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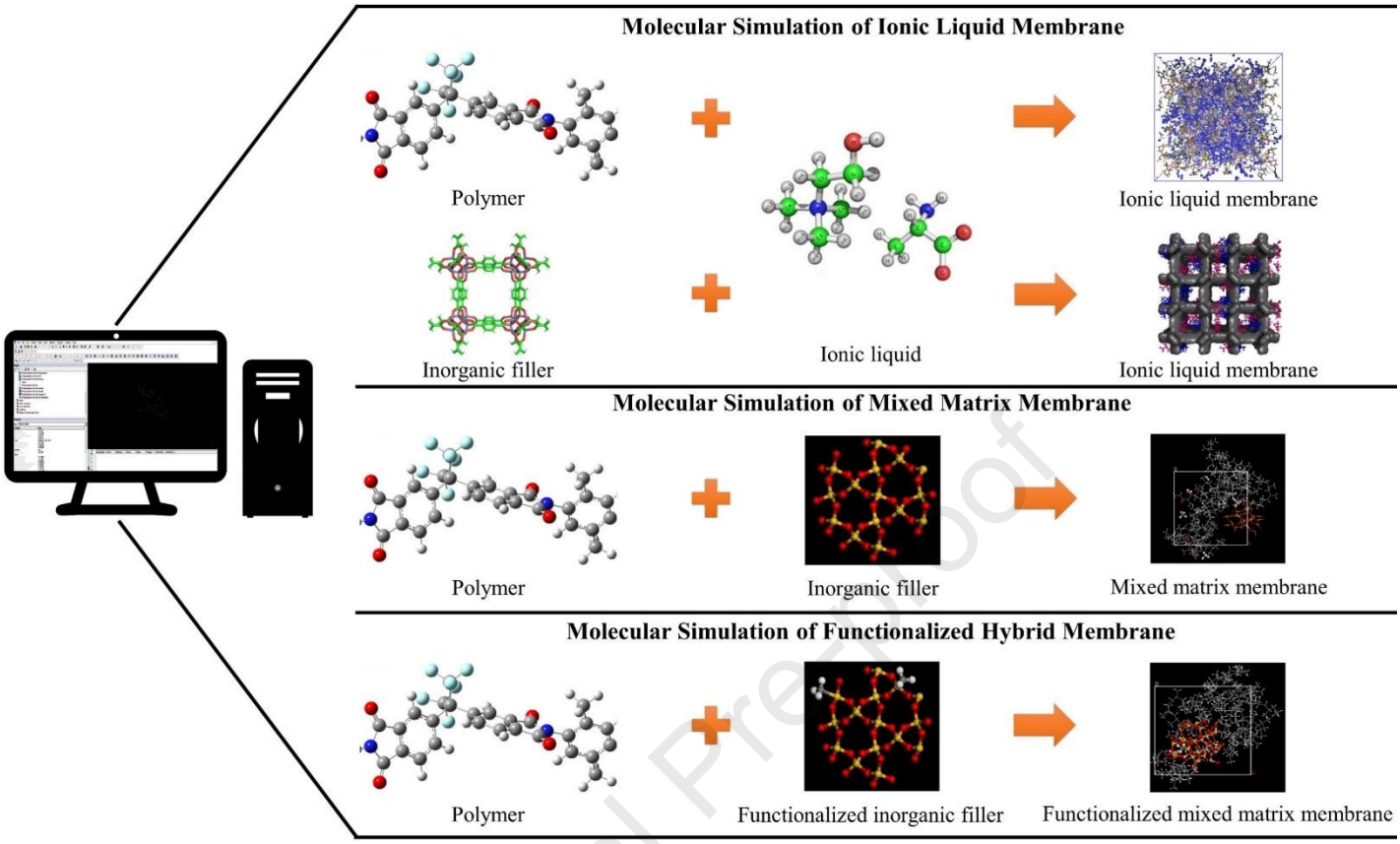
Cia Yin Yee - Writing – Original draft; Data curation; Formal analysis; Investigation, Lam Ghai Lim - Formal analysis; Writing – review & editing; Investigation, Serene Sow Mun Lock – Formal analysis; Supervision; Writing – review & editing; Investigation, Norwahyu Jusoh – Resources; Writing – review & editing; Data curation, Chung Loong Yiin – Resources; Writing – review & editing; Data curation, Bridgid Lai Fui Chin – Resources; Writing – review & editing; Data curation, Yi Herng Chan – Resources; Writing – review & editing; Data curation, Adrian Chun Minh Loy – Resources; Writing – review & editing; Data curation, Muhammad Mubashir – Resources; Writing – review & editing; Data curation

GRAPHICAL ABSTRACT



A systematic review of the molecular simulation of hybrid membranes for performance enhancements and contaminant removals

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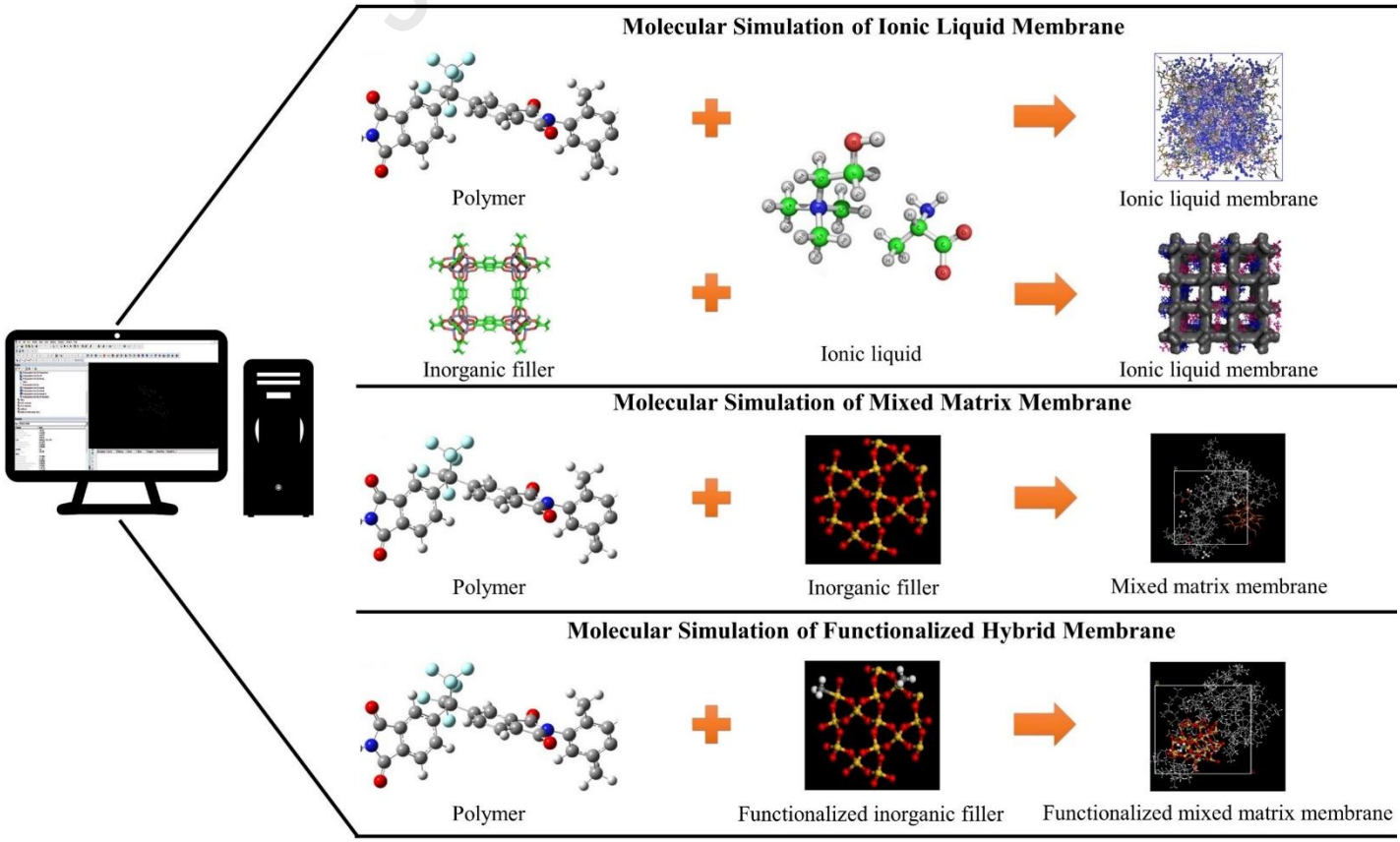
HIGHLIGHTS

- Fundamentals of molecular simulation are reviewed and related to application in hybrid membranes.
- Insight into molecular structural properties of hybrid membranes is presented.
- Simulated transport performance from published literature and mechanism of hybrid membranes are provided.
- Limitation in molecular simulation for membrane separation is discussed.
- Future outlook for molecular simulation of membrane separation is recommended.

GRAPHICAL ABSTRACT



ABSTRACT

Number of research on molecular simulation and design has emerged recently but there is currently a lack of review to present these studies in an organized manner to highlight the advances and feasibility. This paper aims to review the development, structural, physical properties and separation performance of hybrid membranes using molecular simulation approach. The hybrid membranes under review include ionic liquid membrane, mixed matrix membrane, and functionalized hybrid membrane for understanding of the transport mechanism of molecules through the different structures. The understanding of molecular interactions, and alteration of pore sizes and transport channels at atomistic level post incorporation of different components in hybrid membranes posing impact to the selective transport of desired molecules are also covered. Incorporation of molecular simulation of hybrid membrane in related fields such as carbon dioxide (CO_2) removal, wastewater treatment, and desalination are also reviewed. Despite the limitations of current molecular simulation methodologies, i.e., not being able to simulate the membrane operation at the actual macroscale in processing plants, it is still able to demonstrate promising results in capturing molecule behaviours of penetrants and membranes at full atomic details with acceptable separation performance accuracy. From the review, it was found that the best performing ionic liquid membrane, mixed matrix membrane and functionalized hybrid membrane can enhance the performance of pristine membrane by 4 folds, 2.9 folds and 3.3 folds, respectively. The future prospects of molecular simulation in hybrid membranes are also presented. This review could provide understanding to the current advancement of molecular simulation approach in hybrid membranes separation. This could also provide a guideline to apply molecular simulation in the related sectors.

KEYWORDS: Molecular simulation, membrane separation, ionic liquid membrane, mixed matrix membrane, functionalized hybrid membrane

1. INTRODUCTION

In recent years, hybrid membranes have rapidly emerged as a promising technology to circumvent limitation in polymeric membranes for separation process. Hybrid membranes have the advantage of combining two material classes that can potentially modify the resultant structure, which outperform conventional membranes. High selectivity and permeability that are superior to the Robeson plot have been achieved, along with durable and optimized functions suited for specific applications. Different materials have been studied and reviewed for this purpose, but they are mostly limited to state of art research using experimental approach. Recently, computational chemistry has emerged as an indispensable tool to design new generation hybrid membranes with improved separation performance. This enables minimization of intervention from costly and time-consuming experimental method while providing insights at the atomic level, which is challenging or impossible to be measured using laboratory instruments.

Molecular simulation is used to resolve the undiscovered aspects of a system, often much cheaper compared to experiments (Mollahosseini and Abdelrasoul, 2021). Other advantages include the feasibility of designing different simulation perspectives via manipulation of computational approaches. In addition, simulation assists in testing conditions that are almost impossible at laboratory scales and reduces the handling of hazardous materials.

Investigation and analysis of the structural, physicochemical and transport behaviour of molecules through varying types of materials with different system parameters can be accessible at the molecular or atomistic level. The study variables may comprise glass transition temperature (T_g), pore size, fractional free volume, molecular interaction, X-ray diffraction, solubility, sorption and diffusion mechanisms (Dehghani et al., 2017). This has frequently found its application in estimation and calculation of various separation applications, which include gas purification, biomedical engineering and wastewater treatment (Ebro et al., 2013; Hollingsworth and Dror, 2018; An et al., 2019).

Alternatively, membrane system has an emerging role as a recognized eco-friendly separation process due to its low energy consumptions in post-combustion carbon dioxide (CO_2) capture and storage, natural gas sweetening, tertiary-level enhanced oil recovery, dehumidification, separation of acid gases, e.g., hydrogen sulphide (H_2S), sewage treatment, desalination, and pharmaceutical (Brunetti et al., 2015; Le and Nunes, 2016; Vara et al., 2020). In separation process utilizing membrane technology, membrane functions as a selective barrier to allow permeation of one selective permeate while retaining other components (Zolghadr et al., 2021; Manikandan et al., 2022). Permeability and selectivity are critical factors that affect the transport performance of membranes. Permeability of

porous membrane is affected by the permeate molecule size in which larger components have lower diffusion coefficient and vice versa. On the other hand, permeability of non-porous membrane is influenced by the sorption of penetrant molecules into the membrane, its diffusion through the membrane, and desorption at the downstream of the membrane, which is known as the solution-diffusion mechanism (Freeman, 1999). Non-porous dense film membranes transport solute through the pressure difference, concentration, or electric-field gradients on upstream and downstream sides of the membrane (Rackley, 2017). Membrane selectivity is the ratio of permeability of the relevant permeate and retentate passing through the membrane (Zolghadr et al., 2021).

The three core membrane materials used in various industries for separation purposes are organic (polymeric), inorganic (graphene, carbon, zeolite, ceramic, metal, etc) and ionic liquid (He et al., 2018). Polymeric membrane is robust and easy to fabricate, but it has disadvantages of lower performance due to its inherent permeability-selectivity trade-off (Wu et al., 2020) (Freeman, 1999; Wong and Jawad, 2019). Substantial efforts have been ongoing to improve permeability and selectivity of organic membranes to increase its commercial competitiveness. On the other hand, inorganic membranes have excellent permeability, but their fabrication costs are generally higher (Jusoh et al., 2016). Ionic liquids (ILs) are salts made through association of large organic cations with a wide variety of anions, which offer high flexibility in designing new generation advanced materials for contaminant removal (Swati et al., 2021). ILs also inherit downsides, which include high viscosity, high cost, toxicity in abundant amount, which hinder their further expansion in industrial application.

A combination of the aforementioned materials is known as hybrid membrane. Hybrid membranes, a breakthrough of membrane technology, integrating the advantages of polymeric or inorganic or ionic liquid materials together (Jusoh et al., 2016). Hybrid membrane may be a solution to improve and modify the intrinsic property of the pristine material in a less costly manner and to be engineered to a specific use. Some of the crucial parameters for designing an efficient hybrid membrane include the selection of materials for the polymer, inorganic filler and ionic liquid, the composition of the selected materials, and operating conditions (Singh, 2005; Liguori and Wilcox, 2018; Gokulakrishnan et al., 2021).

Acting as an experiment guide, molecular simulation tool can be used to provide atomistic understanding and characterization of the tailor-made combination of membrane materials, its individual polymer, filler and ionic liquid (Keskin and Alsoy Altinkaya, 2019). Currently, comprehensive study of molecular structure of hybrid membranes and their separation mechanism is limited. This may be due to the reason that hybrid membranes are still mainly applied in laboratory settings and have yet to be widely applied in industry (Golzar et al., 2017a). The

excellent separation performance reported in laboratory studies may pave the way for hybrid membranes to expand its use in industry but further elucidation from molecular simulation is required.

In this paper, a systematic review of the recent advances in membrane development for gas separation, water desalination, and wastewater treatment are presented. This includes the basic principles of different membrane processes using molecular simulation, such as ionic liquid membrane (ILM), mixed matrix membrane (MMM), and functionalized hybrid membrane (FHM). Subsequently, recent studies on membrane advances in various applications are reviewed. Lastly, future perspectives on the development of membrane separation using molecular simulation technique are provided.

2. MOLECULAR SIMULATION AND APPLICATION IN MEMBRANE SEPARATION

The advancement and development of membrane appliances and its application software have demonstrated the importance of molecular simulation in understanding, predicting, and validating structure-property relationship of various membranes. In general, molecular simulation works by performing atomistic simulation to elucidate the system evolution, which is majorly based on 1) molecular dynamics (MD) that is a time-dependent evolution of the system and 2) Monte Carlo (MC) simulation that involves randomly sampling of the energy landscape to determine the probability with least value The fundamentals, principals and functionalities underlying molecular simulation and relationship with membrane system is discussed in this section.

2.1 Fundamentals in Molecular Simulation

Molecular simulation aims to replicate properties of a macroscopic (bulk) system using atomistic calculation. However, the largest computers can only simulate systems with about 10^6 atoms, but a realistic macroscopic system has an order of 10^{23} atoms (Alavi, 2020). Thus, periodic boundary conditions are applied to overcome the limitation of molecule numbers in simulations (Shirts et al., 2006; Sharma, 2019). This solves the problem of finite simulation size and removes the surface effects. A crucial factor in MD simulation is the energy function that quantifies the intermolecular or/and intramolecular forces since it determines the simulation speed and accuracy. The energy is often computed based on a force field that defines the atomic bond strength and relationship between atoms in the same molecule and those in others, as shown in Eq. (1).

$$E_{total} = E_{bond}(r) + E_{angle}(\theta) + E_{dihedral}(\phi) + E_{non-bonding}(r) + E_{electrostatic}(r) \quad \text{Eq. (1)}$$

In the energy term, total energy of the system, E_{total}, is characterized by the bonded energy and the non-bonded energy contributions. The bonded energy is consisted of (i) the covalent bond stretching energy terms, $E_{bond}(r)$ (ii) the bond angle bending energy terms, $E_{angle}(\theta)$ and (iii) the torsion angle rotation energy terms, $E_{dihedral}(\phi)$while

the non-bonded energy is described by van der Waals interaction, $E_{van\ der\ Waals}(r)$ and electrostatic force $E_{electrostatic}(r)$ (Lock et al., 2018). The parametrized terms used in force field for energy computation are obtained by fitting with experimental work and mechanical quantum studies from small molecules (Adcock and McCammon, 2006).

In classical MD, the atomic and molecular structures and interactions influence the velocities and positions of the molecules according to Newton's equation of motion. The length is measured in nanoscale and the time, t, is measured in nanoseconds in classical mechanical microscopic description (Cai et al., 2012; Alavi, 2020). Eq. (2) and Eq. (3) describe the aforementioned laws in a basic molecular simulation (Hernández-Rodríguez et al., 2016; Alavi, 2020; Moqadam et al., 2021):

$$F_i = m_i a_i = m_i \frac{d^2 r_i}{dt^2} \quad \text{Eq. (2)}$$

$$F_i = -\nabla_i U(r_i) = \frac{\partial U(r^N)}{\partial r_i} \quad \text{Eq. (3)}$$

where *m*, *r*, and *U* represent the mass of the molecule, the distance between two atoms or molecules, and the potential energy. MD propagates the coordinates and velocities of molecules in time to solve Newton's equations of motion (Jiang et al., 2020). Valid initial conditions of the systems and methods, e.g., the nature of boundary conditions confining the molecules and the inter- and/or intra-molecular interactions, need to be applied beforehand (Alavi, 2020). Maxwell-Boltzmann distribution is applied to assign the initial velocities of the molecules at the simulation temperature. The momentum, p, and position, q,of a complicated system is described in Eq. (4) and Eq. (5) (Mollahosseini and Abdelrasoul, 2021).

$$q(t + \Delta t) = q(t) + \frac{q(t)}{m}\Delta t \quad \text{Eq. (4)}$$

$$p(t + \Delta t) = p(t) + ma(t)\Delta t \quad \text{Eq. (5)}$$

where $a(t)$ is the acceleration as a function of time.

With regards to the initial density during MD in search of the equilibrated structure, measured experimental value especially in the liquid phase can be used as the starting condition. The volumes, molecular position, orientation and energy in the system are varied in isothermal-isobaric (constant *N*, *P*, *T*) MD simulations, the initial density will differ during the simulation. Therefore, the resulting and equilibrated density is only known after completing the computation.

After achieving equilibration state from MD, the general physical properties *A* under canonical ensemble (constant *N*, *V*, *T*) can be calculated using Eq. (6) (Mollahosseini and Abdelrasoul, 2021).

$$A = \iint A(q,p)P(q,p)dpdp \quad \text{Eq. (6)}$$

where $A(q,p)$ is the physical property at equilibrium state and $P(q,p)$ is the probability function of atoms arranged in a molecule.

On the other hand, the MC algorithms operate based on equilibrium statistical mechanics for prediction of probability of varying outcomes via translation, displacement, rotations of molecules or insertion and deletion of sorbates on a simulation cell. Acceptance probability is used to govern configuration of the new structure from the previous state. Example of the probability distribution for a system with *N* molecules under a MC isothermal-isobaric condition is given in Eq. (7) (Corti, 2002).

$$P(\{\boldsymbol{\rho}\},V;T,P)=\frac{\frac{V^N}{N!\Lambda^{3N}}e^{PV/kT}e^{-U(\{\rho\};N,V)/kT}}{\Delta(N,T,P)} \qquad \text{Eq. (7)}$$

where *N* is number of molecules, *P* is pressure, *T* is temperature, ρ is density, *V* is the volume, *U* is the potential energy, *k* is a gas constant.

2.2 Fundamental Approaches Employed in Membrane Simulation

The mean square displacement *MSD* calculates the displacement of particle through the membrane via the MD approach (Bouzid et al., 2018), as shown in Eq. (8).

$$MSD_i=\frac{1}{N}\sum_{i=1}^{n}\{|r_i(t)-r_i(0)|^2\}disrupt \qquad \text{Eq. (8)}$$

The diffusion coefficient *D* is calculated through tracking of the gas molecule displacement via the Einstein self-diffusion correlation (Einstein and Schilpp, 1979) as depicted in (9).

$$D_i=\frac{1}{6N}\lim_{t\to\infty}\frac{d}{dt}\sum_{t=1}^{N}\langle|r_i(t)^2-r_i(0)^2|\rangle \qquad \text{Eq. (9)}$$

In Eq. (8) and Eq. (9), *N* represents the total number of diffusing atoms i within the hypothetical cell under consideration, r_i is the position vector of atom i, $|r_i(t)^2-r_i(0)^2|$ represents ensemble averages of the gas particles MSD, while $r_i(t)$ and $r_i(0)$ depicts the final and initial position vector of the centre of mass of gas molecule over the time span of interest, t.

From MC simulation, the sorption of molecules or ions within the membrane cell of interest can be simulated under different ensembles, which include 1) canonical ensemble to find the preferred locations and energies given a number of sorbates 2) grand canonical (GCMC) ensemble to predict the number of sorbates under fixed simulation temperature and pressure and 3) uniform ensemble to compute the limit of loading of sorbate at low pressure limit in order to know the Henry constant. The solubility coefficient of species i can be found through gradient of the straight line connecting a point on the solubility isotherm to the origin using GCMC method.

$$S_i=\lim_{f_i\to 0}\left(\frac{c_i}{f_i}\right) \qquad \text{Eq. (10)}$$

214 In Eq. (10), c_i and f_i are the total concentration and partial fugacity of sorbates i in the membrane system.

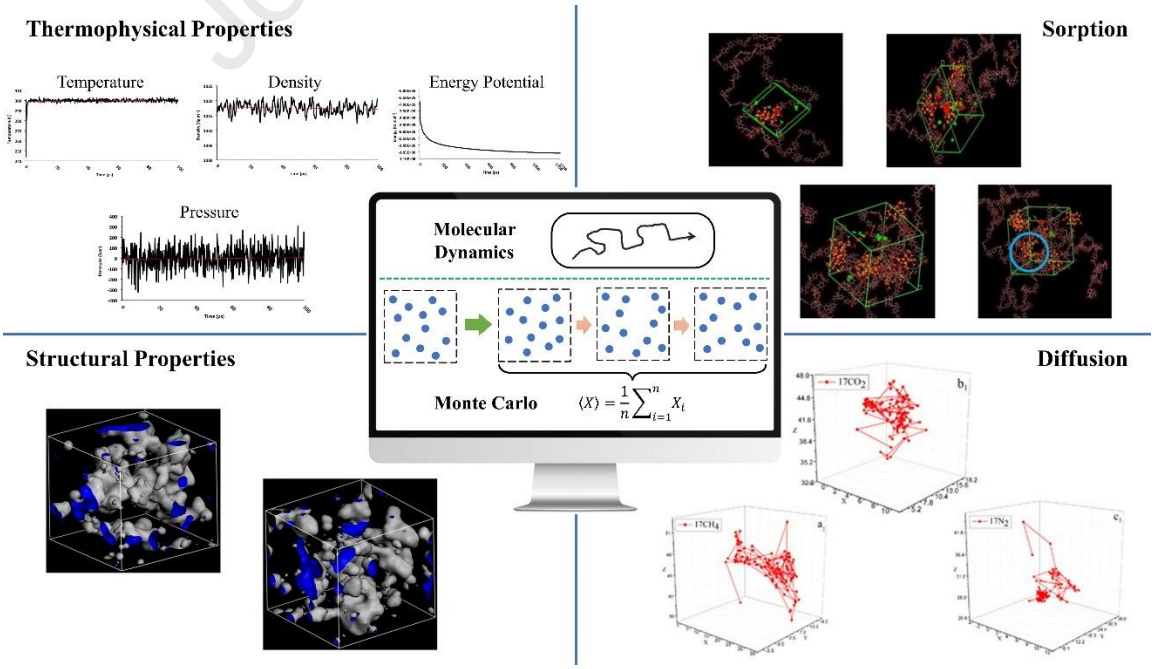
215 Fickian law of diffusion explains the fundamental for all transport phenomenon. The flux, J_i, defines the
216 number of molecules for gas component i that penetrates through a unit area of unit time is directly proportional to
217 the concentration gradient from the region of high to low end, $\frac{dc_i}{dx}$, through the diffusion coefficient, D_i, as depicted
218 in Eq. (11).

219 $$J_i = -D_i \frac{dc_i}{dx} \qquad \text{Eq. (11)}$$

220 Radial distribution function (RDF) also discloses conditions and methods of non-bonding interaction between
221 molecules and the density change at a distance from a specific particle (McCarthy and Vaughan, 2015). It is a
222 probability of finding a particle at a radial distance r from another particle in a random distribution that serves as
223 the centre of reference (Rindt and Gaastra-Nedea, 2015).

224 $$g_{M-i}(r) = \frac{1}{\rho_{M-i} 4\pi r^2} \frac{\sum_{t=1}^{K} \sum_{j=1}^{N_{M-i}} \Delta N_{M-i}(r \to r+\delta r)}{N_{M-i} \times K} \qquad \text{Eq. (12)}$$

225 $g_{M-i}(r)$ is the RDF, N_{M-i} is the total number of membrane molecules, M, and gas species i in the system, K the
226 number of time steps, δr the distance interval, ΔN_{M-i} the number of gas i (or M) molecules between $r + \delta r$ around
227 a M (or gas i) molecule, and ρ_{M-i} the bulk density of membrane system with presence of gas. RDF of gas i around
228 functional groups of the membrane unit can be investigated. Figure 1 summarizes of the fundamentals in molecular
229 simulation.



230

231 **Fig. 1** Fundamentals of molecular simulation including Molecular Dynamics and Monte Carlo simulations

Molecular simulations can be used to demonstrate the adsorption ability, permeability, and selectivity of hybrid membranes. It shows great potential to predetermine the capability, practicality, and functionality of the membrane before proceeding with the actual synthesis of the costly membranes. This section discusses the computation of ILM, MMM and FHM.

3.1 Ionic Liquid Membrane

Two main method of using ionic liquids in membrane materials are supported ionic liquid membrane (SILM) and quasi-solidified ionic liquid membrane (QSILM) (Wang et al., 2016b). SILM consists of a thin microporous support with ionic liquid filled pores (Wang et al., 2016b). QSILM is prepared by casting ionic liquid solution and a special gel to form a thin and stable quasi-solidification film (Wang et al., 2016b). Quasi-solidification of ionic liquid is a reliable way to prevent leakage by the self-assemble of organic molecules as compared to SILM (Wang et al., 2016b). Modelling ILM via molecular simulation aids in capturing the chemical structure stability at small step size modifications, which is not feasible in experiments. Molecular study of ILM along with its application and computed transport performance are provided in Table 1. Figure 2 shows the molecular dynamics simulation for ILM and the structural behaviour of the system, hydrogen bonds between the polypeptide membrane and IL, IL mobility, nanosheet energetic behaviour, and membrane surface topology. Figure 2 (a) discussed the initial structure of A_6D polypeptide membrane molecules and [CHO][GLY] ionic liquids while Figure 2(b) shows the equilibrated structure of the superficial and lateral view of A_6D membrane nanosheet and [CHO] [GLY]. Figure 2(c) and (d) illustrates the interactions between A_6D molecules and [CHO][GLY] ionic liquids and A_6D nanosheet structure with hydrogen bonds formed between polypeptides, respectively.

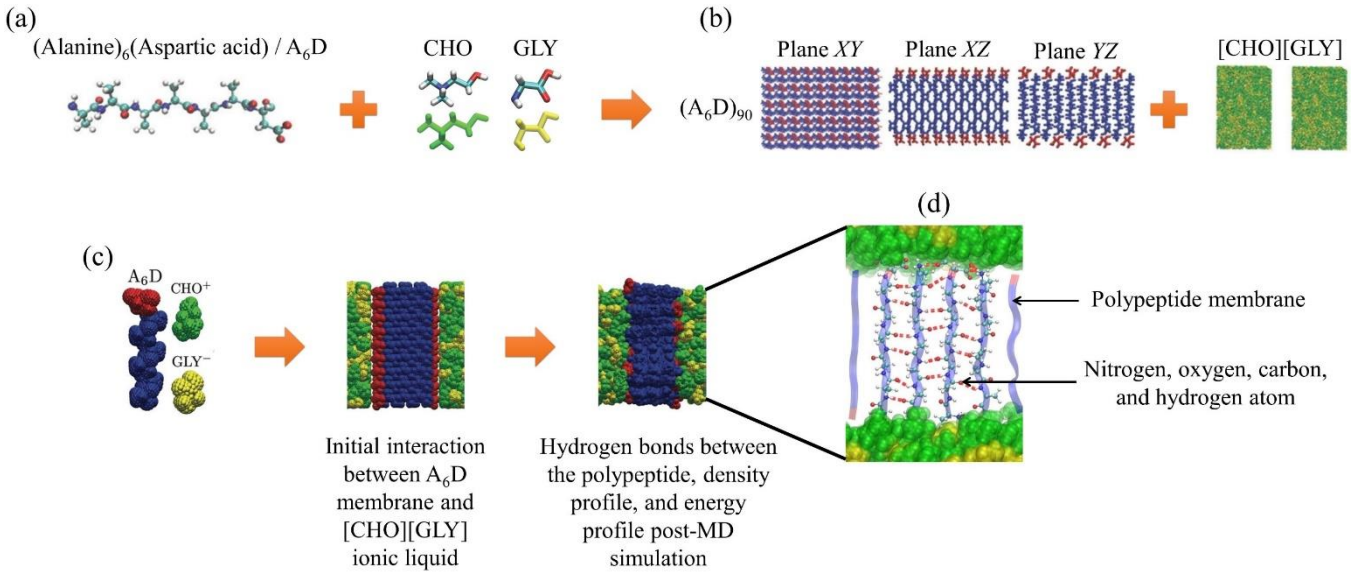


Fig. 2 Molecular simulation studies of the structural behaviour of ILM. (a) Simulated initial structure A_6D polypeptide membrane molecules and [CHO][GLY] ionic liquids. (b) Simulated equilibrated structure of the

superficial and lateral view of A_6D membrane nanosheet and [CHO][GLY]. A = alanine (blue), D = aspartic acid (red), [illegible] and [CHO][GLY] ionic liquids. (d) A_6D nanosheet structure with hydrogen bonds (red dotted lines) formed between polypeptides. Nitrogen, oxygen carbon, and hydrogen are shown in blue, red, cyan, and white colours. Ionic liquid is in green-yellow colour. The molecular interactions between polypeptides are displayed in red-blue ribbon representation. Figures are adapted from Ref. (Alves et al., 2019).

262 Table 1. A review for ionic liquid membrane including the type of materials, research objectives, computational details, application, and separation performance

Studies	Ionic liquid membrane	Study domains	Computation details	Application	Separation performance	Agreement with experimental results
(Abedini et al., 2017)	Ionic polyimides (i-PIs) i-PI+ionic liquid (IL) composite containing $[C_4mim][Tf_2N]$	Prediction of the gas molecules solubility and the adsorption for separation performance relative to the density, fractional free volume (FFV) and surface area of i-PIs and i-PI+$[C_4mim][Tf_2N]$ computed using molecular dynamics and GCMC simulations.	-Simulation method: MD and GCMC - Software: GROningen Machine for Chemical Simulations (GROMACS) 5.0 - Forcefield: TraPPE	Gas separation for CO_2/CH_4	During densification and relaxation of 55 monomers CO_2 solubility is 4 g/L at 1.8g/cm^3 density and solubility increased to 14g/L at 1.58g/cm^3 density.	-
(Budhathoki et al., 2017)	1-n-butyl-3-methylimidazolium bis(trifluoromethyl sulfonyl)imide ($[C_4mim]^+[Tf_2N]^-$ confined in carbon nanotubes and silica nanopores	Prediction of the self-diffusion coefficients of CO_2, CH_4, H_2 and the gas mixtures by MD simulations and sorption isotherms of CO_2, CH_4, H_2, CO_2/CH_4 and CO_2/H_2 using MC simulations through graphite slit pores of 2nm and 5nm widths at 333K and pressures ranging from 1 bar to 200 bar (MC); to 100 bar (MD) with and without confined ionic liquid ($[C_4mim]^+[Tf_2N]^-$ in the pores of carbon nanotubes and silica.	-Simulation method: MD and GEMC -Software: LAMMPS -Forcefield: TraPPE	Gas separation for CO_2/CH_4	At pressure of 2 bar, the solubility of CO_2 is 0.05 mole fraction for bulk IL, 0.1 for IL+2nm slit pore and 0.11 mole fraction for IL+5nm slit pore,	-
(Theng et al., 2017)	Polyvinylidene difluoride (PVDF) in $[C_2bim]^+$ and bromine anion ionic liquid	PVDF membrane with 50 wt%:50 wt% $[C_2bim]^+[Br]^-$:water and PVDF membrane with pure $[C_2bim]^+[Br]^-$ are simulated to measure the P_e, RMSD, and RDF using molecular dynamics. Stability and interaction of PVDF+IL with penetrants were evaluated.	-Simulation method: MD -Software: GROMACS -Forcefield : OPLS	Wastewater separation	This articles revealed that PVDF has stronger interaction to $[C_2bim]^+$ cation (with shortest distance to PVDF after simulation) in comparison to water and bromine anion.	-
(Ying et al., 2018)	Laminated graphene oxide membrane with 1-butyl-3-methyl-imidazolium-tetrafluoroborate $[BMIM][BF_4]$ ionic liquid	The permeability and selectivity of CO_2 through the CO_2-philic $[BMIM][BF_4]$ ionic liquid confined in nanochannels of laminated graphene oxide membrane are investigated.	-Simulation method: MD -Software: LAMMPS -Forcefield : OPLS-AA (GO structure) AMBER ($[BMIM][BF_4]$) -Algorithm: SHAKE	Gas separation i.e. CO_2/H_2, CO_2/CH_4, CO_2/N_2	Permeance of the facilitated CO_2 transportation for the membrane: 68.5 GPU. Selectivities as follows: CO_2/H_2: 24 CO_2/CH_4: 234 CO_2/N_2: 382	-
(Zeng et al., 2018)	Room temperature ionic liquids (RTIL) confined in carbon nanotube (CNT) bundles RTIL used: $[BMIM]^+$ with $[PF_6]^-$, $[SCN]^-$ and $[TF_2N]^-$ anions.	Computation of adsorption and separation of CO_2 from CO_2/N_2 mixtures.$[BMIM][PF_6]$, [BMIM][SCN],	-Simulation method: MC -Software: RASPA 1.1	Gas separation i.e. CO_2/N_2	Adsorption isotherm for CO_2 using $[BMIM][PF_6]$ with carbon nanotubes has highest	-

Studies	Ionic liquid membrane	Study domains	Computation details	Application	Separation performance	Agreement with experimental results
		[BMIM][TF_2N] in CNT bundles was tested using GCMC simulations.	-Forcefield: UFF		loading of 1.1mol/kg at 100kPa.	
(Szala-Bilnik et al., 2019)	i-PI+IL composite membrane IL used: [BMIM] cation in combination with [PF_6^-], [BF_4^-] and [Tf_2N^-]	Investigated molecular level of ionic polyimides (i-PI) and i-PI+IL composite membrane gas adsorption and diffusion characteristics.	-Simulation method: MD and MC - Software: GROMACS - Forcefield: Liquid simulations-all atoms (AA)	CO_2 capture	i-Polyimide with IL of [PF_6^-] has the highest predicted CO_2 solubility of 0.0275g/cm^3 at T_g of 355K.	-
(Tang et al., 2019)	Ionic liquid N-octylpyridiniunm bis(trifluoromethyl) sulfonyl imide [OPY][Tf_2N] modified graphene oxide (IL-GO) incorporated into polyether block amide (PEBA)	Graphene oxide (GO) is modified with ionic liquid (IL) and then incorporated into PEBA membrane. GO and IL-GO is then studied for their water and butanol adsorption performance using molecular simulation. 0.4 wt%, 0.6 wt% and 1 wt% loading of IL- GO on PEBA membrane are investigated.	- Simulation method: MC - Software: Material Studio (MS) 7.0 - Forcefield: COMPASS II	Pervaporation of butanol aqueous solutions	1 wt% IL-GO-PEBA gives highest permeation flux of 460 g/(m^2h).	Pervaporation experiment results shows that IL-GO-PEBA membrane has better performance than pristine membrane with separation factor of 25.92 and permeation flux of 470.68g/(m^2.h).
(Song et al., 2019)	Ionic liquids (ILs) in poly(vinylidene fluoride) PVDF Ionic liquids used: [BMIM][PF_6], [BMIM][Tf_2N], and [BMIM][$B(CN)_4$]	Investigated the interaction of ILs with PVDF, aggregation and separation efficiency using MD.	- Simulation method: MD - Software: GROMACS - Forcefield: All-atom (AA) Algorithm: LINCS	Gas separation for CO_2/N_2	[BMIM][$B(CN_4)$/PVDF has largest solubility of CO_2 and least degree of aggregation.	-
(Rahmani et al., 2020)	3D Graphene (3DGr) supported [EMIM][TF_2N]	Perform simulation to study separation performance of 3DGr supported IL.	- Simulation method: MD and MC - Software: LAMMPS Forcefield: AMBER	Gas separation for CO_2/CH_4	The self-diffusion coefficient of 3DGr supported [EMIM][TF_2N] is 6 x 10^{11} m^2/s	-
(Ishak et al., 2020)	[Chl][Ala]/IRMOF-1 composite membrane	Perform simulation to study the adsorption and stability of [Chl][Ala]/IRMOF-1 and its selective removal of H_2S/CO_2.	- Simulation method: MD - Software: GROMACS - Forcefield: OPLS - Algorithm: LINCS	Gas separation for H_2S/CO_2	Results show preferred adsorption of H_2S with adsorption of $A_{H2S/CO2}$ = 17.954 $molL^{-1}bar^{-1}$ and adsorption selectivity of $AS_{H2S/CO2}$ = 43.159.	
(Cheng et al., 2021)	Ionic liquid in polyimide (PI) structure. PI structures: 6FDA-ODA, 6FDA-DPX and 6FDA-DAM Ionic liquid used: [EMIM] cation in combination with [PF_6^-], [BF_4^-] and [Tf_2N^-]	Author employed molecular design to improve the molecular sieve capability of imidazole ionic liquid in PI composite membrane.	- Simulation method: MD - Software LAMMPS	CO_2 capture	6FDA-ODA (25% IL+PI) has the best performance with MSD of 10Å^2 at 10ns, diffusion of 62 x $10^{-12}m^2/s$	-

Studies	Ionic liquid membrane	Study domains	Computation details	Application	Separation performance	Agreement with experimental results
	ILs/PI system: 25%[EMIM] [Tf_2N]/6FDA-ODA, 50%[EMIM] [Tf_2N]/6FDA-DPX, 75%[EMIM] [Tf_2N]/6FDA-DAM		- Forcefield: Union atom - Algorithm: SHAKE		when CO_2 concentration is 27 wt%.	
(You et al., 2022)	[BMIM][Tf_2N]/polyimide (PI) composite membrane	Studied the effect of different IL concentration in the [BMIM][Tf_2N]/PI composite membrane in CO_2 capture system.	- Simulation method: MD - Software: GROMACS - Forcefield: All-atom - Algorithm: LINCS	CO_2 capture	The self-diffusion coefficient of [BMIM][Tf_2N] of 50 wt% in PI is 90 x $10^{-``}m^2s^{-1}$	-
(Yu et al., 2022)	[BMIM][Tf_2N]/ZIF-8	Simulation of IL encapsulated in ZIF-8 with detailed analysis of CO_2/CH_4 diffusion including the adsorption capability and the study of gas diffusion routes.	- Simulation method: MD - Software: GROMACS - Forcefield: OPLS-AA - Algorithm: LINCS	Gas separation for CO_2/CH_4	CO_2/CH_4 adsorption ratio is doubled from 1.35 to 2.27 when IL is encapsulated to ZIF-8	Computed and experimental diffusion coefficient is in the same magnitude. Simulated diffusion coefficient: CO_2 diffusing in [Bmim][Tf_2N]: 4.3 x 10^{-11} m^2s^{-1} Experimental diffusion coefficient: CO_2 diffusing in [Emim][Tf_2N]: 4.3 x 10^{-11} m^2s^{-1} CO_2 diffusing in [Omim][Tf_2N]: 1.7 x 10^{-11} m^2s^{-1}

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It was concluded that the cyclical relaxation between MD and GCMC can specifically increase the adsorption of CO_2 (Abedini et al., 2017). The i-Pi polymer structure increasingly relaxed while alternating between MD and GCMC, subsequently energy is lowered producing a more stable structure, accepting more CO_2. Addition of $[C_4mim][Tf_2N]$ ionic liquid to i-PI matrix improved the CO_2 adsorption and permeability, making a change on the CO_2 and CH_4 favoured adsorption sites among ligand nitrogen and imidazolium nitrogen, but with negligible change to relative adsorption of CO_2 and CH_4. The i-PI or IL can be functionalized to explore the possibility of increasing the selectivity.

Owing to stronger gas-surface interactions in smaller pores, the decreased in pore width of the empty slit pores increases the gas sorption in the sequence of $CO_2 > CH_4 > H_2$ due to stronger graphite interaction with CO_2 than CH_4 and H_2 (Budhathoki et al., 2017). CO_2 interact with the pore walls of graphite with higher relative interaction energy than CH_4 and H_2, while addition of $[C_4mim][Tf_2N]$ further improved the adsorption of CO_2 in the ILM, with 3-4 times higher diffusion coefficient, higher adsorption capacity and solubility-selectivity of CO_2/CH_4 and CO_2/H_2 in 5nm graphite slit pore than 2nm graphite slit pore. This is due to IL density decrease with increasing graphite pore width, providing more fractional free volume (FFV) creating more voids for CO_2 separation.

It was found that the ionic liquid can stabilize the PVDF structure by reducing the net repulsive force of the model, the computed and measured potential energy and RMSD are lower especially when the ionic liquid weight percentage is increased (Theng et al., 2017). RDF of $[C_2bim]^+$ cation showed higher curve than $[Br]^-$ signifying that$[C_2bim]^+$ has more interaction to PVDF than $[Br]^-$.

[BMIM][BF_4] nanoconfined in laminated graphene oxide has higher resistance to high temperature, enhanced durability and stability under high pressure with increasing CO_2 solubility and selectivity than other gases (Ying et al., 2018). The increment of binding energy between CO_2 and GO-[BMIM][BF_4] promotes CO_2 solubility, due to polarity of C=O bonds of CO_2 forming strong binding between CO_2 and $[BF_4]^-$ anion, resulting in anion layer that offers fast permeance and high selectivity. Increased thickness of GO/[BMIM][BF_4] membrane decreases the permeances for each gas and increases CO_2 selectivity, with 1050nm found to be optimum thickness based on trade-offs between the permeability and selectivity.

Introduction of ionic liquids into CNT channels has increased CO_2 adsorption while keeping the effect of N_2 adsorption at negligible level (Zeng et al., 2018). Strong interaction was observed between [BMIM][PF_6] confined in CNTs and CO_2 gas molecules. However, CO_2 loading in ionic liquid was reduced under humid conditions, where the modelled adsorption isotherm dropped more than half of the original performance in all ionic liquids.

Plasticization effect was observed on the i-PI with addition of ionic liquids leading to reduced T_g and calculated theoretical surface area, but FFV remained the same. (Szala-Bilnik et al., 2019). [PF_6^-] composite membrane has the lowest T_g and [Tf_2N^-] composite membrane has the highest T_g. T_g reduced with increased ionic liquid concentrations above the threshold value of 30 mol%, facilitating CO_2 hopping rates from the void to void in the composite membrane. At low ionic liquid concentration below the threshold value, blocking effect was observed on the CO_2 transport. It was reported that their systems were about two orders of magnitude slower than the range of various polymers disclosed in other studies.

It was found that [OPY][Tf_2N] is hydrophobic with high affinity towards butanol (C_4H_9OH), confining [OPY][Tf_2N] to GO can prevent the pervaporation of IL, and effectively improve the membrane stability and enhance the adsorption selectivity C_4H_9OH/H_2O by approximately 4 folds compared to pure GO (Tang et al., 2019). IL-GO incorporated into PEBA membrane increased the permeation flux and separation factor of the ILM by 18.2% and 31.5%.

CO_2 strongly interacts with ILs in which [BMIM][$B(CN_4)$]/PVDF has the highest solubility compared to [BMIM][PF_6]/PVDF and [BMIM][Tf_2N]/PVDF (Song et al., 2019). The hydrogen bond (HB) numbers decrease in PVDF when IL concentration is increased improving the diffusion of CO_2 in PVDF chains, as the PVDF motion is increased with lesser HB.

It was found that CO_2 diffusion coefficient increases with imidazole ionic liquid concentration (Cheng et al., 2021). Increasing concentration of IL gradually decrease the coordination numbers of 6FDA-DPX (computed PI structure). It indicates that the IL could have shielding effects that weakens the PI chains and ionic liquid interactions. The interaction strength between the anions of IL and gas is in the sequence of [PF_6^-] > [BF_4^-] > [Tf_2N^-]. CO_2 are more attracted to anhydride's partial nitrogen position (N1) in the sequence of 6FDA-ODA < 6FDA-DPX < 6FDA-DAM PI structures.

It was observed that the incorporation of [BMIM][Tf_2N] IL to PI initially decrease the self-diffusion coefficient of CO_2, the IL exhibited blocking effect as the IL are scattered in the composite membrane at low concentrations reducing the FFV(You et al., 2022). As the IL concentration exceed 35 wt%, the IL started to form continuous channels with increased FFV. HB number among PI chains decreased but HB number of PI with IL cation and anion increased as IL concentration increase.

The liquid supported membrane is used extensively for the selective separation of harmful organic compounds and CO_2 separation. Molecular simulation provides a mechanistic understanding of the adsorption, permeability, diffusivity, and selectivity of the model. The relationship between the mechanistic study of ILM structure

compatibilities with the penetrants provides guidance for the design of the system. Molecular simulation model is majorly based on MD and MC simulation method and the methods involved for molecular simulation is provided in section 2 of this paper. MD simulation is a time-dependent evolution of the system and MC simulation involves random sampling of the energy landscape to determine the probability with least value (Chen et al., 2020; Mehana et al., 2021).. The model involved for simulation is provided in computation details in Table 1.

Most of the research group computed ILM for sour gas separation especially CO_2 from CH_4 and N_2 (Gonzalez-Miquel et al., 2011; Budhathoki et al., 2017; Mohammadi et al., 2018; Szala-Bilnik et al., 2019; Cheng et al., 2021). Limited study of computed hybrid membranes are found in other applications such as wastewater treatment (Theng et al., 2017) and pervaporation (Tang et al., 2019). Hybrid membrane is widely applied in many sectors including wastewater treatment, water purification, biogas purification, and etc. Hybrid membrane in CO_2 separation is an emerging sector and most computational research revolves around CO_2 separation; currently, there is scarce computational research for liquid separation and mainly limited to water treatment (Wei et al., 2020; Xu and Jiang, 2020).

Imidazolium based cation was mostly applied during molecular simulation of ILM mainly due to its negligible vapor pressure, good extracting ability and thermal stability (Singh et al., 2018; Subasree and Selvi, 2020). [PF_6^-] and [Tf_2N^-] anions have been computed in the ILMs more often than other available anions especially for CO_2 gas removals (Zeng et al., 2018; Szala-Bilnik et al., 2019; Cheng et al., 2021). This is due to its adsorption ability and lower T_g.

None of the work has reported on the molecular computation of recycling of the ionic liquid in the membrane when it is saturated and the long-term stability of the ILM. Saturation of contaminants in membrane material is a factor for fouling. Membrane regeneration is one of the solutions for this issue (Deqian, 1987). Regeneration techniques for contaminants saturated membrane includes physical, chemical, and physio-chemical methods (Deqian, 1987; Ebrahim, 1994). However, the regeneration is a process, which is difficult to be carried out using molecular simulations software thus far. It is challenging to simulate a chemical reaction equilibrium molecularly (Smith and Qi, 2018). Additionally, the function is challenging and computationally expensive because MD-based future predictions are only about the next 2-3 s of the processes (Mollahosseini and Abdelrasoul, 2021). Despite algorithm advancements, characterizing various types of motion in macromolecular systems that involve extremely broad range of time scales, which is typically applicable to glassy state membrane that requires time scale from tens of femtoseconds (covalent bond vibrations) to years (long-term stability), is not realizable. In this regard, MD is an

insufficient approach for correctly sampling the dynamics and properly equilibrating these systems (Vergadou and Theodorou, 2019).

The common forcefield used for simulation of ILM model includes AMBER, COMPASS, and OPLS All-Atom (AA). AMBER forcefield covers all parameters to facilitate simulation of organic molecules like ionic liquids (Cornell et al., 1995), COMPASS forcefield covers broad range of organic polymers and inorganic with organic hybrid membrane (Asche et al., 2017); while OPLS All-Atom can reproduce organic liquids' condensed phase properties accurately (Murzyn et al., 2013).

Key accomplishments in addition of IL to MMM may improve the permeability, the selectivity, or both, synergising with filler. They combine the advantage of easy operation of membrane and high solubility liquid stripping process. Molecular simulations aided in screening of IL in membrane (Gonzalez-Miquel et al., 2011; Song et al., 2019) without needing to perform various costly experiments at the preliminary stage.

3.2 Mixed Matrix Membrane

Molecular simulation enables the study of interaction of the molecules in MMM, important and crucial data such as permselectivity, FFV, density analysis, XRD are some of the parameters that could be simulated and analysed prior to experimental analysis. Molecular studies of MMMs, their application and separation performance are summarized in Table 2. Figure 3 shows the molecular dynamics simulation for MMM and the molecular view of the system.

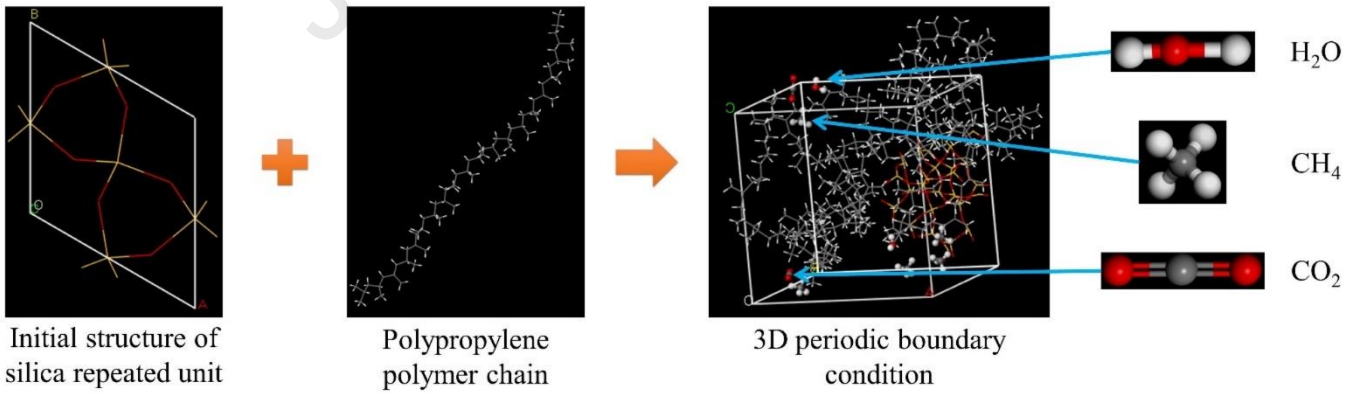

Fig. 3 The configuration of constructed MMM of polypropylene polymer (white) and SiO_2 (red-orange). Its interactions with feed and permeate gas (H_2O, CH_4 and CO_2) are shown.

374 Table 2 A review of mixed matrix membrane including the type of materials, research objectives, computational details, application, and separation performance

Studies	Mixed matrix membrane	Study Domain	Computation Details	Application	Separation Performance	Agreement with experimental results
(Keskin, 2010)	$Zn(bdc)(ted)_{0.5}$ (zn = zinc; bdc = 1,4-benzenedicarboxylic acid; ted = triethylenediamine)	Self-diffusivities and adsorption isotherms with different composition of $Zn(bdc)(ted)_{0.5}$, computed using MD simulations at room temperature	- Simulation method: MD and MC - Forcefield: Universal	Gas separation for CH_4/H_2	At fugacity of 10bar, $Zn(bdc)(ted)_{0.5}$ has adsorptive selectivity of 50 for CH_4/H_2.	-
(Golzar et al., 2014)	Nanosized silica particles filled poly(oxy-1,4-phenylenesulf-onyl-1,4-phenyleneoxy-1,4-phenyle-neisopropylidene1,4-pheny-lene) (PSF) membranes	Prediction of the diffusivity and solubility of gases including nitrogen, oxygen, carbon dioxide and methane through the MMM using MD. Studied the transport behaviours of gases in the PSF nanocomposite with different concentration of the nanosized silica particles membranes.	- Simulation method: MD and MC - Software: Material studio - Forcefield: COMPASS - Algorithm: Metropolis	Gas separation for CO_2/CH_4, CO_2/N_2, CO_2, O_2	At 20% silica and 80% polysulfone, the predicted diffusivity of O_2, N_2, CO_2 and CH_4 are 16.05, 6.41, 5.21 and 1.89 (x 10^{-8} cm^2/s).	Simulated diffusivity and experimental diffusivity of O_2, N_2, CO_2, CH_4 have difference of 20-30%.
(Wang et al., 2016a)	Amorphous poly(ether imide) (PEI) polymer with boron nitride nanotubes (BNNT) BNNTs of the zigzag types, nanotubes of (3,0), (7,0) and (12,0) nanotubes with diameters of 9.5Å, 5.6Å, 2.5Å. The three polymer composites are named PC3, PC7 and PC12.	Prediction of the possibility of utilize a new type of polymer composites namely the amorphous poly(ether imide) (PEI) and boron nitride nanotubes (BNNTs). The diffusivities, solubilities and FFV in the PEI-BNNTs composites were computed using MD.	- Simulation method: MD - Forcefield: Universal	Gas separation for CO_2/CH_4	PC12 has the highest computed solubility of 105.55cm^3/atm of CO_2.	PEI simulated solubility and measured solubility of CO_2 has a difference of 35%.
(Dehghani et al., 2017)	Poly (amide-6-b-ethylene oxide) (PEBA 1657)/ Faujasite (FAU)	Poly (amide-6-b-ethylene oxide) (PEBA 1657)/Faujasite (FAU) mixed matrix membrane is simulated to study the structural and transport properties.	- Simulation method: MC - Software: Materials Studio - Forcefield: COMPASS - Algorithm Metropolis	Gas separation for CO_2/N_2	PEBA 1657/Faujasite has a T_g of 204.1K. The CO_2 diffusivity is 0.0517 and CO_2 permeability is 89.23 Barrer with FAU composite of 20% at 298K.	-
(Hwang et al., 2018)	ZIF-8 metal organic framework dispersed in 6FDA-DAM polymer	Applied molecular modelling to microscopically study on the MOF/polymer. A record on the change of CO_2 concentration in the ZIF-8/6FDA-DAM membrane is unfolded through microimaging by IR microscopy.	- Simulation method: MD and MC - Forcefield: AMBER	Gas removal for CO_2	Atomic simulations revealed the presence of the microvoids of 9Å at the MOF/polymer interface and accumulation of CO_2in these microvoids.	-
(Tan et al., 2018)	- Zeolitic imidazole framework-8 (ZIF-8)-Polyimide (PI) - Alumina-PI	In depth study of 3-(aminopropyl)triethoxysilane (APTES) for promoting the synthesis of polyimide (PI)/zeolitic imidazole framework-8 (ZIF-8) and alumina/PI MMMs experimentally and verified through molecular simulation	- Simulation method: MD - Forcefield: Material Studio	Gas separation i.e. CO_2/N_2	PI/ZIF composite membrane with 3 layers of polyimide base gives Permeance: 93.47 GPU CO_2/N_2 selectivity: 7.50.	-

(Kong and Liu, 2019)	Porous organic cage (POC)/ polymer of intrinsic microporosity (PIM-1) Discrete CC3 cages/PIM-1 -> micromixed MMM CC3 crystal/PIM-1 -> macromixed MMM	Construction of macromixed and micromixed MMM of a CC3 and PIM-1 using MD to assess permeability and steady state adsorption amount of CO_2 and N_2 at pressure from 1-13 bar, selectivity, diffusivity, density, void size distribution and free volume.	- Simulation method: MD - Software: GROMACS - Forcefield: OPLS-AA	Gas separation for CO_2/N_2	Macromixed MMM (MMM-83) has permeability of 44000barrer and selectivity of 10.4, highest performance among other membrane composite.	
(Liu et al., 2019b)	Pebax-1657-based mixed matrix membrane doped with MoS_2 nanosheets	Applied molecular simulation on Pebax-1657 based membrane doped with MoS_2 nanosheets to study the CO_2 solubility and CO_2/N_2 solubility selectivity. Characterization is done on the fabricated MMM as well.	- Simulation method: MD - Software: Material Studio - Forcefield: PCFF	Gas separation i.e. CO_2/N_2	Pebax membrane doped with 4.76 wt% MoS_2 nanosheets had the best performance, with CO_2 permeability of 67.05 barrer and CO_2/N_2 selectivity of 90.61.	Highly correlated with experimental results.
(Monsalve-Bravo et al., 2020)	Polyimide based MMM with MFY-type zeolite Polyimide based MMM with carbon molecular sieve (CMS)	Employed equilibrium molecular dynamics to assess the permeation of gas through MMM with interfacial defects.	- Simulation method: MD and MC - Software: LAMMPS - Forcefield: PCFF - Algorithm: Force-Biased (FBA)	Gas separation i.e. CO_2/CH_4	PI/CMS based MMM has Permeability: 18 Barrer CO_2/CH_4 selectivity: 70	Simulated and experimental permeability and selectivity has percent error of 5%.
(Riasat Harami et al., 2019)	Zeolite 4A embedded into polydimethylsilocane (PDMS)	Elaboration of the physical movements of molecules and understanding the structural properties and identifying the solubility coefficients of CO_2, CH_4, C_3H_8 and H_2 gaseous molecules in PDMS/Zeolite 4A of different loadings.	- Simulation method: MD and MC - Software: Material Studio - Forcefield: COMPASS	Gas separation	CO_2 solubility coefficient at 298K with 10 wt% zeolite 4A in PDMS is 33.10×10^{-4} $cm^3(STP)/cm^3(polymer)cmHg$	Solubility of H_2 at 318K in simulation and experimental results has percent error of <5%.
(Amirkhani et al., 2020)	Poly(ether-b-amide) (PEBA) filled by different amounts of nano ZnO (0, 0.1, 0.3, 0.5 0.75 and 1 wt %)	Fabricated ZnO filled PEBA MMMs for characterization with permeability and T_g investigated experimentally. Prediction on the structural properties and gas transport performance is simulated.	- Simulation method: MD and MC - Software: Materials Studio - Forcefield: COMPASS - Algorithm: Verlet	Gas separation i.e. CO_2/CH_4, CO_2/N_2	At 0.5 wt% loading of ZnO, the MMM, CO_2 Solubility: 3.97×10^{-3} $cm^3(STP)/cm^3(polymer)cmHg$ CO_2 Diffusivity: $33.3 \times 10^{-7}(cm^2s^{-1})$) CO_2 Permeability: 132.29 Barrer.	CO_2 permeability and CO_2/CH_4 selectivity were reduced compared to single gas experiments.
(Lock and Yiin, 2020)	α-Quartz/PSF α-Cristobalite/PSF α-Tridymite/PSF (PSF with 15, 20, 25, 30, 35 wt% amount of silica polymorphs)	Pioneered in simulation of incorporation of nanosized SiO_2 in the form of varying polymorph configurations (α-Quartz, α-Cristobalite, α-Tridymite) into Polysulfone (PSF) to investigate its feasibility to improve gas separation.	- Simulation method: MD - Software: Materials Studio - Forcefield: COMPASS	Gas separation i.e. CO_2/CH_4	PSF with 25 wt% of α-Cristobalite at 25^0C has CO_2 Solubility: 5.31 $cm^3(STP)/cm^3$ [STP]cmHg CO_2 Diffusivity: 5.72×10^{-8} cm^2/s CO_2 Permeability: 39.98 barrer	-

(Riasat Harami et al., 2020)	Polycarbonate (PC)/*p*-nitroaniline(pNA)/zeolite 4A	Molecular simulation to determine the diffusivity and solubility coefficients of gas ^{molecules} within the MMM.	- Simulation method: MD and MC - Software: Materials Studio Forcefield: COMPASS	Gas separation	Neat PC CO_2 Diffusivity: 4.01 x 10^{-7} cm^2/s CO_2 Permeability: 7.21 Barrer PC/5% pNA/30% 4A CO_2 Diffusivity: 1.94 x 10^{-7} cm^2/s CO_2 Permeability: 4.05 Barrer	-
(Wei et al., 2020)	Polyacrylate (PAR) / Zeolitic-Imidazolate Framework (ZIF-8 and ZIF-93)	Prediction of the performance on desalination of water of PAR/ZIF and the swelling degree of the MMM.	- Simulation method: MD - Software: GROMACS - Forcefield: OPLS-AA	Water desalination	All MMMs rejects 100% of sodium and chloride ions.	-
(Zhao and Jiang, 2020)	Porous organic cage (POC) incorporated into polymer of intrinsic microporosity (PIM-1): MMM1 (1 cage/13 PIM-1 chains) MMM2 (1 cage/20 PIM-1 chains) MMM3 (1 cage/28 PIM-1 chains)	Studied the MMMs formed by POC(PB-1A)/PIM-1 on their degree of swelling, salt rejection and water permeability using molecular simulation	- Simulation method: MD - Software: GROMACS - Forcefield: OPLS-AA - Algorithm: Leap-frog	Water desalination	MMM1 has the highest permeability of 10^{-5} kgm/m^2hbar and 99% salt rejection. MMM2 and MMM3 has 100% salt rejection but permeability of $<10^{-5}$, $>10^{-6}$.	-
(Asif et al., 2021)	Silica/polysulfone for separation of gas with varying concentrations (i.e., 30% CO_2/CH_4, 50% CO_2/CH_4, and 70% CO_2/CH_4) and silica content (i.e., 15–30 wt%)	Performed molecular simulation to predict the solubility, diffusivity and selectivity of CO_2/CH_4 through the silica/polysulfone MMM with different gas concentrations and silica content. The respective separation performances are investigated.	Simulation method: MD and MC Software: Materials Studio Forcefield: COMPASS	Gas separation for CO_2/CH_4	15 wt% of silica in PSF has lowest CO_2 solubility of 2.0 $cm^3(STP)/cm^3atm$ but highest solubility selectivity of CO_2/CH_4 of 30. The solubility and selectivity provided is at 30% CO_2/CH_4.	Simulated and experimental density has less percent error of <5%.
(Salahshoori et al., 2021b)	Polysulfone-polyethylene glycol-silica (PSF-PEG-Silica)	Studied the effect of silica loading, temperature, and pressure on the transport performance for CO_2, CH_4 and N_2 gases.	Simulation method: MC and MD Software: Material Studio Forcefield: COMPASS	Gas separation for CO_2/CH_4 and CO_2/N_2	20 wt% of silica incorporated to PSF-PEG MMM at 25^OC and 10 bar gives CO_2 permeability of 14.76 Barrer CO_2/CH_4 selectivity of: 25.44	

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It is observed that there is high adsorption selectivity of CH_4 using $Zn(bdc)(ted)_{0.5}$ and high permeance for H_2 (Keskin, 2010). H_2 molecules are relatively small to the pore size resulting in the high permeance and faster diffusion through the MMM resulting in higher H_2/CH_4 selectivity. The adsorption selectivity using $Zn(bdc)(ted)_{0.5}$ is claimed to be notably higher than different MOFs, IRMOF-1, IRMOF-8, IRMOF-10, and CuBTC. The calculations are performed with the assumption of ideal condition of the membrane.

Incorporation of silica to PSF matrix reduced and disrupted the efficient chain packing of PSF, producing microvoids in the matrix of the PSF membrane (Golzar et al., 2014). This increases the FFV and average cavity size. Thus, the separation performance and transport properties of the PSF/silica MMM is more superior than pure polysulfone membrane.

The BNNT nanotubes in the polymer created larger fluctuation in free volume distribution as demonstrated in the cavity size distribution of the composite membrane improving the solubilities and self-diffusivities of CO_2 in polymer-BNNT, facilitating gas permeabilities and separation properties (Wang et al., 2016a). This is evident via increased concentration of gas molecules within the membrane materials as reported by C. Wang et. al.

With the addition of 20 wt% of FAU nanomaterials, the CO_2 permeability increases with a decrease of T_g as compared to pure PEBA 1657 (Dehghani et al., 2017). It was predicted that both the transport and structural properties are enhanced due to the more pathways that facilitates CO_2 transport through the membranes. Presence of pores in FAU increases the pathways, increasing its concentration would improve the permeability of penetrant molecules.

The MOF/polymer interface is observed to have microvoids formation and is more pronounced at high pressure (Hwang et al., 2018). The weak interactions of -OH and -NH at ZIF-8 surface and $-CF_3$, $-CH_3$ and -CO at 6FDA-DAM resulted in well-defined microvoids delimited by anchoring points of the molecules' interaction. The CO_2 molecules accumulation are preferred at these microvoids indicating that there might be a layer at the interface of MOF serving as the initial step of mechanism with high CO_2 affinity. It serves an indication of filler-polymer compatibility. From the IR time resolved images, it is found that CO_2 molecules transport through the filler, which may imply the CO_2 mass transport through the "highway" especially at high pressure. Similar transport patterns were predicted in molecular dynamics.

It is found that APTES treated alumina can improve adhesion between alumina-PI during synthesis allowing formation of up to 5 layers of defect-free PI dip-coated alumina-supported PI membrane with improved compatibility (Tan et al., 2018). Molecular simulation demonstrated lower binding energy (-16.00 kcal/mol) for

model containing APTES than model without APTES (26.96 kcal/mol) indicating stable membrane system with the presence of APTES.

There is no profound improvement of CO_2 permeability when discrete CC3 molecules are dispersed in the PIM-1 membrane matrix in micromixed MMMs; while there is notable enhancement of gas permeability without selectivity trade-off in macromixed MMMs (Kong and Liu, 2019). The micromixed MMM is constructed by adding CC3 cages, while macromixed MMM is constructed by adding CC3 crystal. The gas permeation performance for both type of MMMs is different because macromixed CC3 crystal disturb the packing of PIM-1 chains creating reasonably large pores in the interface, promoting gas permeation; while PIM-1 can pack tightly around the micromixed CC3 cage resulting in no notable change in void size distribution with no performance improvement.

It is observed that the MMM has strong affinity towards CO_2 due to added MoS_2 in the MMM which contributes to high CO_2/N_2 selectivity (Liu et al., 2019b). The adsorption of CO_2 molecules increased with increasing pressure indicating that the simulated results agree with rubbery polymer matrix properties, in which the sorption behaviour is usually related to Henry's Law.

For both of the polyimide based MMM with MFY type zeolites and CMS, it is observed that there is polymer rigidification with reduced permeability at the interfacial region of the polymer-adsorbent interface in non-ideal simulations (Monsalve-Bravo et al., 2020). Macroscale simulations reveal that if the filler particle size is optimum, it can maximize the permeability of gas in non-ideal MMMs. The CO_2/CH_4 permselectivity is influenced by the finite uniform and non-uniform particle size distribution's interfacial resistance. Particle size distribution (PSD) effect on gas permeability performance is investigated in ideal and non-ideal conditions of the MMMs. The non-uniform PSD in ideal condition has negligible effect to the permeability while in ideal condition it has more notable effect to the permeability. This work is one of the first fundamental approach in studying both ideal and non-ideal MMMs in simulation.

The gas solubility coefficients are found to be in decreasing order of $C_3H_8 > CO_2 > H_2 > CH_4$ through the MMM (Riasat Harami et al., 2019). The article demonstrated that higher zeolite content increases the T_g and decreases the gas solubility. This could be due to the non-sorbent zeolite materials substituted fraction of polymer chains, which adsorb gaseous molecules less effectively, as explained by H. Riasat Harami et. al. The reduction in solubility is in agreement with other experimental research (Adams et al., 2011; Tahir et al., 2018). With further zeolite loading, the solubility reduction effect decreases due to more channels and pores from the increased loading amount of zeolite 4A nanoparticles (Riasat Harami et al., 2019). The MMM is capable to adsorb more gas molecules in lower temperature than higher temperature.

It was revealed that PEBA membrane loaded with 0.5 wt% ZnO results in increased permeability for CO_2 compared to the pristine PEBA membrane as the FFV is found to increase (Amirkhani et al., 2020). Higher CO_2 permeability is acquired when the feed pressure and temperature is increased while CH_4 and N_2 has negligible changes on the transport performance. The plasticization effect of the MMM stimulates gas transport.

The increment weight percentage of silica polymorphs, as the inorganic filler, increases the free volume and T_g, which translates to the enhancement of the gas solubility, diffusivity and permeability of CO_2 and CH_4 but compromised on its CO_2/CH_4 selectivity (Lock and Yiin, 2020). The increase in free volume is due to the inorganic filler disrupting the polymer chain packing creating bigger void spaces. The addition of silica polymorphs has reduced the mobility of the polymer chain causing increment of the T_g, in consistent with experimental findings (Ahmad et al., 2015; Najafi et al., 2018; Vatanpour et al., 2022). It is predicted that the most optimum MMM according to gas permeability enhancement is addition of 25 wt% of α-Cristobalite, a polymorph configuration of SiO_2, to polysulfone matrix. This work has pioneered in molecular simulation study of SiO_2 polymorphs for enhancement of gas separation.

When zeolite and pNA is incorporated into PC, deterioration of permeability is observed which can be associated with the gas kinetic diameter where CH_4 has the most significant reduction while O_2 and H_2 has the least reduction (Riasat Harami et al., 2020).

It is found that in different PAR/ZIF MMMs, PAR of bulk region demonstrated same swelling degree and void size distribution (from <5Å enlarged up to 13Å) (Wei et al., 2020). This implies that the presence of ZIF mostly does not affect the microstructure of PAR. Due to hydrophobic characteristic of ZIF-8, during swelling, the PAR/ZIF-8 interface stays intact, exhibiting comparable interaction with PAR and water. ZIF-93 is hydrophilic with considerably stronger interaction with water than the polymer matrix, PAR. Increasing ZIF content in PAR/ZIF-8 membrane decreases the permeability of water but for PAR/ZIF-93 MMMs the water permeability remains the same. All the MMMs can reject salt permeation. Hydrated diameter of Na^+ (7.16Å) and Cl^- (3.7Å) ions are bigger than ZIF-8 (3.4Å) and ZIF-93 (3.7Å), enabling MMMs to retain the salt molecules.

3 MMMs are constructed with different POC/PIM-1 ratios for water desalination with MMM1, MMM2, and MMM3 having 1 POC/13 PIM-1 chains, 1 POC/20 PIM-1 chains, and 1 POC/28 PIM-1 chains, respectively (Zhao and Jiang, 2020). The swelling degrees are 69.3% in MMM1, 64.9% in MMM2 and 56.6% in MMM3 higher than the swelling degrees in pristine PIM-1 membrane. This is because embedding porous PB-1A cage to PIM-1 increases the free volume of MMM. MMM1 rejects approximately 99% of salt, while MMM2 and MMM3 rejects 100% of salt. MMM1 is the thinnest, most porous and allows ions to permeate, while MMM2 and MMM3 the PIM-

1/POC ratios increase, decreasing the membrane porosity and hence rejects ion permeation. The MMMs enhance 20–30% separation performance from pure PIM-1 as reported by Z. Zhao and J. Jiang.

As the gas concentrations increase, the gas permeation for gas mixture also increases in the following order 70% CO_2/CH_4 > 50% CO_2/CH_4 > 30% CO_2/CH_4 (Asif et al., 2021). As the silica content incorporated in polysulfone increases, the transport properties including diffusivity, solubility, and permeability of the penetrant molecules are steadily increasing until 25 wt.% of silica contents, followed by a decrease of the transport properties with 30 wt.% of silica contents. The enhancement of the diffusion of the binary gases is because of more void space when silica weight percentage is increased.

The incorporation of silica into PSF-PEG MMM improved the permeability and selectivity (Salahshoori et al., 2021b). The silica nanoparticles prevent softening effect of CO_2 on the polymeric membranes by reducing the mobility of the polymeric chains improving membrane rigidity, and the strong interactions of silica with CO_2 molecules improves the selectivity of CO_2 (Salahshoori et al., 2021b). The increase in permeability could be due to the selective surface area when silica nanoparticles are uniformly distributed in the polymer matrix (Salahshoori et al., 2021a). It could also be due to the interaction of the polymer chain with silica via hydrogen bonding, increasing the solubility of polar gases, in this case CO_2 (Golzar et al., 2017a; Setiawan and Chiang, 2019).

Computation of MMM mainly focuses on CO_2 separation from CH_4 followed by CO_2 removal from N_2 and O_2 (Kong and Liu, 2019; Liu et al., 2019b; Riasat Harami et al., 2019; Lock and Yiin, 2020; Monsalve-Bravo et al., 2020). Limited works have reported on computation of MMM for water treatment (Wei et al., 2020; Zhao and Jiang, 2020).

Metal organic frameworks particularly ZIF-8 is mostly used for dispersion into a polymer matrix during molecular simulation (Hwang et al., 2018; Tan et al., 2018; Wei et al., 2020) followed by silica (Golzar et al., 2014; Asif et al., 2021).

Majority of the research work focused on the accuracy of computed separation performance and properties of the inorganic membrane incorporated into polymeric membrane but however overlooked the transport performance of the membrane as the membrane physically aged and the possibility of plasticization by the inorganic filler. The solubility, selectivity, permeability, and durability of the membrane in long term application lacks study due the limitation of computational method not being able to simulate the physical aging because of the time span and physical wear and tear that could not be naturally occurring in simulation.

MMM with different inorganic fillers that are studied using molecular simulation studies are emerging, including metal oxide-based MMMs, particularly SiO_2, MOF based MMM, zeolite based MMM, and CNT based

MMM. Metal oxides are most widely accepted inorganic fillers for improvement of membrane by their different pore size, increasing chain mobility of membrane, low cost, good availability and so on (Zhu et al., 2021). MOF have ultra-high surface area, with higher packing capacity, low density, etc (Qian et al., 2020). Zeolite has gained much attention in gas separation in recent years due to its insolubility in water, microporosity, and wide range of structure with molecule sized dimension (Krishna and van Baten, 2010). CNT can be categorized into single walled CNT (SWCNT) and multi walled CNT (MWCNT) and the properties are very attractive due to their high aspect ratio (length to diameter), high thermal conductivity, flexible, etc (Wang et al., 2020).

From the molecular simulation studies, higher amount of filler tends to agglomerate and form clusters in the polymer membrane (Kim et al., 2007). Appropriate amount of filler in the polymer chain matrix is found to disrupt the polymeric chain of the membrane, producing more voids and subsequently more FFV that facilitates molecules permeation (Kim et al., 2007; Golzar et al., 2014; Lock and Yiin, 2020). With molecular simulation tools, the intrinsic properties of MMM such as the molecular sieving ability, dispersion ability, surface area and transport performance can be decoded (Riasat Harami et al., 2019).

3.3 Functionalized Hybrid Membrane

Hybrid membrane functionalization is one of the efficient techniques to further enhance properties of the membrane. Its application to hybrid membranes in many fields has progressed rapidly in recent years especially in carbon capture and storage. The functionalities can be thoughtfully tailored to reduce membrane swelling issue, increasing both permeability and selectivity, and increase the strength of the membrane for large scale application. From Table 3, applications of molecular simulation for functionalized polymer in fermentation, gas separation, biomedical application such as purification of medicine from natural source are enumerated. Surface modification processes via different methods have been assessed and developed for the membrane with enhanced properties. Mostly, researchers can study on the non-bonded forces, the van der Waals force, interfacial energy, RDF, solubility coefficient and intrinsic characteristics of the modified membrane using molecular simulations.

Figure 4 illustrates the performance of functionalized hybrid membrane which improves the MMM's hydrophobicity, compared to a normal hybrid membrane. The left hybrid membrane in Figure 4 illustrates membrane swelling when solvent molecules permeate into the membrane matrix, occupying the voids of the membrane and subsequently dilate the membrane; while the right hybrid membrane in Figure 4 illustrates the functionalized hybrid membrane without swelling.

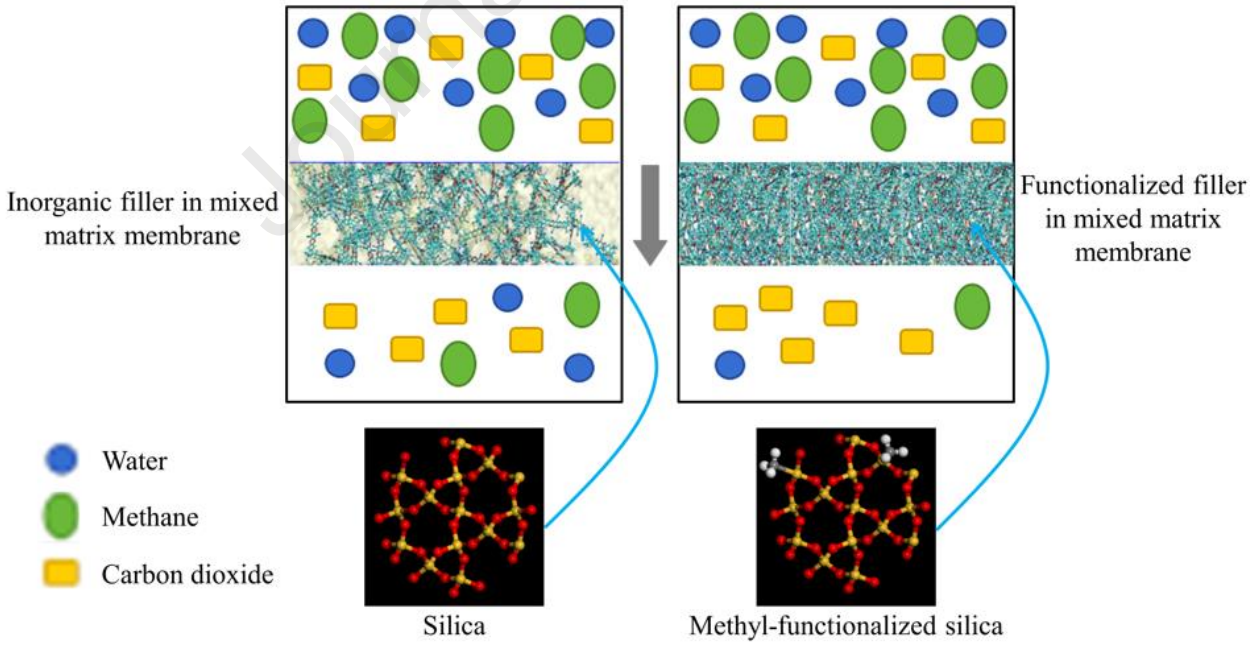

Fig. 4 A graphical illustration of functionalization of hybrid membrane in improving separation performance in both selectivity and permeability with improved membrane characteristic of its hydrophobicity (reduce membrane swelling issue) with the functionalization of the silica with hydrophobic functional group (Lee et al., 2022). Figure adapted from (Liu et al., 2019a).

528 Table 3 A review of functionalized hybrid membrane including the type of materials, research objectives, computational details, application, and separation performance

Reference	Functionalized Hybrid Membrane	Study Domain	Computation Details	Application	Separation Performance	Agreement with experimental results
(Kim et al., 2007)	Single welled carbon nanotubes (SWNT) functionalized with octadecylammonium (ODA) and polysulfone (PSF) as the polymer matrix	Fabrication of SWNTs functionalized ODA dispersed in polysulfone polymer matrix nanocomposite membranes. Gas adsorption and permeability performance were investigated using the MMM prepared.	Simulation method: MC	Gas separation for CO_2/CH_4	10 wt% SWNT/PSF has: CO_2 permeability of 5.19 Barrer CO_2 diffusivity of 6.48±0.51 x 10^{-8} cm^2/s	-
(Yani and Lamm, 2009)	Octahydrido silesquioxane (OHS) or octaaminophenyl silsesquioxane (OAPS) functionalized polyhedral oligomeric silesquioxanes (POSS) with polyimide (PI) as polymer matrix	Applied MD for molecular understanding of PI and POSS MMM behaviour. The effect of functional groups OHS and OAPS on PI are examined. The Glass transition temperature (T_g), radial distribution function and PI chains mobility with POSS molecules in the functionalized MMM are determined.	- Simulation method: MD - Software: LAMMPS - Forcefield: Hybrid-COMPASS	Gas separation	Mean Square Displacement of 10.45 wt% OHS-POSS/PI is 63Å, highest as compared to other functionalized membrane loaded at different weight percent.	-
(Kasahara et al., 2016)	Amino acid ionic liquids (AAILs) with polytetrafluoroethylene (PTFE).	Prediction of the AAILs/PTFE membrane's physical properties including the density, viscosity, FFV and transport properties such as N_2/CO_2 absorption capacities using molecular dynamics.	- Simulation method: MD - Software: MS + GROMACS - Forcefield: AMBER - Algorithm: LINC	Gas separation for CO_2/N_2	[aN_{111}[Gly]-based FTM at 5kPa CO_2 partial pressure has: CO_2 permeability of 3000 Barrer CO_2/N_2 selectivity of 110	-
(Park et al., 2016)	Polar groups -OH or -NH_2 functionalized multi walled carbon nanotubes (MWCNTs) and co-polyimide (P84)	The macroscopic CNT dispersion through P84 matrix is examined for its transport behaviour using MD and macroscopic CNT dispersion in P84 matrix using mesoscale simulations	- Simulation method: MD and mesoscale simulation - Software: Materials Studio - Forcefield: COMPASS forcefield	Water treatment	MWCNT of hydroxyl groups functionalized CNT has solubility parameter of 23.2 ±1.3 $(J/cm^3)^{1/2}$ MWCNT of amine groups functionalized CNT (CNT-NH_2) has solubility parameter of 24.2 ±1.0 $(J/cm^3)^{1/2}$	Both simulated and experimental results show non-functionalized MWCNT and P84 are not compatible.
(Golzar et al., 2017b)	- 0.5-3.0 wt% Pristine single-walled carbon nanotubes (p-SWCNT) embedded into PIM-1 - 0.5-3.0 wt% Pristine multi-walled carbon nanotubes (p-MWCNT) embedded into PIM-1 - Polyethylene glycol (PEG) functionalized SWCNT (*f*-SWCNT) embedded into PIM-1	Prediction of the transport properties of gas mixtures including CO_2, CH_4, N_2 and O_2 into the pristine PIM-1 membrane and MMM based on PIM-1 using molecular simulations.	- Simulation method: MD and GCMC - Software: Materials Studio - Forcefield: PCFF	Gas separation CO_2/CH_4, CO_2/N_2, CO_2/O_2	PIM/*f*-SWCNT(2%) is the MMM that have highest diffusivity of 24.76±4.78 x 10^7 cm^2/s and high solubility of 789.54±89.43 x 10^3 cm^3(STP)/cm^3(PIM/*f*-SWCNT)cmHg	The simulated density and the available experimental density of the membranes have percent error of <5%.

	- Polyethylene glycol (PEG) functionalized MWCNT (*f*-MWCNT) embedded into PIM-1		- Algorithm: Verlet			
(Pazirofteh et al., 2017)	Polyethylene (PEG) functionalized Polyhedral oligomeric silesquioxanes (POSS) embedded into PEBA 1657 or PEBA 2533	Prediction of transport and structural behaviour and properties of PEG functionalized POSS dispersed in both polyether block amide namely PEBA 1657 and PEBA 2533 using molecular dynamic simulation.	- Simulation method: MD and Monte Carlo - Software: Materials Studio - Forcefield: COMPASS	Gas separation	PEBA 1657 +30% PEG functionalized POSS performance is the closest to the Robeson upper bound with CO_2 permeability of 100 Barrer and CO_2/CH_4 selectivity of 70.	Simulated T_g and experimental T_g for both PEBA 1657 and PEBA 2533 has percent error of <5%
(Ahmad et al., 2018)	$-NH_2$ and $-NH-COCH_3$ functionalized metal organic frameworks (MOFs) in 6FDA-DAM polymer MOF used: UiO-66 (Zr-BDC)	Evaluation of the functionalized MOF/6FDA-DAM separation performance and pristine 6FDA-DAM performance.	- Simulation method: MD - Software: LAMMPS - Forcefield: AMBER	Gas separation for CO_2/CH_4	Best separation performance membrane: 14 wt% UiO-66 MMM (P_{CO2} = 1912± 115 Barrer, $\alpha_{CO2/CH4}$= 31 ± 1) 16 wt% UiO-66-NH_2 MMM (P_{CO2} = 1223 ± 123 Barrer, $\alpha_{CO2/CH4}$= 30 ± 1)	
(Mosadegh et al., 2020)	Sulfonic acid or amine functionalized-faujasite/ poly(ether-block-amide) FAU/PEBA(P8) P8 is PEBA membrane with 8% concentration.	The author functionalized zeolite FAU with sulfonic acid and amine for incorporation to PEBA. The structural properties and transport behaviour are investigated using molecular modelling.	- Simulation method: MD and GCMC - Software: Materials Studio	Gas separation for CO_2/CH_4	P8FAU-NH_2(1 wt%) has the highest ideal CO_2/CH_4 selectivity of 45 and permeability of 9 Barrer at 3.48 (1000/T, K^{-1})	Simulation data and experimental data has percent error of <5%.
(Liu et al., 2021)	Hollow silica Porous liquid (SPL) functionalize into Pebax-1657 matrix.	Applied Molecular Simulation to verify the improved interaction of the functionalized MMM and CO_2 molecules by analyzing the interaction parameters including the transport properties.	Simulation method: GCMC	Gas separation for CO_2/N_2	The functionalized MMM gives: CO_2 permeability up to 229.5 Barrer CO_2N_2 selectivity of 71.1	Experimental and modelled both exhibit good permeability with percent error of <5%.

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At lower loadings of SWCNT (5 wt% & 10 wt%) in polymer matrix, the permeability and diffusivity is high as all gas permeates through the carbon nanotubes in SWCNT's diffusive tunnels and the dispersion of nanotubes in the polymer matrix are well dispersed (Kim et al., 2007). However, at higher SWCNT loadings (15 wt%), the tortuosity throughout the agglomerated SWCNT domains restricts further permeability. Also, there is an observed decrease in CH_4/H_2 experimental selectivity which conforms with CH_4/H_2 selectivities in SWCNTs as predicted by atomistic simulation. Addition of functionalized SWNTs to PSF matrix improve the selectivities and permeabilities of smaller molecules.

Incorporation of 11.25 wt% OAPS into the PI polymer matrix exhibit an increase of T_g while a decrease of the T_g is observed when OHS is incorporated into the PI matrix (Yani and Lamm, 2009). Through RDF calculations, it is found that the PI-OHS contacts' density is higher than PI-OAPS contacts' density. PI chains are more closely packed around OHS than OAPS. OHS molecules are positioned in a more orderly manner than OAPS molecules in the nanocomposite membranes. Introduction of OAPS reduced the PI mobility while OHS slightly increased the PI chains mobility.

The molar and FFVs decreased with decreasing AAIL size, enabling increased carbon dioxide adsorption and decreased N_2 absorption (Kasahara et al., 2016),. It was found that the more the number of amino groups in the AAILs, the CO_2 absorption increase. Multi-amino functionalized AAILs are suitable under humid condition as water molecules aids CO_2 absorption by the AAILs' second amino group.

The solubility parameter of pristine MWCNT and P84 shows the largest variance in value between all CNTs and P84, which may indicate poor affinity towards each other (Park et al., 2016). Experimental results confirmed that P84 and non-functionalized MWCNT do not mix well and have low mutual compatibility. However, functionalized MWCNTs and P84 have similar solubility parameters, indicating better miscibility and dispersion of functionalized MWCNT in P84 polymer matrix and validated with experimental data. The functional groups must be embedded into the MWCNTs model (with limitation of 0.5-1.0 wt% concentration) for good dispersion through the P84 matrix. If functional groups exceed limit of 1 wt%, the model will show strong phase separation. The number of functional groups shall not exceed a specific limit, else the apolar-polar repulsion between polar heads and carbon together with polar-polar and apolar-apolar interactions occur resulting in phase separation.

Improvement of the transport properties including permeability, diffusivity and solubility is observed with the incorporation of either pristine CNT or PEG-functionalized CNT particles up to 2 wt% into the PIM-1 membranes, without compromising on the selectivity, and starts to decrease beyond 2 wt%, while selectivity remains the same (Golzar et al., 2017b). PIM-1/*f*-SWCNT membrane gives the highest diffusivity and permeability; PIM-1/*f*-MWCNT

gives the highest CO_2 selectivity. It is found that the resulting functionalized MMM (up to 2 wt%) contains polar hydroxyl group that have affinity for the adsorption of quadrupolar CO_2 gas, beyond 2 wt% there is a discontinuity of nano gaps due to agglomeration of the CNTs imposing resistance of diffusing gas through the membrane.

Membranes with PEBA 2533 shows higher permeability as compared to PEBA 1657 although results showed otherwise for permselectivity (Pazirofteh et al., 2017). The T_g for POSS-PEG/PEBA 1657 and POSS-PEG/PEBA 2533 membranes decreased with the increase of POSS-PEG nanoparticle content. The incorporation of nanomaterial increases the free volume and polymer chain flexibility.

Functionalized UiO-66 with 20 wt% of UiO-66-NH_2 and UiO-66-NH-$COCH_3$ observed improvements in both CO_2 permeability and CO_2/CH_4 selectivity contributed by the decreased T_g and FFV increment due to the disruption to the polymer chain packing (Ahmad et al., 2018).

According to M. Mosadegh et. al. (2020), the blending of sulfonic acid or amine functionalized FAU fillers to P8 interrupted the P8 polymer chains which increase the FFV, improving the gas diffusion. Improved adsorption and the transportation of gas molecules is facilitated due to the polar groups' presence on the surface of FAU. Amine-FAU/P8 (1 wt% amine) gives better performance for CO_2/N_2 selectivity of 117, while SO_3-FAU/P8 (1 wt% SO_3) gives higher CO_2/CH_4 selectivity of 31 (Mosadegh et al., 2020).

The as prepared hollow silica-based porous liquids functionalized Pebax-1657 has shown increment of 241.9% of CO_2 permeability and increment of 90.2% of CO_2/N_2 selectivity as compared to the pure Pebax-1657 (Liu et al., 2021). The SPL disrupted Pebax chain arrangement, and the hollow cavity of the porous liquid serves as a pathway for gas transport. The CO_2-philic moieties derived from the porous liquid leads to improved CO_2 selective permeation, overcoming the 2008 Robeson upper bound.

Computed FHM exhibits superior results and tailored to its application. During computation of FHM, it is found that functionalized components of the membrane modify the membrane structure where the cavity and pore size are suited to the desired molecular sizes for permeation and retention of respective contaminant molecules, modify the membrane polarity or modify the membrane contaminant-philicility (Yani and Lamm, 2009; Park et al., 2016; Liu et al., 2021).

A number of molecular simulation works have reported on the use functionalization of CNTs (Kim et al., 2007; Park et al., 2016; Golzar et al., 2017a) mainly due to its high surface area and good material properties, such as high mechanical strength and good thermal conductivity (Singh et al., 2016). The base polymer material may exhibit reduced mobility when incorporated with functionalized inorganic compound (Yani and Lamm, 2009). Thus, polymer with flexible backbone can be considered for application in future studies.

The incorporation of special functional groups in IL yields task specific IL for facilitated transport membranes besides solution-diffusion mechanism. Sulfonate or amine functionalized hybrid membrane can increase the membrane's polarity and its affinity for CO_2 (Kasahara et al., 2016; Mosadegh et al., 2020). PEG functional groups exhibit high permeability without compromising on the selectivity of the hybrid membrane (Golzar et al., 2017a; Pazirofteh et al., 2017).

A few researchers have focused the computation of FHM on gas separation for CO_2 from mainly CH_4. Only one has reported on the computation of FHM for water treatment (Park et al., 2016). The limited number of studies indicates that this section might still be new. This observation suggests more studies are warranted to understand its value and create deeper insight on FHM. The simulation work is also in very small/microscopic scale. It lacks macroscopic representation of the actual scale application and the separation performance in aggressive environment, large scale and the long-term application is not known. The FHM are also normally assumed homogeneous if they have similar or T_g that are near.

Table 4 shows the available data for the enhancement of hybrid membranes from the research work collected from Table 1, 2 and 3.

Table 4 Tabulation of performance enhancement between the pristine membrane and hybrid membrane

Reference	Parameter	Pristine membrane	Hybrid Membrane	Improvement (Folds)
Ionic Liquid Membrane				
(Abedini et al., 2017)	CO_2 solubility, mol/(L.atm)	0.075	0.066	0.88
(Budhathoki et al., 2017)	CO_2 solubility, mol fraction	0.025	0.075	3
(Ying et al., 2018)	CO_2 permeance, GPU	17	68.5	4.03
(Zeng et al., 2018)	CO_2 loading, mol/kg	3.75	5.5	1.47
(Szala-Bilnik et al., 2019)	CO_2 MSD (x $10^{-9}cm^2s^{-1}$)	2.3	7.63	3.32
(Tang et al., 2019)	Butanol Adsorption, nmol/g	0.39	2.83	7.25
(Rahmani et al., 2020)	CO_2 Diffusivity (x $10^{-11}m^2/s$)	2.8	6	2.14
(Ishak et al., 2020)	CO_2 Diffusivity, nm^2/ps	397.183	60.067	0.15
(You et al., 2022)	CO_2 Diffusion coefficient (x 10^{-11} m^2s^{-1})	130	120	0.91
Mixed Matrix Membrane				
(Golzar et al., 2014)	CO_2 Permselectivity	25.3	23.2	0.92
(Dehghani et al., 2017)	CO_2 Permselectivity	20.11	57.83	2.88
(Kong and Liu, 2019)	CO_2 Diffusivity (x 10^{-9} m^2/s)	0.12	0.15	1.25

Reference	Parameter	Pristine membrane	Hybrid Membrane	Improvement (Folds)
(Liu et al., 2019a)	CO_2 permeability (Barrer)	46	67	1.46
(Riasat Harami et al., 2019)	CO_2 solubility	33.1	11.32	0.34
(Amirkhani et al., 2020)	CO_2 Permselectivity	25.7	29.13	1.13
(Mosadegh et al., 2020)	CO_2 permeability (Barrer)	70	110	1.57
(Riasat Harami et al., 2020)	CO_2 permeability (Barrer)	7.21	4.05	0.56
(Wei et al., 2020)	Water permeability (x 10^{-7} L.m/(h.m^2.bar))	3.3	4.5	1.36
(Salahshoori et al., 2021a)	CO_2 Permeability (Barrer)	7.9	14.76	1.87
Functionalized Hybrid Membrane				
(Kim et al., 2007)	Permeability (Barrer)	3.9	5.19	1.33
(Pazirofteh et al., 2017)	Permselectivity	1	1	1
(Ahmad et al., 2018)	Permeability (Barrer)	997	1912	1.92
(Liu et al., 2021)	Permeability (Barrer)	70	229.4	3.28

It is observed that around 70% of the ILM, 80% of the MMM and 100% of the FHM shows improvement from its pristine membrane. The best separation performance of hybrid membrane is with ionic liquid, giving four times higher compared to GO-based membranes without ionic liquid and above the Robeson upper bound (Ying et al., 2018), followed by functionalized hybrid membrane and mixed matrix membrane.

4. CONCLUSIONS AND FUTURE PERSPECTIVES

In conclusion, molecular simulation approaches aid to unravel molecule interactions with the environment and complex materials in complementary to experiments. Although the computational method may become more heavily dependent upon in the future, the Molecular Dynamics-based prediction process is still a complicated and challenging task. Precise data input and sufficient timescale must be provided to converge the simulation into more reliable and accurate outcomes. It was observed from the review that via proper design and selection of ionic liquid, inorganic material or functionalized material using molecular simulation, the separation performance of polymeric membrane can be enhanced by a few times ranging from two to four folds. Functionalized hybrid membranes are observed to have better overall improvement in separation performance, while ionic liquid membranes and mixed matrix membranes have a combination of enhanced and deteriorated performance compared to its pristine membrane. This finding highlights the importance of elucidation of suitable hybrid membrane material and its gas transport properties

by molecular modelling, a potential solution to reduce time consuming experiments due to trial and error for tailoring new hybrid membrane materials in the laboratory for various application (Smith and Qi, 2018).

A comprehensive molecular simulation along with justifications from theoretical calculations can provide researchers with vast details and parameters of the system. This can lead to the design and development of tailormade and engineered materials at the most optimum separation. Hence, molecular simulation is expected to continuously contribute to the testing of new applications for various fields such as sour gas removal in the energy sector to reduce global warming, water and wastewater treatment to protect human from harmful element in water, water desalination which is a solution to source for fresh water for industrial/domestic use and human consumption, and etc. In particular, the removal of CO_2 is important in reducing the concentration in the atmosphere responsible for global warming and wastewater treatment could protect human from harmful elements found in water and ensure maximum amount of water to be reused especially in places with limited freshwater source.

Based on the recent advances in molecular simulation, the followings are the aspects that would gain attraction in the research and development of molecular simulations.

4.1 Innovative Membrane Modifications and Combinations

The explorations of new membrane materials are required for new applications. Although membrane modifications will find their niche in terms of small-scale development, there may be limitations during large scale production of the membranes. More molecular simulation research is required to interpret the roles of new materials in the membrane structure, morphology, and effect on solute transport.

Studying the safety and environmental aspects of the membrane modification will be beneficial for real life applications. Careful selection of materials should be given for tailor-made modified membranes that are important for enhancement in the aspects of selectivity, diffusivity, and intrinsic properties. This will lead to breakthrough in optimizing membrane performance.

4.2 Environmental Aspects

The inevitable large-scale applications and non-scientific disposal of membrane materials pose severe threat to environments, especially those non-biodegradable membranes with polymer base made of ethylene, polycarbonate, polystyrene, polyvinyl chloride, polypropylene, and polyester. Future direction of membrane industries should emphasize on the development of sustainable polymer in an economical manner. This can be achieved with

transformative basic research using materials derived from renewable feeds. Simulation based study functions may serve as the starting gate to explore new materials that are environmentally friendly and practical for application.

4.3 Long Term Techno-Economic Studies of Membrane Advancement Application

Although many improvements can be observed from the advancement of membrane technology, the diversity and operating range of actual large-scale membrane-based separation remains limited. The separation performance of the membrane materials in aggressive actual conditions is unknown despite proven to improve separation and mechanical strength performance in simulations. These materials are highly attractive for future considerations due to their advantages of portable and easy maintenance.

A number of studies have reported new and interesting applications with membrane advancement in many areas in small scale but none have reported on the large scale and long-term operation of the processes (Fu et al., 2021; Jiang et al., 2021; Moqadam et al., 2021; Zhang et al., 2021). The technical barriers in molecular modelling include membrane physical aging, fillers, and ionic liquid having plasticization effect to the membrane. In addition, multiscale modelling for system description and hybrid membrane homogeneity are normally presumed to be homogenous. These challenges shall be addressed to achieve a more reliable modelling outcome.

For the membrane operation to perform, techno-economic assessment of the process at pilot scale is necessary. This will resolve many issues like the viability, profitability, swelling control and mitigation, and the membrane susceptibility to complex feed materials. Such studies are costly and time-consuming, but successful outcomes will lead to a more sustainable membrane separation operation. Solitary membrane process may not be able to perform well, but the overall process can be improved when incorporated with filler or ionic liquid.

Reliable simulation and modelling can be used to predict the performance of the new hybrid membrane in which it can provide guidelines on the operating conditions of the process. This reduces the amount of time in conducting the experimental study. A new way of bringing the advancement of membrane separation technology to real-life applications is highly promising for the decades to come.

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Conflicts of Interest

There are no conflicts to declare.

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Authorship contribution statement

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HIGHLIGHTS

- Fundamentals of molecular simulation are reviewed and related to application in hybrid membranes.
- Insight into molecular structural properties of hybrid membranes is presented.
- Simulated transport performance from published literature and mechanism of hybrid membranes are provided.
- Limitation in molecular simulation for membrane separation is discussed.
- Future outlook for molecular simulation of membrane separation is recommended.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: