# A new approach for predicting gas separation performances of MOF membranes

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A B S T R A C T

Metal organic framework (MOF) membranes are widely used for gas separations. Permeability and selectivity of MOF membranes can be accurately calculated using 'the detailed method' which computes transport diffusivities of gases in MOFs' pores. However, this method is computationally demanding therefore not suitable to screen large numbers of MOFs. Another approach is to use 'the approximate method' which uses self-diffusivities of gases to predict gas permeabilities of MOF membranes. The approximate method requires fewer amounts of time compared to the detailed method but significantly underestimates gas permeabilities since mixture correlation effects are ignored in this method. In this work, we first used computationally demanding detailed method to calculate permeabilities and selectivities of 8 different MOF membranes for Xe/Kr and Xe/Ar separations. We then compared these results with the predictions of the approximate method. After observing significant underestimation of the gas permeabilities by the approximate method, we proposed a new computational method to accurately predict gas separation properties of MOF membranes. This new method requires the same computational time and resources with the approximate method but makes much more accurate predictions for gas permeabilities. The new method that we proposed in this work will be very useful for large-scale screening of MOFs to identify the most promising membrane materials prior to extensive computational calculations and experimental efforts.

## 1. Introduction

Energy efficient gas separation methods such as membrane-based gas separations have gained significant attention in the recent years. Research on finding new membrane materials to achieve high-performance gas separations has increased dramatically [1]. Metal organic frameworks (MOFs) are considered as a new class of nanoporous membrane materials that are composed of metal ions connected with organic ligands [2]. MOFs have well-defined pore structures [3], large surface areas (500–6500 $m^2$/g) [4], high porosities, good thermal and mechanical stabilities which make them strong candidates for gas separation processes [5,6]. MOFs have been widely used for adsorption of $CO_2$, $CH_4$, $H_2$, and $N_2$ in addition to the separation of several gas mixtures including $CO_2/CH_4$, $CH_4/H_2$, $CO_2/N_2$, and $CO_2/H_2$ [7–11]. Separation of noble gas mixtures using membranes has recently attracted researchers' attention due to the high cost of cryogenic distillation of air to produce pure noble gases [12,13]. MOFs can be highly promising membrane materials for separation of noble gases. However, it is not practical to examine the potential of all MOF membranes in this area using purely experimental techniques due to the very large number of available MOFs in the literature. Screening MOFs using computational methods is very useful to identify the MOF membranes that would achieve high gas permeability and high selectivity for noble gas separations. Development of efficient and accurate computational screening methods plays an important role in selecting promising MOF membranes to direct experimental efforts, time, and resources to these promising materials.

Predicting gas permeability and selectivity of new membrane materials is computationally demanding. The most comprehensive method to model crystalline nanoporous membranes was suggested by Sanborn and Snurr [14,15]. This method requires computing the matrix of Onsager coefficients [16–18], which relates gas fluxes with the driving forces in irreversible processes, at a wide range of loadings in the membrane material using equilibrium molecular dynamics (EMD) simulations. This type of computation requires significant amount of time. Once the EMD data and gas adsorption data, obtained from grand canonical Monte Carlo (GCMC) simulations, are collected and fitted to continuous functions, Sanborn and Snurr's method can be applied with confidence under all possible operating conditions of the membrane.

Their method has been used in the literature to predict flux of $CH_4$/$CF_4$ mixture and diffusivities of $CF_4$ and n-alkanes in faujasite zeolite membranes [14,15]. Throughout the remainder of this paper, we will refer to this method as 'detailed method' and results of the detailed method will be considered as the 'correct' answers for gas permeabilities of membranes.

A simpler version of the detailed method suggested by Keskin [19] is based on calculating transport diffusivities of gases from the EMD simulations using the Onsager coefficients at the specific loadings in the membrane rather than at a wide range of loadings. In this method, the permeate side of the membrane is assumed to be under vacuum and this assumption simplifies the problem relative to the more general situation considered by the detailed method. This approach still requires significant computational resources since computing the Onsager coefficients from EMD simulations is very demanding. In order to eliminate this computationally demanding step, Krishna and van Baten [20] developed an 'approximate method' which requires computing self-diffusivities of gases instead of the Onsager coefficients. Gas permeabilities and selectivities of several MOFs for equimolar $CO_2$/$CH_4$, $CH_4$/$H_2$, $CO_2$/$N_2$, and $CO_2$/$H_2$ mixtures were computed using the approximate method in the literature [8,21–23]. This method is valid for equimolar gas mixtures and the loadings used for calculation of the self-diffusivities do not need to necessarily match with the adsorbed loadings of the gases at the membrane surface. Keskin and Sholl [24] modified the approximate method for arbitrary bulk gas compositions and evaluated self-diffusivities of gas mixtures at their corresponding adsorbed compositions calculated from the GCMC simulations. They applied modified approximate method to several MOF membranes including IRMOF-1, IRMOF-8, IRMOF-9, IRMOF-10, IRMOF-14, CuBTC, Zn(bdc)(ted)$_{0.5}$, and COF-102 for $CH_4$/$H_2$, $CO_2$/$H_2$, and $CO_2$/$CH_4$ separations. Their results showed that approximate method is accurate for gas/MOF systems if the mixture correlation effects are not important. Otherwise, significant deviations from the detailed method can be observed for some gas pairs/MOFs [24]. We recently used the approximate method to evaluate the noble gas separation performances of several MOFs and predicted Xe, Kr, and Ar permeabilities, as well as Xe selectivities of MOF membranes for Xe/Kr and Xe/Ar mixtures under various operating conditions [25]. In order to evaluate the accuracy of the approximate method to predict the potential of MOF membranes for noble gas separations, it is necessary to compare predictions of the approximate method with the results of the detailed method. In other words, the detailed method demonstrates the 'real' gas separation performance of the MOF membranes, whereas the approximate method makes predictions on the selectivity and permeability of the MOF membranes by neglecting correlation effects between gas species although these effects can be important for some MOFs.

In this work, we first used computationally demanding detailed method to calculate 'real' gas permeability and selectivity of 8 MOF membranes for Xe/Kr and Xe/Ar separations. We then compared these results with the predictions of the approximate method. After observing the cases where approximate method fails to make accurate predictions for gas permeability of MOF membranes, we proposed a new method alternative to the approximate method for fast and accurate screening of MOF membranes. This new method requires the same computational time and resources with the approximate method, but makes much more accurate predictions. We discussed the cases where the detailed, approximate, and new methods agree and deviate from each other. The new method that we proposed in this work will be very useful for large-scale computational screening of MOFs to efficiently identify the most promising membrane materials prior to extensive experimental efforts.

## 2. Computational methods

As an extension of our previous computational studies on predicting noble gas separation performance of MOF membranes [25,26], we studied the same set of MOFs which are IRMOF-1 (isoreticular MOF), ZIF-2 (zeolite imidazolate framework), ZIF-3, ZIF-10, Zn(bdc)(ted)$_{0.5}$, CPO-Ni (coordination polymers of Oslo), CPO-Co, and CuBTC. Detailed information about the structural properties of these MOFs can be found in our early work [26]. Molecular simulations were performed to compute adsorption and diffusion of noble gas mixtures, Xe/Kr and Xe/Ar, in these MOFs. This information was then used to predict gas permeability and selectivity of MOF membranes by three different modeling approaches: detailed method, approximate method, and new method.

### 2.1. Molecular simulations

Experimental XRD data was used to determine the atomic positions of MOFs [26]. We carried out all molecular simulations assuming rigid frameworks because it was previously shown that molecular simulations using flexible and rigid MOFs give similar results and agree with the experimental noble gas adsorption data of MOFs [25]. Grand Canonical Monte Carlo (GCMC) [27] and Equilibrium Molecular Dynamics (EMD) [28,29] simulations were used to calculate adsorption and diffusion of Xe/Kr and Xe/Ar mixtures in MOFs, respectively. All simulations were performed at room temperature up to 25 bar. After cryogenic distillation of air, a mixture of 80% Kr and 20% Xe is obtained therefore, compositions of the gas mixtures were set as Xe/Kr:20/80 and Xe/Ar:20/80 [30].

The Dreiding [31] force field was used in GCMC and EMD simulations to describe the MOF atoms since simulations performed with this force field agreed with the experimental measurements of noble gas adsorption in MOFs [26]. Universal Force Field (UFF) [32] parameters were used for the metal atoms of MOFs since they are not available from the Dreiding force field. Spherical Lennard-Jones (LJ) 12–6 potentials were used to model Xe ($\varepsilon/k_B = 221$ K, $\sigma = 4.01$ Å), Kr ($\varepsilon/k_B = 166.4$ K, $\sigma = 3.63$ Å) and Ar ($\varepsilon/k_B = 119.8$ K, $\sigma = 3.4$ Å) [33,34]. The Lorentz-Berthelot mixing rules were employed to calculate gas-MOF and gas-gas LJ cross interaction parameters. The intermolecular potentials were truncated at 13 Å and the simulation box was increased up to $4 \times 4 \times 3$ to ensure that it contains enough gas atoms at the lowest loadings to increase the statistical accuracy of the simulations. Periodic boundary conditions were applied in all simulations [27,35].

In GCMC simulations, the temperature and fugacity of the adsorbing gases were specified and the number of adsorbed molecules was calculated at equilibrium. At the lowest fugacity of each system, simulations were started from an empty MOF matrix. Each subsequent simulation at higher fugacity was started from the final configuration of the previous run. Simulations consisted of a total of $3 \times 10^7$ trial configurations with the last half of the configurations used for data collection. Mixture GCMC simulations were carried from 0.1 bar to 25 bar. The pressure was increased by 0.1 from 0.1 bar to 1 bar, by 1 from 1 bar to 10 bar, and by 5 from 10 bar to 25 bar for every Xe composition (from 0.1 to 0.9 at 9 compositions) in the Xe/Kr and Xe/Ar mixtures. All these calculated data was fitted to continuous functions for each component in Xe(1)/Kr(2) and Xe(1)/Ar(2) mixtures as shown below:

$$c_1 = \frac{h_1 f_1}{h_2 f_1 + h_3 f_2 + h_4} + \frac{h_5 f_1}{h_6 f_1 + h_7 f_2 + h_8}$$
$$c_2 = \frac{s_1 f_2}{s_2 f_1 + s_3 f_2 + s_4} + \frac{s_5 f_2}{s_6 f_1 + s_7 f_2 + s_8}$$

$$(1)$$

Here, $c_i$ is the adsorbed loading (molecules/unit cell) calculated