from the addition of particles in the membrane mechanical stability was observed. Modarress et al. [49] analyzed nanosized silica particles in polysulfone for O_2, N_2, CO_2 and CH_4. They initially compared condensed-phase optimized molecular potential for atomistic simulation studies (COMPASS), polymer-consistent force field (PCFF), and Dreiding force field for membrane unit simulation and compared membrane density to experimental data from elsewhere [50]. A COMPASS forcefield was selected as the most suitable, and gas sorption and diffusion were analyzed considering bulk periodic units. In two posterior studies, the dispersion of different amounts of silica nanoparticles in PS was analyzed considering different CO_2/CH_4 binary mixtures composition [51] and the effect of different polymorphs of SiO_2 nanoparticles (α-Quartz, α-Cristobalite, α-Tridymite) [52]. In both cases, the methodology followed consisted in the combination of GCMC and EMD simulations to determine the solubility, diffusivity and permeability coefficients for different filler loadings and gas mixtures. Additionally, qualitative analysis of selective sorption sites depending on the filler and gas mixtures was discussed.

Pasquinwlli et al. [53] simulated the interactions between rigid Poly-(p-phenylene biphenyltetracarboximide) (BPDA–PDA) and multi-walled carbon nanotubes (MWCNTs). They analyzed different morphologies, arrangements, and loadings of MWCNTs in the polymer matrix, focusing on their structural and mechanical properties depending on the filler and its orientation in the polymeric matrix.

2.2.2. Zeolites

In one of their works, Harami et al. [54,55], summarized a methodology to perform the modeling of MMMs composed by LTA zeolite in polydimethylsiloxane (PDMS) considering GCMS and EMD. In [54], the study was focused on the effect of the temperature and filler loading on the sorption properties of several gases (H_2, CO_2, CH_4 and C_3H_8). EMD simulations were carried out to prepare and characterize the simulated membranes in terms of X-ray diffraction and glass transition temperature with zeolite loadings up to 50% in PDMS, sorption distribution was also analyzed. Other of their works considered zeolites as fillers in MMMs and followed similar methods including FAU zeolite in polyether block amide (PEBA) [56,57]. These studies used the same methodology, constructing a bulk amorphous cell composed of the polymer chains and the filler. Particularly, the effect of d-spacing of the polymeric chains was analyzed by building the MMM unit at a lower temperature [57].

Another computational study combined with experimental work considering the functionalization of FAU zeolite with different groups (-SO_3 from Nafion and -NH_2 from 3-aminopropyl triethoxysilane (APTEOS)), combined with PEBA as the polymeric matrix, for CO_2, CH_4, and N_2 [58]. In this study, the bulk construction cell was prepared similarly to other works, combining the filler (functionalized when applied) with PEBA chains considering different loadings. GCMC and EMD simulations were performed and successfully compared to the corresponding experimental data considering loadings from 0.5 to 5wt.%. Effects of the gas mixture, temperature, and operating pressure were also considered in the study.

Contrasting to the previously described works, Dutta and Bhatia [59] focused their study on describing the interactions of zeolite and polymer at the atomic level. They designed a layer-based unit cell, in which the MFI zeolite unit cell was sandwiched between two polyimide polymer-filled regions. The research was oriented to determine the role of polymer rigidification and filler particle size on CO_2/CH_4 sorption and dynamic behavior.

2.2.3. Metal-Organic Frameworks

MS can be used to understand the microstructure of MMMs. A periodic unit composed of ZIF-7 and polybenzimidazole (PBI) polymer was prepared to perform GCMC and EMD simulations for H_2 and CO_2 separation [60]. They analyzed the effect of ZIF-7 loading in the membrane considering 1 to 3 ZIF-7 clusters in the polymer. The maximum void size per membrane, depending on filler loading, was analyzed. The maximum void size per membrane was found to increase with an increase in loading. Additionally, as in previous GCMC+EMD studies, gas sorption and transport were evaluated in the bulk unit and compared with gas permeation experimental data at high temperatures, obtaining a fair agreement between both. The use of computational studies has been also utilized to analyze non-ideal microstructures, such as the case of polymer rigidification in the interphase [61]. In this study, CO_2 high-pressure was exposed to the ZIF-8/Matrimid®5218 structure to analyze the interphase and the ZIF-8 structural properties. The modeled system was validated by the agreement of experimental sorption data with sorption isotherms produced by GCMC simulations.

Then, the interest in the analysis of the interphase MOF/polymer resulted in the use of a different methodology using atomistic studies. Semino et al. [62] developed a methodology to analyze the interactions of MOF/polymer by combining Density Functional Theory (DFT) calculations and force field-based simulations. The approach relied on the correct independent model of both components, followed by the use of DFT calculations to determine the most stable arrangement of the materials as layers, especially attending to the terminal functional groups. Factors such as interaction sites, filler external surface coverage, porosity, and polymer rigidity were evaluated through radial distribution and rotation angles of specific groups in the interface, free volume, and pore size distribution, among others. This methodology was later extended to other works. UiO-66 with PIM-1, polystyrene (PS), polyethylene glycol (PEG) as polymers, and HKUST-1 with poly(vinyl alcohol) were also evaluated in Semino *et al.* [63,64], respectively. In Semino *et. al.* [65], combining once again ZIF-8 and PIM-1, the effect of including defects on ZIF-8 in ZIF-8/polymer interphase was analyzed. A "defect containing" ZIF-8 was designed as a result of leaving out the terminal atoms on the ZIF-8 unit: -OH groups and imidazole moieties linked to Zn external atoms. These modifications at the terminal groups led to minor changes in the interphase. However, these studies did not include any gas separation in their analysis. However, posterior studies have introduced simulated gas permeation studies with the constructed layer-by-layer membrane. MOFs such as UiO-66 [66,67], ZIF-8 [22], ZIF-67 [68] and NUS-CO_2 [69] have been studied combined with several high permeable polymers. For the study of ZIF-67 [68], the layer was introduced to model a composite membrane, where the dense layer was

composed of a MMM. GCMC simulations were utilized to determine the sorption properties in the membrane, being able to determine the sorption selectivity along the membrane structure, and more especially at the interphase. For the dynamic behavior in this type of structure, NEMD methodology was applied, specifically called concentration gradient driven MD (CGD-MD) [22]. The transport of the molecules through the different layers was quantified along with the membrane structure and their residence time. In this regard, a specific study [67] focused on the effect of defect-engineered UiO-66 nanoparticles with crosslinked poly(ethylene glycol) diacrylate (PEGDA) was carried out. In this work, two potential UiO-66 structures (non-defective and with missing linkers) were compared in terms of sorption and dynamic studies for CO_2/N_2 separation. The authors used a macroscopic model in a reverse use of the model (from MMM to single filer/polymer permeability) to quantify the effect of those engineered defects in the experimentally prepared membranes. Therefore, the combination of the layer-by-layer membrane preparation approach with NEMD studies allowed to obtain fundamental information in terms of gas transport along with the different components, and at their interphase. Furthermore, the tunability characteristic of MOFs have also motivated the introduction of targeted defect engineering which had a key impact at the interphase. These recent studies present an initiative of analyzing non-ideal structures from the fillers and the corresponding effect on the polymer.

2.2.4. Other fillers

Porous Organic Cages have also been included as fillers in MMMs and analyzed by molecular simulations. Kong and Liu [70] performed a NEMD simulation, mimicking a gas permeation experiment, with a MMM composed of a porous organic cage (CC3) embedded in a PIM-1 polymer matrix. They simulated the gas transport following the solution-diffusion model and the driving force was kept constant with a Constant Pressure Difference MD Simulation (CPDMD) in which the gas transported through the membrane is added again to the feed side. Two mixing methods were followed, considering different sizes of the CC3 to be mixed in the polymeric matrix, showing the most favorable results for larger CC3 particles and in fair agreement with experimentally observed behaviors.

Another work using CC3 and 6FDA-DAM as polymeric matrix [71] studied the separation mechanism of C_3H_6 and C_3H_8 combining GCMC simulations and EMD comparing polymeric membrane to 20wt.% of dispersed CC3 following a bulk approach. The separation improvement by including the highly porous filler was successfully attributed to an upgrade in the diffusivity selectivity towards C_3H_6. The analysis of the trajectory of the molecules from EMD allowed to associate the selectivity improvement to the window and cavity size of CC3.

The modeling of both filler and polymer in the same system has provided practical information regarding structural and gas separation properties. Different approaches have been followed, being the most followed a combination of sorption and dynamics simulations, instead of NEMD simulations. Trending fillers are still predominantly focused on MOFs, with a few works focused on other fillers, which still leaves work to extend these methods to new appealing fillers, such as the novel COFs highlighted in Section 2.1., and novel polymers.

2.3. Three Components – MMMs

Few studies are published combining more than two components (polymer and filler), as the ones gathered in Section 2.2. However, recent studies have approached a ternary system, which goes along the trend in terms of experimental works. The motivation for including further modifications in a typical binary MMM gathers from the need of overcoming the limitations of existing MMMs concerning materials' compatibility issues and the search for a higher separation performance. Harami *et al.* [72] analyzed the gas separation performance along with the structural characteristics of polycarbonate filled with p-nitroaniline and LTA zeolite. In this work, p-nitroaniline was utilized as a plasticizer and co-dispersed along with zeolite particles in the polymeric matrix. Regarding the computational study, a bulk periodic system was prepared with different loadings, and several gases were considered (CH_4, CO_2, H_2, N_2, and O_2) to analyze their potential. GCMC and EMD simulations were used to analyze the structural properties of gas transport. Experimental work was combined with molecular simulations to analyze the effect of including an IL in a MMM composed of PEBAX polymer and γ-Al_2O_3 particles [73]. The membrane was prepared as a bulk, where gas permeability was also calculated using combining EMD and GCMC. Two different ILs were compared by modifying γ-Al_2O_3 particles prior to their utilization in the preparation of MMMs. the molecular simulations allowed to relate the membrane separation improvement, separately in terms of solubility and diffusivity, to the chemistry of each IL.

As previously mentioned, one typical approach is the inclusion of an IL in the membrane, and the enhanced results have opened the questions of its role in gas separation and membrane properties. Dutta and Bhatia [74] analyzed via MS the gas transport, anti-plasticization, and interfacial interactions between ZIF-8 and 6FDA-durene MMMs, and the impact of the incorporation of IL in the interface. A layer-based membrane was prepared, where the IL was located between MOF and polymer, determining the CO_2 and CH_4 sorption and transport properties through GCMC and EMD, respectively. Though the gas permeability was compromised, a higher selectivity was reached. The swelling effect of the membranes at higher pressures was determined, showing no apparent negative influence of the IL in the system. The appeal of evaluating the incorporated IL via atomistic simulations also relies on identifying the appropriate combination among the infinite combinations of IL-MOF-polymer, and analyzing the role of IL in each configuration [11].

In this regard, Fig. 3 schematically represents both membrane construction options, enumerating some of the advantages. The bulk description of binary or higher number of components has typically analyzed the effect of filler loading and other process variables, such as temperature, pressure, and mixture composition. The membrane is constructed as a periodic unit cell without orientation in space or driving force for sorption and dynamic studies. Despite this, the membrane prepared in the bulk model is closer to a real MMM system. The filler can be modified prior to incorporation in the polymeric matrix, as in the preparation of IL@MOF composites or modification of radical groups. In case of adding a new element to the MMM, it will randomly incorporate it achieving the equilibrated structure. However, the number of atoms increases when considering the concentration of particles of microporous materials and the homogeneous nature of the system. Especially in a multi-component system with ILs, the degree of freedom of arrangement is large, and a larger number of atoms must be considered in order to create an appropriate model. On the other hand, the layer method is focused on understanding the polymer-filler

interphase impact along with gas transport, facilitating its description through each material/interphase. Additionally, it reduces such degrees of freedom and focuses on the phenomena of interest. For the gas molecules transported through the membrane, it is first assumed that diffusing molecules always penetrate the interior of the microporous material. This process is reasonable by the fact that MMM uses the high diffusion coefficient in microporous materials to achieve a high permeability. Also, the layer-based model has a larger fraction of the interfaces than the bulk model. This means that diffusion through interfaces can be simulated more efficiently and with a high control degree.

Simultaneously, attending to other recent simulation works, different from MMMs, most recent advances in simulation studies for polymeric studies have approached other phenomena such as plasticization [75,76], the effect of water and solvent from the preparation routes [77]. Phenomena such as plasticization of polymers at interfaces can also be simulated in the layer-by-layer model more efficiently than in the bulk model. However, in actual MMM, not all molecules are diffusing in a porous material, and there may be various diffusion paths. In addition, multi-component separation systems are more complicated. For such problems, the layer-based model is not very informative, and the bulk model gives results closer to real systems.

Nevertheless, both approaches allowed for obtaining a comprehensive description, characterization, and analysis at a fundamental level of the membrane and its components. In addition, their relative simplicity, especially in the bulk approach, has motivated their extension to other membrane systems, from pristine polymeric structures to three-component membrane structures and diverse types of fillers. However, they require an extensive experimental characterization, and novel combinations are limited to well-described components. Additionally, observations at an atomic level will be hardly confirmed with experimental techniques. These matters will be more extensively discussed in Section 3.
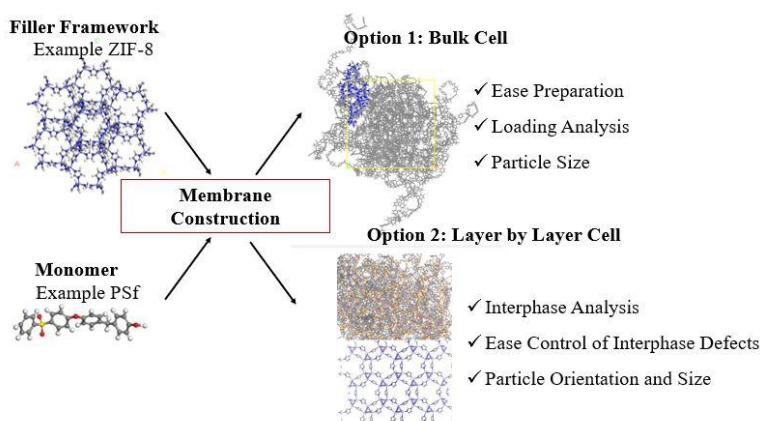

Fig. 3. Schematic classifications of approaches followed for MMMs conjunct construction models of polymer/filler in molecular dynamics and potential advantages for their selection.

Table 2
Summary of molecular simulation works for gas separation processes in MMMs.

Filler	Filler	Polymer	Gas	No. of components	Approach	Target	Ref.
Metal oxide	Fe$_2$O3	PEBA	CO_2, CH_4, N_2	II	GCMC + EMD	Material description	[47]
	ZnO	PEBA	CO_2, CH_4	II	GCMC + EMD	Material description	[46]
Silica	Silica	PS	O$_2$, N$_2$, CO_2, CH_4	II	GCMC + EMD	Material description Selection of suitable force field	[49]
	Silica	PTMSP	H$_2$, O$_2$, N$_2$, CO_2, CH_4, n-C_4H_{10}	II	MD	Material description Particle size impact	[48]
	Silica	PS	CO_2, CH_4	II	GCMC + EMD	Filler loading and process variables description (gas mixture	[51]
	Silica (different polymorphs)	PS	CO_2, CH_4	II	GCMC + EMD	Filler morphology, filler loading effect, process variable effect	[52]
Carbon	MWCNTs	BPDA–PDA	-	II	Force field description and MD	Structural analysis – filler morphology and mechanical stability	[53]

Table 2 *(continue)*

Filler	Filler	Polymer	Gas	No. of components	Approach	Target	Ref.
Zeolite						Materials description	
	Silicalite	PI	CO_2, CH_4	II	GCMC + EMD (layer system)	Polymer-filler interphase analysis Particle size effect	[59]
	Zeolite 13X	PEBA	CO_2, CH_4, N_2	II	GCMC + EMD	Materials description	[56]
	FAU	PEBA	CO_2, CH_4, N_2	II	GCMC + EMD	Materials description Effect of temperature in preparation	[57]
	Zeolite 4A	PDMS	H_2, CO_2, CH_4, C_3H_1	II	GCMC + EMD	Materials description	[54]
	Zeolite 4A	PDMS	H_2, CO_2, CH_4, C_3H_1	II	GCMC + EMD	Materials description	[55]
	FAU, FAU-SO_3, FAU-NH_2	PEBA	CO_2, CH_4, N_2	II	GCMC + EMD	Materials description External functionalization	[58]
MOF	ZIF-8	PIM-1	-	II	Combination of DFT and Force field MS	Structural analysis of polymer-filler interphase	[62]
	ZIF-8	PIM-1	-	II	Combination of DFT and Force field MS	Structural analysis of polymer-filler interphase and MOF defects	[65]
	UiO-66	PIM-1, PVDF, PS, PEG	-	II	Combination of DFT and Force field MS	Structural analysis of polymer-filler interphase	[63]
	HKUST-1	PVA	-	II	Combination of DFT and Force field MS	Structural analysis of polymer-filler interphase	[64]
	NUS-8	PIM-1	CO_2, CH_4, N_2	II	GCMC + NEMD (layer system)	Sorption and transport description along membrane, interphase analysis	[66]
	UiO-66	PEGDA	CO_2, N_2	II	GCMC + EMD (layer system)	Sorption and transport description along membrane, interphase analysis, defect engineering	[67]
	ZIF-67	PEBA and PES (support)	CO_2, CH_4, N_2	II	GCMC + EMD	MMM and composite membrane analysis	[68]
	NUS-8	PIM-1	CO_2, N_2	II	GCMC + NEMD (layer system)	Sorption and transport description along membrane, interphase analysis, MOF functionalization	[69]
	ZIF-8	PIM-1	CH_4, H_2	II	GCMC + NEMD (layer system)	Comparison of layer-by-layer to single filler/polymer modelling	[22]
	ZIF-7	PBI	H_2, CO_2	II	GCMC + EMD	Material description	[60]
	ZIF-8	PA	CO_2, CH_4	II	GCMC + MD	Plasticization effects under high pressure	[61]
	16 different MOFs from CSB	PI (several grades) Hyflon AD60X, Teflon AF-2400, PTMSP, among others	H_2, CO_2, CH_4	I	GCMC+EMD – Maxwell/modified Felske models	Screening	[28]
	Cu-BTC, ZIF-8, IRMOF-1, ZIF-8, ZIF-90	PDMS, PS, PI, Matrimid, Ultem, PPEES, 6FDA-DAM	CO_2, N_2	I	GCMC+EMD – permeation models	Screening Framework flexibility of the filler particles, filler loading and operation temperature	[29]
	16 different MOFs from CSB	CA, Matrimid, PS, SPEEK-3, PEBA, 6FDA-DAM, PIM-1	CO_2, CH_4	I	GCMC+EMD – permeation models	Screening Flexible MOF structure impact	[30]
	5629 MOFs from CoRE MOF (2019)	PSF, Matrimid, PU, PPEES, and ODPA-TMA, among others	O_2, N_2	I	GCMC+EMD – permeation models	Screening Flexible MOF structure impact	[31]
	15 different types of ZIFs	PI (several grades) Hyflon AD60X, Teflon AF-2400, PTMSP, among others	H_2, CO_2, CH_4, N_2	I	GCMC+EMD – Maxwell/modified Felske models	Screening	[32]
	9 different types of ZIFs	Matrimid, Ultem, 6FDA-DAM, and PPEES	H_2, CO_2, CH_4	I	GCMC+EMD – permeation models	Screening	[24]
	MOF-5, Cu-BTC, ZIF-8, MEFMEQ	-	H_2, CH_4	I	GCMC+EMD NEMD	Materials and performance description Methodology applicability	[21]
	CAU-1	-	CO_2, CH_4, H_2, N_2, He, Kr and Xe	I	NEMD	Gas transport description (pure and mixture)	[33]
COF	288 COFs from CoRE COF database	-	CO_2, H_2	I	GCMC+EMD – permeation models	Screening of novel materials, description of forcefield and potential candidates for target separation	[36]
	572 COFs from CURATED COF database	-	H_2, CH_4	I	GCMC, EMD, DFT	Screening for target separation, forcefield and simulation model analysis	[37]
	41 3D and 268 2D from CoRE COF database	PDMS, PEBA, PIM-7, SBS	CH_4, N_2	I	GCMC+EMD – permeation models	Screening for target separation	[40]
POC	CC3	PIM-1	CO_2, N_2	II	NEMD	Materials and performance description Preparation, materials mixing analysis	[70]
	CC3	6FDA-DAM	C_3H_6, C_3H_8	II	GCMC + EMD	Mechanism study and comparison to experimental data	[71]
Zeolite + plasticizer	Zeolite 4A + p-nitrolaniline	PC	H_2, O_2, CO_2, CH_4, N_2	III	GCMC + EMD	Materials description	[72]
Alumina + IL	Alumina + IL	PEBA	CO_2, N_2	III	GCMC + EMD	Effect of IL incorporation and effect IL chemistry	[73]
MOF+IL	ZIF-8 [BMIM][BF$_4$]	PI	CO_2, CH_4	III	GCMC + EMD (layer system)	Structural and gas transport analysis of polymer-filler interphase	[74]

3. Key Experimental Characterizations to Address Emerging Materials

Molecular simulations are capable of modeling membrane structural properties and gas separation performance. They can be used to identify the best configurations of novel materials for specific gas separation processes and to obtain a fundamental understanding of their performance. However, the definition of the model, assumptions, parameters, the selection of a force field of the constituents, and their interactions strongly affect the calculated membrane properties. Accordingly, the validation of the simulation conditions is important. Approaching a summary of the experimental requirements to support coherently the atomistic modeling, this section aims to gather the most frequent and minimum set of experimental data utilized for MMMs. The criteria behind this list have been supported by taking as base the frequently used techniques from the papers described in previous Section 2.2 and Section 2.3.

Moreover, this section seeks to guide future research works looking forward to optimally combining emerging and novel materials experimental with fundamental atomistic studies for MMMs.

3.1. Structural characterization

Regardless of the membrane construction method followed, adequate structural characterization of the prepared membrane is required. The validation of the constructed model will not only assure the working of a representative model for the gas separation properties, forcefield, and methodology, but also extrapolate the potential observations and analysis. Several structural parameters can be obtained from molecular simulations and compared with experimental data. However, it must be into account the reliability of directly comparing molecular level-specific ideal structures, defects, or interphase layers to experimental values containing all these possible arrangements. To effectively determine the accurateness of a model, one unique structural characteristic will not fulfill the necessary information to validate it. In this section, the most utilized parameters and their challenges are summarized in the following.

The membrane density is described as the weight of the material enclosed in the periodic unit cell. An amorphous system with a low density is constructed by NPT ensemble dynamic simulation (Constant Number of particles, Pressure and Temperature), followed by a NVT ensemble simulation (Constant Number of particles, Volume and Temperature). The objective of this first step in the simulation is to achieve the equilibrium of the cell parameters, density, and energy of the structure. Therefore, the membrane density is a direct parameter obtained from the membrane construction and can roughly be compared to the experimentally estimated membrane density. The simulation time has been required for this construction has varied depending on the size of a cell and components, being typically between 250-500 ps for polymers such as PSf and PEBA in a cell of approximately 40 Å [46,51,57]. Another possibility, following the same method, considers the presence of a specific gas fugacity, e.g. CO_2. This latter option has been previously used to analyze the potential plasticization of polymeric membranes [75,76]. The membrane cell construction follows the same method previously described, with the extra component of CO_2 molecules considering different gas fugacity values, to ultimately compare with gas sorption isotherms. Then, performing a NVT

ensemble simulation equilibrates the membrane cell and reduces the system energy, as the polymeric chains achieve their most stable arrangement. After the equilibration of the structure using NVT, this ensemble is further used to obtain ensemble-averaged properties, such as the structural membrane characteristics (e.g. density, free volume, crystallinity properties), or sorption of gas guest molecules.

Glass transition temperature is commonly referred to in simulation studies and used to validate the model. To calculate the glass transition temperature, the membrane density or the membrane-free volume at different temperatures is modeled for, and afterward, calculate the inflection point of the resulting curve. Following Fox and Flory's theory [49,55,74], the temperature of this point will be the membrane glass transition temperature.

Another structural characteristic that can be of importance is the X-ray diffraction pattern of the polymeric matrix and the fillers. This property can be easily obtained for the bulk structure and compared to experimental data, along with the analysis effect of adding the filler into the membrane crystallinity or d-spacing.

The structural properties described above are mainly analyzed in bulk systems. Once the validation of the materials has been confirmed, the same model characteristics and materials have been employed modifying the membrane construction to a layer-by-layer configuration. In the layer-based model, it is of interest to analyze the change in the membrane density along the cell [63,67,74]. Although possible to similarly perform this analysis in bulk cells, membranes constructed by layers allow for quantifying the interphase or defects size to later relate to gas separation properties.

However, while these parameters can be related to the experimental values, it is highly limited due to the scale of the atomic simulations. The experimentally determined membrane density will not have the accuracy of a periodic cell at the molecular level. Additionally, experimental techniques will not measure the atomic-level defects found in the membranes, and therefore, a unique structural property will not properly validate the system. Therefore, the combination of the characterized membrane cell with the gas separation performance (following Section 3.2.) is key for validation of the modeled membrane.

3.2. Gas Performance

Once the membrane has been constructed adequately, the interactions of different gases with the simulated membrane can be performed. Experimentally, the gas performance of prepared membranes is characterized by the membrane permeability towards a specific gas. On the other hand, in molecular simulations, the gas performance description is not straightforward. The utilization of membrane-like simulations, such as NEMD, offers a description of the permeation considering the solution-diffusion model directly. However, the most typical approach has been to separate the sorption and diffusion phenomena, similarly to the single-component simulations (Fig. 2), which require a set of assumptions regarding the gas behavior. Fig. 4 gathers a schematic representation of the typical methodology to determine the gas permeability using GCMC and EMD simulations. This approach has been widely followed for two and three-component modeling following a bulk membrane preparation.
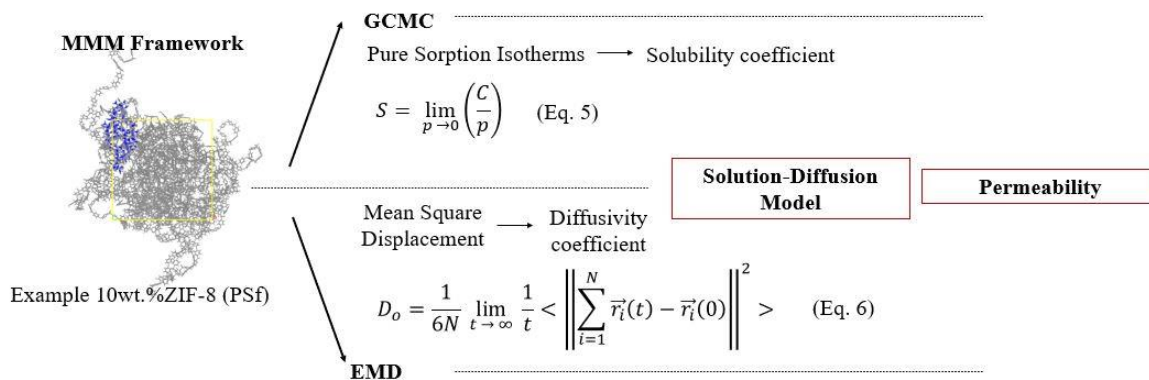

MMM Framework

GCMC

Pure Sorption Isotherms ⟶ Solubility coefficient

$$S = \lim_{p \to 0}\left(\frac{C}{p}\right) \quad \text{(Eq. 5)}$$

Example 10wt.%ZIF-8 (PSf)

Mean Square Displacement ⟶ Diffusivity coefficient

$$D_o = \frac{1}{6N} \lim_{t \to \infty} \frac{1}{t} \left\langle \left\| \sum_{i=1}^{N} \vec{r_i}(t) - \vec{r_i}(0) \right\|^2 \right\rangle \quad \text{(Eq. 6)}$$

EMD

Solution-Diffusion Model

Permeability

Fig. 4. Schematic representation of GCMC+EMD methodology followed for MMMs. Embedded equations refer to the Solubility coefficient calculation (Eq. 5), and calculation of the diffusivity coefficient from the mean square displacement of gas molecules (Eq. 6).

The sorption behavior has been typically described through gas sorption isotherms from GCMC simulations after performing a NVT dynamic simulation, from which solubility coefficients are estimated (Eq. 4). The dynamic movement of inserted gas molecules is analyzed after using NPT ensemble. The diffusivity coefficient is calculated from the mean squared displacement of gas molecules along time in the designed structures, as stated in the Einstein relationship (Eq. 6). In contrast to the previous method described in Section 2.1., the permeability calculation relies on the solution-diffusion model, in which the product of calculated solubility and diffusivity coefficient is equal to the membrane permeability. No corrections of self-diffusivity to transport diffusivity are typically considered in this method, being of more importance to the duration of the EMD simulation.

The gas molecules suffer different stages in an EMD simulation: the ballistic, sub diffusive, and Fick's diffusive regimes [78]. The transition of one regime to other can be directly related to the slope of the log(MSD) versus log(t) graph. To determine the diffusivity coefficient considering Einstein relationship, the slope of the double logarithmic relation must tend to the unit. Depending on the polymer density, temperature and the gas penetrant considered, the simulation time required can drastically increase, compared to the modeling of the single filler or a highly permeable polymer.

Regardless of the approach selected in the molecular simulation, a proper experimental characterization will be required for validation. Novel membranes will require experimental efforts to accompany the simulation studies to effectively address the potential of certain materials (as in the case of high-throughput screenings), or the description of molecular-level. While the membrane permeability is typically the key parameter to address a membrane performance, the separation of solubility and diffusivity will even facilitate more the correspondence to simulated data. In the first case, the typical comparison will be through NEMD simulations or the combination of GCMC+EMD. NEMD approach allowed to reliably determine the gas sorption and transport properties and to successfully compare with experimental data, a gas flux is obtained from the simulation. An overestimation of the simulated permeability for the GCMC+EMD approach and an underestimation, in the case of NEMD, is typically obtained. Moreover, while fillers are typically characterized through sorption isotherms (which can be obtained directly from GCMC simulations), studies with pure polymeric materials have traditionally analyzed sorption phenomena through sorption isotherms [75,76], but it is not common for MMMs.

These performance properties, along with the structural properties previously described, will be key for simulation works model MMMs in the future.

4. Recent Developments and Future Perspective

One of the advantages of using molecular simulations is the possibility to simulate conditions that are rarely tested experimentally [33,48]. Additionally, molecular simulations have been positively used in the development of screening studies, since actual membranes and experiments are limited due to difficulties in membrane preparation and experimental characterization [11,31,39]. However, a validation of the designed membrane and forcefield model is important to perceive and relate the simulation results to the real system. In this regard, Section 3 describes the most typical membrane characteristics that will allow a more straightforward model validation. Moreover, the atomic-level analysis will vary depending on the orientation and organization of the MMMs components. The layer-based method infers a key factor in MMMs, which is the interphase polymer-filler analysis [22,69]. With the methodological development of molecular simulations such as NEMD, the number of simulations for such complex systems will increase as computer power increases.

The macroscopic models have evolved over the years from the ideal Maxwell permeation model towards a more descriptive set of parameters, as one of the leading disadvantages of MMMs involves the appearance of non-ideal and non-selective structures by the combination of both materials. The layer-based model has efficiently addressed this issue and recent works have introduced externally functionalized and modified fillers, and the incorporation of the third component through different approaches, following the experimental research trend. Therefore, there is an increasing interest leading towards merging the concept of macroscopic models with non-idealities (Table 1) and molecular simulation studies (Table 2). In this regard, NEMD has the potential to merge these two concepts, because it can directly simulate a non-ideality system and check the difference with the macroscopic models [22].

A potential advantage of merging NEMD simulations with a bulk membrane arrangement will allow for analyzing other non-idealities at the interphase caused by particle size, loading, aggregation, and similar, as the ones described in Fig. 1. Additionally, the bulk model has also the advantage of representing the MMM more realistically. Future research efforts with strong and improved computational resources will preferably analyze the gas molecules transport in the bulk model with a heterogeneous distribution of the filler, and a proper description of the gas molecules permeation paths. Additionally, future novel methodologies may integrate the analysis of phenomena such as membrane plasticization and other structural modifications in simulated MMMs.

Therefore, molecular simulations present the potential to be applied in the future to novel and emerging materials for the development of MMMs, especially through computational screening and deep-analysis fundamental methods. However, the extension of their application will strongly depend on the complicated and realistic structure modeling of MMMs and the availability of experimental data for its validation.

5. Conclusions

The objective and scope of the study will vary. Here, they have been classified depending on the number of elements included in the atomistic study. The simulation of a unique component in the MMM, that is, the filler, has the advantage of performing high-throughput screening simulation studies. This approach has successfully analyzed different fillers using up-to-the-date and ready-to-be-simulated structural databases, considering easily tunable gas separation target and operation. Their main limitations, however, rely on the availability of practical information for proper simulation of emerging materials and their potential MMMs Typically, this approach considers a combination of atomical-level modeling of the filler with macroscopic information of the polymer. In this regard, the selection of the polymer will be of high importance to properly select the denominated MMM macroscopic permeation model (Table 1).

The successful integration of these studies in emerging fillers, such as COFs, will require coordinated research efforts in both simulation and experimental works.

On the other hand, the description of the whole MMM (polymer, filler, and potential third component) in a common framework has equally attracted research efforts. The main objective in this approach has been limited to a certain combination of materials, and the computational effort in the membrane construction becomes more important. This method allows to directly obtain molecular-level information on the structural and gas separation properties, so as the filler-polymer interactions, along with other factors such as the effect of loading and the operating conditions (temperature, pressure, and gas mixture composition). A systematic route to represent and obtain permeation data from a MMM with different and new pairs of fillers and polymers has trended among the simulation studies, being recently extended to more complex systems. Future works will be expected to include more emerging fillers, such as COFs, along with the polymer in the simulated membrane cell. The attractiveness of this approach is focused on the potential evaluation of a more realistic system, directly compared to experimental data, either membrane structural properties or gas separation performance. The potential of especially analyzing certain phenomena, such as the interactions of the component at the interphase (with and without engineered defects or modifications) and the use of NEMD simulations expand the use of molecular-level description. However, the computational effort to use in several membrane systems limits the combinations to study, being more interesting to perform in those which present the potential for certain gas separation.

Nevertheless, the current state-of-the-art in the use of molecular simulations has proven the versatility and efficiency of using molecular simulations to successfully describe the gas separation in MMMs with different approaches and materials.

Nomenclature and Acronyms

6FDA	Hexafluoroisopropylidene bisphthalic dianhydride
AIMD	Ab initio molecular dynamics
BPDA-PDA	Poly-(p-phenylene biphenyltetracarboximide)
BTC	Benzene-1,3,5-tricarboxylate
c	Gas concentration
CA	Cellulose acetate
CDB	Cambridge database
CGD-MD	Concentration gradient driven molecular dynamics
COF	Covalent organic framework
COMPASS	Condensed-phase optimized molecular potential for atomistic simulation studies
CoRE	Computation-ready, experimental
CPI	Colorless polyimide
CURATED	Clean, uniform, and refined with automatic tracking from experimental database
DFT	Density functional theory
D_0	Corrected diffusivity coefficient
DAM	Diaminomesitylene
DCP-NEMD	Dual-control plane nonequilibrium molecular dynamics
D_t	Transport diffusivity coefficient
EMD	Equilibrium molecular dynamics
f	Fugacity
FAU	Faujasite zeolite
GCMC	Grand canonical Monte Carlo
IL	Ionic liquid
IL@MOF	IL supported by MOF or IL@MOF composite
J	Flux
L	Membrane Thickness
MD	Molecular dynamics
MFI	Type of zeolite
MMM	Mixed matrix membranes
MOF	Metal organic framework
MSD	Mean square displacement
MWCNT	Multi-walled carbon nanotubes
NEMD	Non-equilibrium molecular dynamics
NPT	Constant Number of particles, pressure and temperature
p	Pressure
P	Gas permeability
PA	Polyamide
PC	Polycarbonate
PBI	Polybenzimidazole
PCFF	Polymer-consistent force field
PDMS	Polydimethylsiloxane
PEBA	Polyether block amide
PEG	Polyethylene glycol
PEGDA	Poly(ethylene glycol) diacrylate
PI	Polyimide
PIL	Poly-ionic liquid
PIM	Polymer of intrinsic microscopy
PPEES	Poly(1,4-phenylene ether-ether-sulfone)
PS	Polysulfone
PTMSP	Poly(1-trimethylsilyl-1-propyne)
PVA	Poly(vinyl alcohol)
PVDF	Polyvinylidene Fluoride

SPEEK-3	Sulfonated aromatic poly(ether ether ketone)
T	Temperature
t	Time
TFC	Thin film composite
UFF	Universal force field

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