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An Atomistic Perspective on Diffusion and Permeation of Hydrogen and Isotopes through Engineered Nano-Porous Silica Membrane using Molecular Dynamics Simulations

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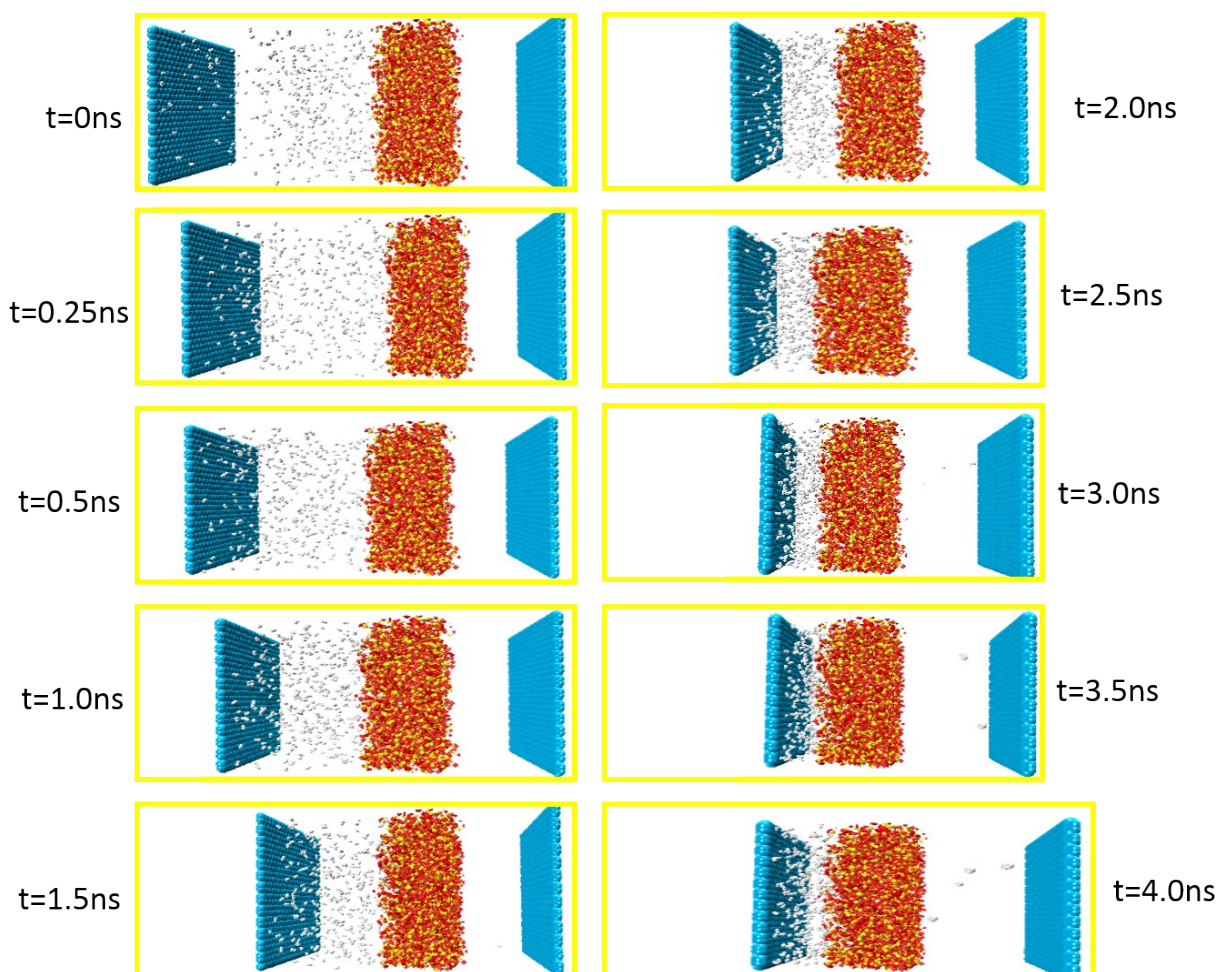


Figure S1. Time evolution images for H₂ permeation through silica density model of 2.0 g/cm³(permeating molecules were maintained at T=300K, pressure of P atm was applied on feed piston in positive x direction and 1 atm on permeate piston in negative x direction).

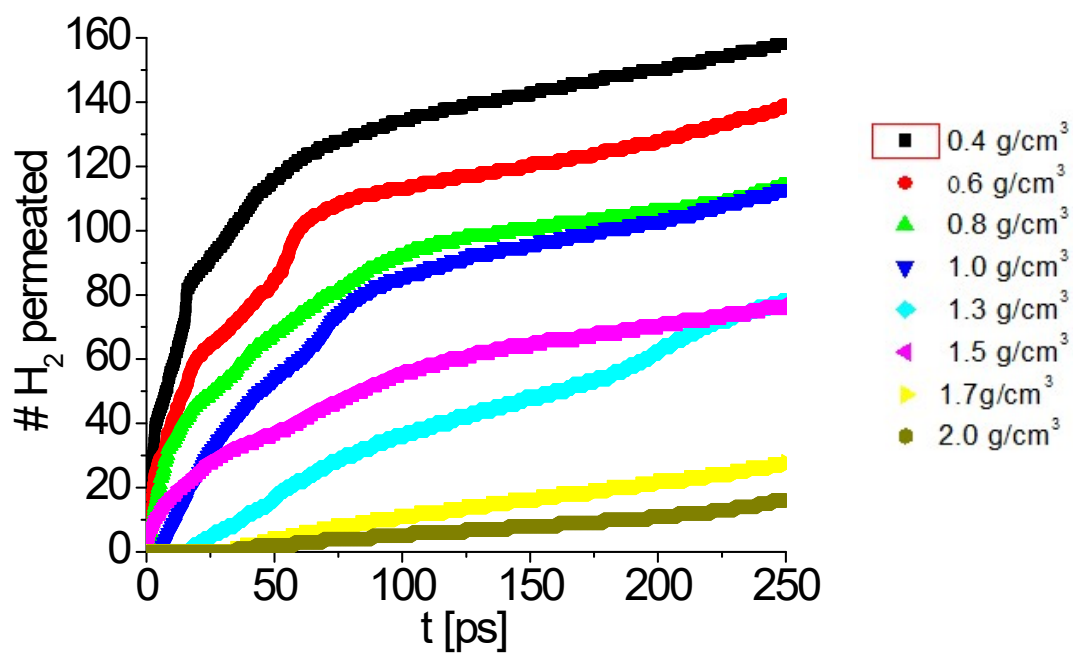


Figure S2. Time evolution of permeation profiles for H₂ gas as an effect of membrane density model (respective to section 3.2).

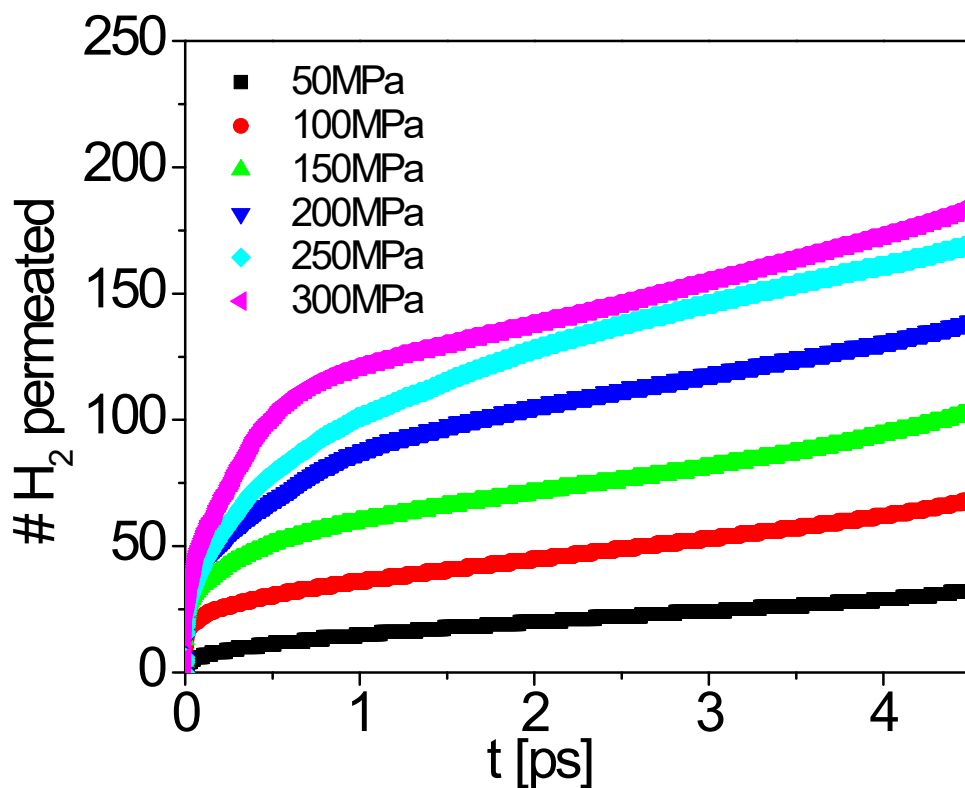


Figure S3. Time evolution of permeation profiles for H₂ gas as an effect of pressure for silica model 2.0 g/cm³ (respective to section 3.3).

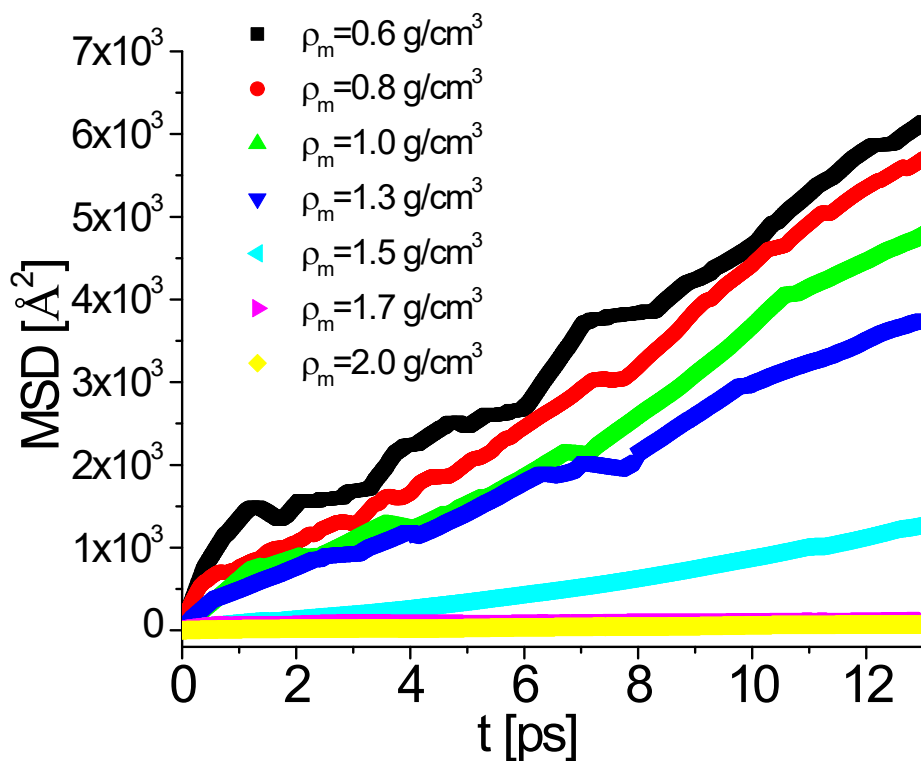


Figure S4. MSD profiles for H₂ permeation through silica membrane of different density model 0.4 g/cm³ to 2.0 g/cm³.

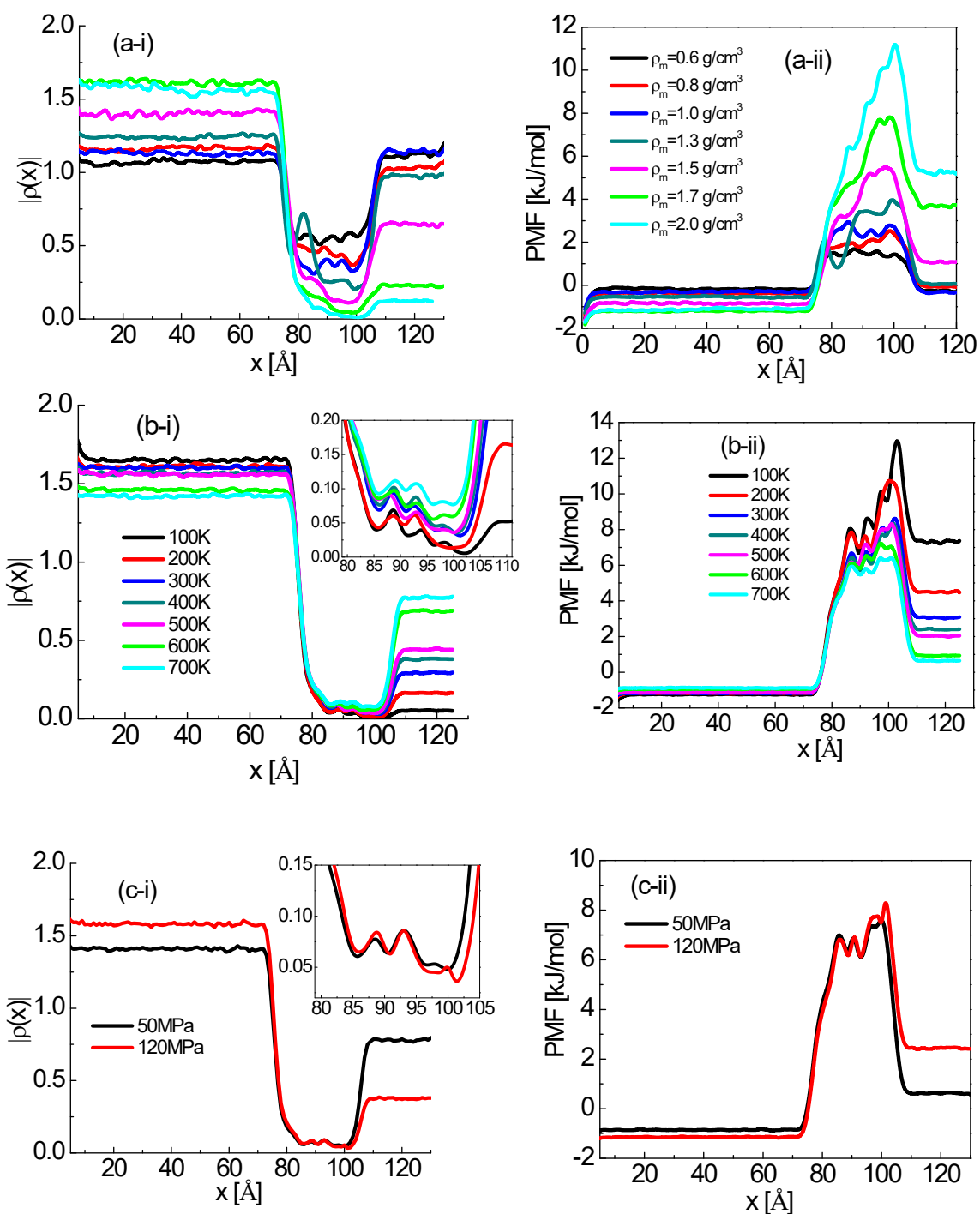


Figure S5. Population distribution (left figures a, b, c -i)) and PMF profiles (right figures a, b, c, -ii) for H_2 as an effect of (a) membrane density (at $T=300K$, $P=1atm$), (b) temperature (for membrane density model $2.0 g/cm^3$) and (c) pressure gradient (for membrane density model $2.0 g/cm^3$ at $T=300K$).

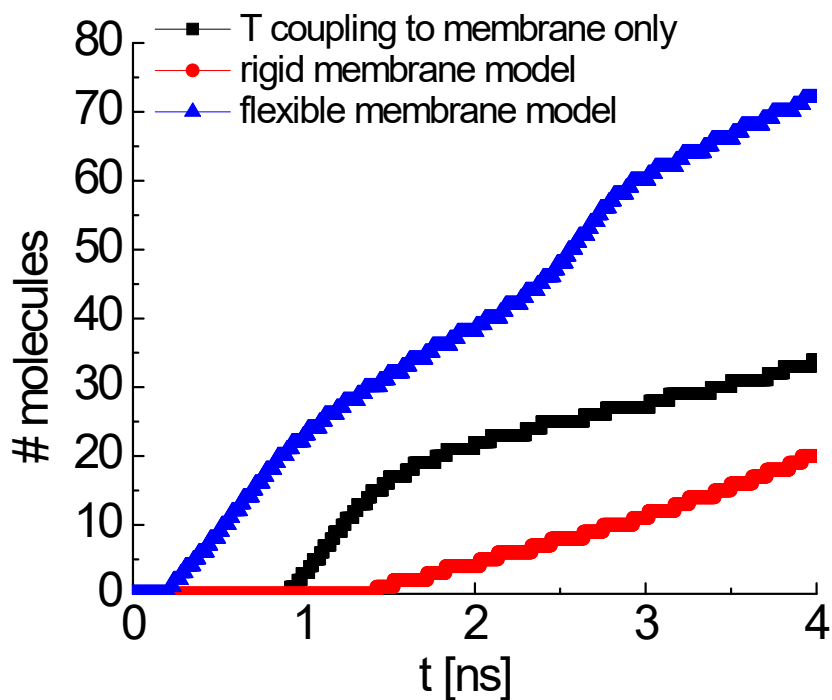


Figure S6. Permeation profiles for H₂ permeation through silica membrane of density model 1.5 g/cm³ for (black line) thermostat coupling applied to membrane atoms only, (red line) rigid membrane model with thermostat coupling to membrane + permeating gas, and (blue line) flexible model with thermostat coupling to membrane + permeating gas.

Table S1. Comparison of Permeability with the available literature.

Reference	Permeability [moles/m ² -sec-Pa] @ 300K temperature
Shelby, 1977(Shelby, 1977a)	1.04×10^{-11}
Lee et al., 1966(Lee, 1963)	2.7×10^{-9}
Perkins et al., 1971(Perkins and Begeal, 1971)	3.7×10^{-12}
Dong et al, 2008(Dong et al., 2008)	3.5×10^{-7}
Yoshioka et al., 2008(Yoshioka et al., 2008)	10^{-7}
Present Study	0.32×10^{-7}

Text S1. Mechanism for gas transport through membranes

There are several mechanism for gas transport through membranes, which depend on the mean free path of permeating gas molecules and the pore size of membrane. In general, the gas transport in membranes can occur with Poiseuille flow, Knudsen diffusion, surface diffusion, capillary condensation, molecular sieving and solution-diffusion. Sometimes, depending on the conditions and the properties of the permeating molecules, two or more of these processes can occur simultaneously.

A brief overview of possible permeation mechanism is as followed-

1. Viscous flow:

If pore diameter is larger enough than mean free path of a permeating molecule, the permeating molecule frequently has a collision with other permeating molecules than membrane pore wall. This situation is understood as permeation by so-called viscous flow. In this transport mode, separation of molecular mixtures by membrane permeation is impossible. In this case, the permeability is obtained by relation -

$$P = \frac{\varepsilon \eta r^2}{8 \mu R T} p_{av} \quad (S1)$$

Where ε is the porosity, μ is the viscosity, η is the shape factor (assumed to be equal to the reciprocal tortuosity of the medium), r is the pore radius, and p_{av} is the mean pressure.

2. Knudsen diffusion:

Knudsen diffusion occurs when the pore size is larger than the molecule size but smaller than the mean free path λ of the gas molecule. In this regime, collisions occur primarily between gas molecules and the pore wall, rather than between the gas molecules themselves. The collisions are elastic, so there is no tendency for the molecules to interact with the surface, although the direction of rebound is random.

Gas transport by Knudsen diffusion occurs in the gaseous state without involvement of adsorption because the interaction between diffusing molecules and pore wall is negligibly small. In this case, the permeability is estimated using relation -

$$P = \frac{2\varepsilon\eta r v}{3RT} \quad (S2)$$

vis the molecular velocity given by: $v = \sqrt{\frac{8RT}{\pi M}}$

In case of Knudsen diffusion - separation factor α of typical gas mixture is derived from the square root of ratio of molecular weight of permeating gases.

3. Surface diffusion:

Surface diffusion occurs when gas molecules cannot escape from the surface potential field because the interaction between the inner surface and gas molecules becomes strong compared to their kinetic energy. Surface diffusion occurs when at least one component in the feed adsorbs preferentially on the membrane surface. The transport of adsorbing gas through membrane pores is a sequence of four stages

1. diffusion of adsorbing molecules through the feed bulk to the vicinity of the membrane surface;
2. reversible sorption of the molecules to the membrane surface;
3. transport of the adsorbed molecules through the membrane pores by surface diffusion;
4. desorption of the molecules from the membrane surface to the permeate bulk.

In case of surface diffusion, the permeability is calculated from relation -

$$P = P_o \exp\left(\frac{-\Delta H_a - \Delta E_{sd}}{RT}\right) \quad (S3)$$

Where $(-\Delta H_a - \Delta E_{sd})$ is the energy barrier for diffusing molecules to permeate through membrane (Oyamaetalii, Journal of the Japan petroleum Institute, 54 (5), 298-309 (2011))

4. Capillary Condensation:

Capillary condensation is the process by which multilayer adsorption from the vapor into a porous medium proceeds to the point at which pore spaces become filled with condensed liquid from the vapor.

5. Molecular Sieving:

Molecular sieving separates gas molecules using membrane pores that have roughly same size as the molecules themselves. Typical pore sizes for molecular sieving are < 2 nm.

For the case of molecular diffusion, ideal gas approximation of bulk gas phase outside of a membrane is adopted and molecular diffusion in a pore occurs under chemical potential gradient as a driving force for permeation.

Permeability, P can be obtained by

$$P = \frac{\int_{p_1}^{p_2} \frac{D'}{RT} dp}{p_1 - p_2} = \frac{D'}{RT} \quad (S4)$$

D' is thermodynamic corrected diffusion coefficient that satisfies the “Darken equation.

Transport mechanism	Pore diameter (nm)
Knudsen diffusion	2-50
Surface diffusion	1-3
Capillary condensation	2-10
Molecular sieving	0-2
Solution diffusion	0

Depending on pore size, a mixture of mechanism can be followed during permeation.

Considering the small pore size of simulated membranes (for density model of 1.5 g/cm³ and higher) which is roughly same as kinetic diameter of the permeating molecules, the molecular sieving process for permeation of H₂ and isotopes in these membranes can be expected. Also, the observed permeability ratio was different from Knudsen selectivity parameter, which confirm that Knudsen like permeation is not the dominant mechanism of transport for considered cases. However, it might be possible that combination of Knudsen and molecular diffusion happens while the transport of H₂ and isotopes through silica membrane (density model of 1.5 g/cm³ and higher)

In case of molecular sieving process, the permeability of diffusing gases are observed to be pressure independent (*Chang et al. Chem. Engg. Sci. (2006) 61, 3974 – 3985*). However, these studies are performed only at low pressure range (1-10MPa). To be noted, the permeation mechanism may change while implication of large pressure gradient as applied in present article (50MPa-350MPa). Implication of such a streamlined high pressure, may alter the mean free path of permeating molecules. In the present study, linear increase in permeability and diffusivity with pressure indicates the liquid like permeation of hydrogen and isotopes in high pressure regime. The similar linear increasing flux profiles with increasing pressure for H₂ permeation through vitreous silica (of similar density model) has also been reported by experimental studies of Rundgren et al. (*J. Appl. Phys., 100 (2006) 104902-5*). Velioglu and Keskin in their studies about H₂/CH₄ mixture permeation through MOF membranes, also reported the linear increase in H₂ flux with increasing pressure (*J. Mater. Chem. A 7 (2019) 2301-2314*)

Text S2. Error bar

Error bars were represented by standard deviation, which indicates the dispersion from the average value. The standard deviation for average pore size was estimated from distribution profile, using the following relation¹–

$$\sigma = \sqrt{\frac{\sum_{i=1}^n (x_i - x_{avg})^2}{n-1}} \quad (S5)$$

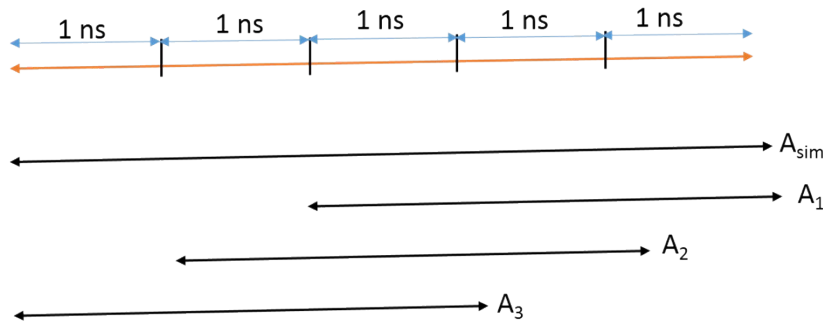
Where

x_{avg} = average pore size

x_i = value of i^{th} pore size

n = number of sample points

However, for permeation and diffusivity, the standard deviation was estimated using following methodology –



A_{sim} = average estimated from complete simulation trajectory of 5ns

$A_{i(i=1,2,3)}$ = average estimated from simulation trajectory of 3ns (as shown above)

$$\sigma = \sqrt{\frac{\sum_{i=1}^3 (A_i - \langle A \rangle_{sim})^2}{3}}$$

1. Gregory V. Hartland, Statistical Analysis of Physical Chemistry Data: Errors Are Not Mistakes, J. Phys. Chem. C **2020**, 124, 11, 5889–5892.