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Grand challenges in membrane transport, modeling and simulation

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1 Introduction

Today, membranes play an increasing role in separation processes across a wide range of industries, including water treatment, biomedical applications, bioseparations, and gas separations (Yeom et al., 2022). Numerous different membrane types exist, which can be broadly categorized as either porous or non-porous, where pores may be or may not be filled with a separate phase from the bulk solvent and membrane phases. In addition, various driving forces exist - pressure, concentration, electric field, etc.—that lead to transport across the membrane. For a porous membrane, solute transport is usually governed by convective flow through the pores. Micron-sized pores are used to reject particles such as cells and cell debris while at the other end of the size range, nanoscale pores act as molecular sieves, selectively allowing smaller molecules to pass through. Nanoscale domains in non-porous (dense) membranes control separation selectivity and permeability by manipulating solute distribution and diffusivity. These nanostructures can also influence solute behavior, like adsorption/desorption at membrane interfaces. At intermediate pore sizes, convection and diffusion may both play a significant role in solute transport as is often observed for nanofiltration membranes. In addition surface properties such as charge can have a significant effect on performance.

Simulation and modeling play an increasingly important role in the design of these separation processes. Computational methods offer the possibility of enabling rational design of new membranes and membrane processes (Kancherla et al., 2021; Samei and Raisi, 2022), supporting the optimization and understanding of complex membrane-based systems. They can be used to examine molecular interactions that lead to adsorption and desorption of species as well as fouling. This can guide the development of new membranes leading to improved performance. Nonetheless, the simulation and modeling of membrane separation processes presents a range of formidable challenges that demand our attention. In this contribution, we delve into the existing hurdles relating to simulation and modeling. Our aim is to highlight these issues and emphasize the need for increased focus by researchers engaged in the simulation and modeling field.

This article is divided into three sections. The first focuses on the membrane casting process and modeling of membrane structure. The second section discusses simulation of separations using dense membranes, which includes, gas separations, pervaporation, and perstraction. The final section discusses separations involving porous membranes. Some membranes, such as those used for reverse osmosis, forward osmosis, dialysis, etc. may be considered at the boundary between dense and porous membranes and have been included with dense membranes.

2 Challenges in modeling membrane formation and structure

The specific process used to create a membrane largely determines its structure and, in turn, its separation properties and performance. For instance, porous and dense membranes are typically formed through distinct mechanisms, which leads to distinct challenges (Wang et al., 2022). Modeling the formation process is important for understanding how controllable changes to the fabrication protocol can adjust membrane function. It is important to distinguish between modeling of the actual formation process and the development of algorithms that predict the resulting membrane structure. As we will highlight, there are many valid procedures, differing widely from the real formation process, that produce membrane structures reflecting experimentally determined properties. This is not indicative of the value of the models—rather, predictions of how formation conditions affect the final structure of the membrane are important for both future modeling studies as well as engineering design. However, accurate predictions of structure do not indicate a causal link to the details of formation. Due to the scarcity of real-time experimental data, models are often judged solely on their ability to produce *final structures* matching experiments. We encourage, instead, careful consideration and a statement of the limitations of a particular modeling technique and to strive towards an understanding of precisely which features of the membrane formation process, or the final structure, are emulated.

2.1 Porous membranes

Many models have been developed for predicting pore geometry, however, accurately representing the complex and often irregular pore structures within membranes can be challenging. Though there has been interest in producing membranes through electrospinning (Chiao et al., 2022; Aijaz et al., 2023) or controlling block-copolymer morphologies (Nunes, 2016; Hampu et al., 2020), the primary mechanism for forming porous membranes is through phase inversion (Tang et al., 2021). This involves inducing solid–liquid phase separation through a non-equilibrium process to modify either temperature and/or solution composition (either through evaporation of solvent or introduction of a non-solvent).

For detailed surveys of porous membrane formation modeling techniques, we direct readers to a comprehensive recent review by Tang et al. (2021). Modeling techniques can roughly be divided into four categories: continuum models, phase-field (or, more generally, mean-field) treatments, coarse particle-based simulations, and atomistic particle-based simulations. Continuum models can capture long time and length scales associated with the phase inversion process, but do not directly provide details on the molecular or meso-structure of the formed membrane. Such features are inferred heuristically by tracing the time-series of composition or temperature within regions of the precipitating polymer solution through a known phase diagram. While this methodology helps to rationalize and improve membrane formation processes, the requirement of significant experimental data (e.g., thermophysical properties) pertaining to the specific system of interest remains a barrier to the rapid computational exploration of novel polymeric species or more complex fluid mixtures.

While phase-field simulations can provide approximate dynamics of phase separation across a wide range of length-scales, and hence directly predict morphologies, they are limited by a similar lack of generality to unknown systems. Specifically, such simulations are only chemically specific to the extent of known data, typically utilizing simple Flory–Huggins or polynomial models of thermodynamics. While the possibility of introducing further information on chemical structure through more sophisticated thermodynamic models exists, the computational feasibility and limit for improving phase-field simulations in this manner remains to be clarified.

Particle-based simulations can provide chemical specificity, enhanced transferability to new systems, and resolution at a molecular scale. However, this comes at increased computational expense and hence smaller overall length and time scales that can be explored. In dissipative particle dynamics (DPD), molecules are represented as coarse blobs experiencing both molecular as well as hydrodynamic forces. Unlike fully atomistic models, DPD simulations can currently reach the length and time scales necessary for observing the formation of membrane meso-structures. Currently, atomistic simulations are not commonly used to model membrane formation but are more typically employed to study nanoscale membrane properties once an overall structure is known. A major challenge lies in identifying ways to couple models at different scales in a single simulation. Complications arise from the strong coupling during phase inversion of fluid dynamics, mass transport, and thermodynamics, all in an intrinsically non-equilibrium, non-steady-state setting.

2.2 Non-porous membranes

Dense membranes are frequently produced through interfacial polymerization to ensure a very thin film that ensures selectivity, while minimizing overall membrane resistance (Ji et al., 2000; Wang et al., 2021). Though interfacial polymerization takes place over smaller length and time scales than phase inversion, it introduces the unique challenge of modeling chemical reactions simultaneously with mass transport and phase separation. Non-porous membranes often have intricate molecular structures that require accurate representation in simulations. Obtaining detailed structural information can be challenging, both for synthetic and complex natural membranes.

Dense membrane formation modeling employs some of the same methods as for porous membranes. However, a greater emphasis is placed on atomistic simulations and phase-field treatments are excluded due to phase separation of the thin film occurring in tandem with the growth of polymer chains rather than their nucleation or diffusion. Continuum models of interfacial polymerization focus on reaction–diffusion mechanisms, both analytically and numerically, varying in the detail with which polymer chains are treated (Berezkin and Khokhlov, 2006). Though some techniques predict chain length distributions or changes in diffusivities of polymers or monomers with degree of polymerization, details of the actual chain configurations or their chemical structure are not present.

DPD simulations emulating polymerization through aggregation of monomers have provided a more detailed view of the interfacial polymerization process (Oizerovich-Honig et al., 2010). Berezkin and Kudryavtsev (2013) used a multiscale framework to couple DPD simulations to continuum-based numerical simulations of the monomer diffusion. While the rigor of such methods requires further validation, this represents an important step in coupling simulation approaches at different scales. Working in between DPD and atomistic resolution, Muscatello et al. (2017) introduced a coarse-grained model of interfacial polymerization that accounts for molecular shape and bonding specificity. While accurately capturing many experimental observations, these simulations were still limited by the size of the simulation box and discrete, finite number of available reactants.

At an atomistic scale, models to this point have not focused on the exact process of membrane formation, but instead on "unphysical" algorithms (heuristic with no accurate representation of the actual physics of the formation process) for generating dense amorphous membranes that correspond to experimental structures (Harder et al., 2009; Luo et al., 2011; Ridgway et al., 2017; Liu et al., 2022; Vickers et al., 2022). A number of software packages exist for generating amorphous, long-chain polymer structures with atomistic resolution (Abbott et al., 2013; Gissinger et al., 2020; Zhang et al., 2023). Applications of such tools, in particular the most flexible, REACTER framework (Gissinger et al., 2020), may prove fruitful for investigating the interfacial polymerization process. It is important to note, however, that all such tools heuristically simulate reactions. Simulations that accurately represent reactions, and thus on some level include quantum dynamics, are too computationally expensive to study dense membrane formation on informative time and length scales. However, neural-network potentials that accurately reproduce bond breaking and forming in quantum simulations at a similar computational cost to classical dynamics (Smith et al., 2017; Zhang et al., 2018) represent an additional interesting future possibility. While application of such toolsets and models may lead to additional molecular-level insights, multiscale models will likely be necessary to fully capture dense membrane formation at all relevant time and length scales. For instance, if we wish to predict the impact of a porous support with even small pores of tens to hundreds of nanometers, atomistic simulations will quickly become intractable. Such considerations again reinforce the necessity of improved coupling between models at different scales.

3 Challenges in membrane simulation and modeling in non-porous membranes

3.1 Elucidating transport mechanisms

While macroscopic fluid flow through pores dominates transport in porous membranes, non-porous membranes are typically considered to involve a solution-diffusion mechanism of transport. In the case of reverse osmosis, or more generally when solvent significantly swells a membrane, there has been recent debate over the balance between homogeneous diffusion and diffusion through nanoscopic pores (Hegde et al., 2022; Heiranian et al., 2023; Wang et al., 2023). While the picture of clusters of water "hopping" between fluctuating nanoscale voids in reverse osmosis membranes has been established in molecular dynamics simulations (Shen et al., 2016), it has been elusive to validate experimentally. Further, most efforts to date have focused heavily on polyamide membranes for desalination. A significant challenge lies in uncovering mechanistic understanding of transport in novel membrane materials.

While solvent, water in particular, has been the focus of many studies of transport through membranes, exploring solute transport is also important and can provide critical insights into the mechanism of transport (Shen et al., 2016). Unfortunately, this is a tremendous challenge for solutes, such as ions, with very low solubility in the membrane phase or nanoporous channel. The reason is that passage of such a solute becomes an incredibly rare event, occurring only on the order of microseconds at the fastest. While a single event is potentially within the realm of state-of-the art molecular dynamics simulations (at great computational expense), a meaningful statistical sample for determining flux would require hundreds of such events at a minimum. While non-equilibrium pulling of ions through a membrane provides insight into nanoscale pathways through a membrane (Luo et al., 2011), rigorous estimates of transition rates of ions are only recently emerging through the application of advanced sampling techniques (Shoemaker et al., 2022).

3.2 Accounting for non-equilibrium effects

Transport across a membrane is by definition a non-equilibrium process. Non-equilibrium approaches in molecular simulations introduce external forces or biases to perturb the system from its equilibrium state. Non-equilibrium methods enable the exploration of specific processes, transitions, or reactions that may not occur spontaneously in equilibrium simulations. The information obtained from these simulations is particularly valuable for understanding membrane-related phenomena, as they provide a level of detail and resolution that surpasses what is achievable through experimental techniques alone (Mollahosseini and Abdelrasoul, 2021). This computational approach aids in deciphering the intricacies of membrane structure, composition, and dynamics, offering insights that can inform and guide experimental studies. Moreover, the knowledge gained from classical equilibrium molecular dynamics simulations and non-equilibrium approaches plays a pivotal role in advancing the design of the next-generation of reverse osmosis (RO) membranes, fuel cell-energy production, and blood purification through hemodialysis. The challenge is to ensure that the simulated system represents reality.

Most typically, non-equilibrium driving forces are introduced into molecular dynamics simulations through net applied forces (per unit area) to all or some subset of solution-phase molecules in order to emulate a transmembrane pressure difference (Heiranian et al., 2022). This may take the form of a solid interface that acts as a piston (Shen et al., 2016; Shoemaker et al., 2022; Wang et al., 2023), a constant acceleration or force applied to all solvent-phase molecules

(Jiao et al., 2022), or a force applied to only a small region of solvent-phase molecules (Monet et al., 2023). The latter has the advantage of being generalizable to any external driving force, not just pressure gradients. It also promises steady-state simulations without the transient effects associated with rigid boundaries displacing a fixed amount of fluid. Further innovations for applied non-equilibrium gradients will be crucial moving forwards, particularly those that rigorously couple to macroscopic fluid transport theories or simulations.

3.3 Finite-size effects and multiscale modeling

As mentioned in Section 2.2, there is already uncertainty concerning the atomic-level structure of dense membranes. Further, we expect significant variations in membrane morphologies for the size of a typical membrane structure simulated in a particle-based simulation. While in a macroscopic membrane, numerous polymer and void configurations might be observed, a simulation only samples a small snapshot of this diversity. Liu et al. (2022) have recently explored the effect of random differences in membrane morphology on permeance of water. They found that membrane density and pore volume strongly correlate with equilibrium water mobility, and, in turn, water flux. Along with other recent studies highlighting the heterogeneity of simulated membrane structures (Vickers et al., 2022), this emphasizes a current need for examinations of finite-size effects on molecular simulation results. Recent work by Haji-Akbari and coworkers (Shoemaker et al., 2022) has highlighted the potential of elegant theoretical corrections but requires generalization to additional systems.

An additional challenge involving finite sizes relates to the fluctuations and mesoscale structural shifts of simulated membranes. In particular for polymeric membranes, the size of the simulated system sets the size of the polymer chains and effectively the length scale for voids and related fluctuations. Even with periodic boundary conditions, the membrane and its constituent polymer chains can be thought of as being somewhat analogous to a fluctuating surface with a fixed period of oscillation. Currently, it is not well-appreciated what size is necessary for these fluctuations to appear “bulk-like,” or reach the macroscopic limit. Beyond flexible polymeric membranes, general strategies to enable mesoscopic structural transitions of the membrane material are currently not available. While coarse-grained simulations, such as DPD, can capture these structural transitions, rigorous methods are largely unavailable for linking them back to atomistic resolutions at which diffusive transport is represented realistically. While purely geometric back mapping strategies have a long history (Peter and Kremer, 2009), they do not ensure rigorous sampling of the atomistic ensemble. Recent strategies based in machine learning show promise (Sidky et al., 2020; Monroe and Shen, 2022), but this remains an open research area that will likely grow in the future.

3.4 Membrane fouling

Unlike porous membranes, fouling on non-porous membranes does not involve steric blocking of pores, but instead the adsorption of foulants at a continuous interface. When the layer of adsorbents, or “cake” grows large enough, it can obstruct the passage of water or other solutes, hindering the separation process. Fouling at a variety of interfaces has been extensively investigated with a variety of models and resolutions and will not be discussed at length here. Despite extensive literature, strategies for reducing fouling are still limited by lack of molecular-level mechanistic knowledge and strategies for manipulating features at this same scale to tune solute-surface interactions. Foundational studies examining the influence of nanoscale heterogeneity, both geometrical (Xi et al., 2017) and chemical (Monroe et al., 2021), on solute adsorption are still limited to model systems and are just at the beginning of exploring realistic materials.

4 Challenges in membrane simulation and modeling in porous membranes

Porous membranes are classified into the following categories. Pressure driven processes include microfiltration (MF), ultrafiltration (UF), and nanofiltration (NF). Temperature driven processes include membrane distillation (MD) (Hitsov et al., 2015; Dong et al., 2021) while partial pressure-driven processes include blood oxygenation and dehydration. Other driving forces include osmotically-driven process such as pressure restarted osmosis (PRO) and forward osmosis (FO) and electrically driven process such as electrodialysis (ED) (Pismenskiy et al., 2006). Simulation and modeling of these porous membranes have many significant challenges e.g., using an appropriate adsorption isotherm for adsorptive membranes, description of fouling, etc.

4.1 Pore structure and size distribution

Many models have been developed for predicting pore geometry, however, accurately representing the complex and often irregular pore structures within membranes can be challenging. While modeling the membrane pores, considering transport phenomena is essential. Different types of diffusion can occur through porous membranes such as surface diffusion, molecular diffusion (Brownian motion), and Knudsen diffusion. As there are different types of diffusion mechanisms present in the system, it leads to complexity in the modeling process (Bukowski et al., 2021). Moreover, fully atomistic model of the amorphous mesoporous materials are not frequently employed due to the time-consuming nature of generating representative structures. Typically, simple models are favored for simulating pore structure. For instance, pore network models are a popular choice for modeling diffusion through mesoporous materials. This model assumes simple pore shapes such as long smooth cylinders, which are not physically realistic. Hence, tortuosity, τ, is generally used as an adjustment factor to correct for such deficiencies in the models (Bukowski et al., 2021).

Another challenge is to predict the connectivity of pore networks in mesoporous materials experimentally. This is often measured experimentally by mercury porosimetry measurements or nitrogen adsorption methods. Moreover, tomographic imaging techniques are unable to visualize amorphous porous materials at a resolution better than a few nanometers, which makes it difficult for accurate models to be created (Bukowski et al., 2021).

As mentioned in Section 2.1, simulation-derived porous structures are far from perfect reflections of reality. For instance, the timescales within DPD are significantly shorter than real-world cases, particularly in the case of the temperature induced phase separation (TIPS) process, which takes several seconds to complete the formation of a membrane pore geometry. Despite time and length scales of several microseconds and micrometers respectively, this is insufficient for realistically replicating the exact conditions of large-pore membranes. As membranes pores can vary in size, shape, continuity, and distribution, it remains difficult to create a precise model that accurately reflects real-world conditions.

4.2 Membrane fouling

Membrane fouling, where particles or solutes block the membrane pores or deposit irreversibly on the membrane surface, can significantly affect process efficiency. During membrane filtration, foulants have the strong potential to be attracted towards the membrane surface due to drag forces. Hence, a concentration gradient builds up near the interface of the membrane compared to the bulk solution. In addition, cake formation occurs when increasing amounts of foulants deposit on the membrane surface and pore blocking occurs when the foulants or particles smaller than the membrane pores are trapped and adsorbed onto the pores wall (Yang et al., 2022). There are many studies which focus on modeling and simulation techniques, such as computational fluid dynamics (CFD) (Yan et al., 2016), Monte Carlo simulation (Chen et al., 2005) and artificial neutral networks (ANN) (Corbatón-Báguena et al., 2016), for predicting fouling behavior. However, there are challenges due to the diverse nature of foulants, such as physical structure, conformation, chemistry, functionality, and charge, which is a very important concern while modeling fouling behavior. Another concern is model validation. For example, ANN can play a crucial role in selecting the optimum operating conditions and maximizing performance; however, this involves trial-and-error processes to determine the best architecture. It is important to direct attention to this because such procedures may not consistently provide reasonable results and extrapolations (Jawad et al., 2021).

4.3 Transport phenomena

Modeling the transport of solutes through membranes involves intricate phenomena such as diffusion, convection, and adsorption. There are successful models reported in literature for diffusion (Wijmans and Baker, 1995), convection (Boon et al., 2011), and adsorption (Weber et al., 1991). Nevertheless, acquiring these processes precisely in simulations requires sophisticated models. In addition, accurately modeling the interactions of the fluid flow and solute transport can be challenging.

4.4 Multiscale modeling

Membrane separation processes occur at multiple scales, from the molecular level to the macroscopic system level. Recent multiscale modeling work by Cooper et al. (2023) illustrates the necessity of resolving details across various length scales. The authors first use self-consistent field theory to generate triblock copolymer membrane structures, then parametrize a kinetic Monte Carlo model for estimating water diffusivities based on DPD simulations in select, simple geometries. By comparing to their previous studies utilizing only field theory (Howard et al., 2020) and DPD, (Aryal et al., 2020), respectively, they find that including information on the conformations of hydrophilic chains extending into the pores changes the relationship between diffusivity and pore geometric features. This study highlights how ignoring physics at a specific scale can drastically change conclusions. Recent techniques for switching between field theories and coarse-grained molecular dynamics in a single simulation are promising methods for more efficiently accessing longer length scales while explicitly retaining information on chain conformations (Lequieu, 2023).

Another exemplary study of multiscale modeling comes from investigations of membrane fouling. In early studies of fouling, non-covalent interactions between proteins and the membrane surface were not considered. Curcio et al. (2018) improved the multiscale modeling of fouling in ultrafiltration membranes with consideration of the interaction between bovine serum albumin and a membrane surface. Still, integrating these scales into a comprehensive model can be a challenging task.

5 Outlook

The modeling of membrane processes clearly involves a myriad of physical phenomena occurring across a broad range of time and length scales. No single model can capture all relevant physics within a membrane, indicating a grand challenge in rigorously linking models within multiscale frameworks (Borg et al., 2018; Curcio et al., 2018; Nikfar et al., 2020), where, ideally, models at different scales interact. High-resolution simulations can be computationally intensive, requiring substantial computational resources. This can limit the feasibility of simulating large-scale industrial processes. It is often difficult to obtain experimental data for validation, especially for new membrane materials and configurations. Accurate validation is crucial for ensuring the reliability of models. Real-time experimental monitoring across all relevant length and time scales remains difficult, making detailed comparisons with experimental results another grand challenge. There are opportunities to more closely link modeling results to experiments through direct calculation of experimental observables. For instance, it is best practice in atomistic simulations to calculate scattering patterns (of X-rays, neutrons, etc.) to compare to experimental data rather than comparing to the interpretation of this raw data.

Author contributions

JM: Writing–original draft, Writing–review and editing. CT: Writing–original draft, Writing–review and editing. SRW: Conceptualization, Data curation, Formal Analysis, Funding acquisition, Investigation, Methodology, Project administration,

Resources, Software, Supervision, Validation, Visualization, Writing–original draft, Writing–review and editing.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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