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# Thermophysical properties of H<sub>2</sub>/gas/brine system under subsurface storage conditions: molecular simulations and thermodynamic modeling

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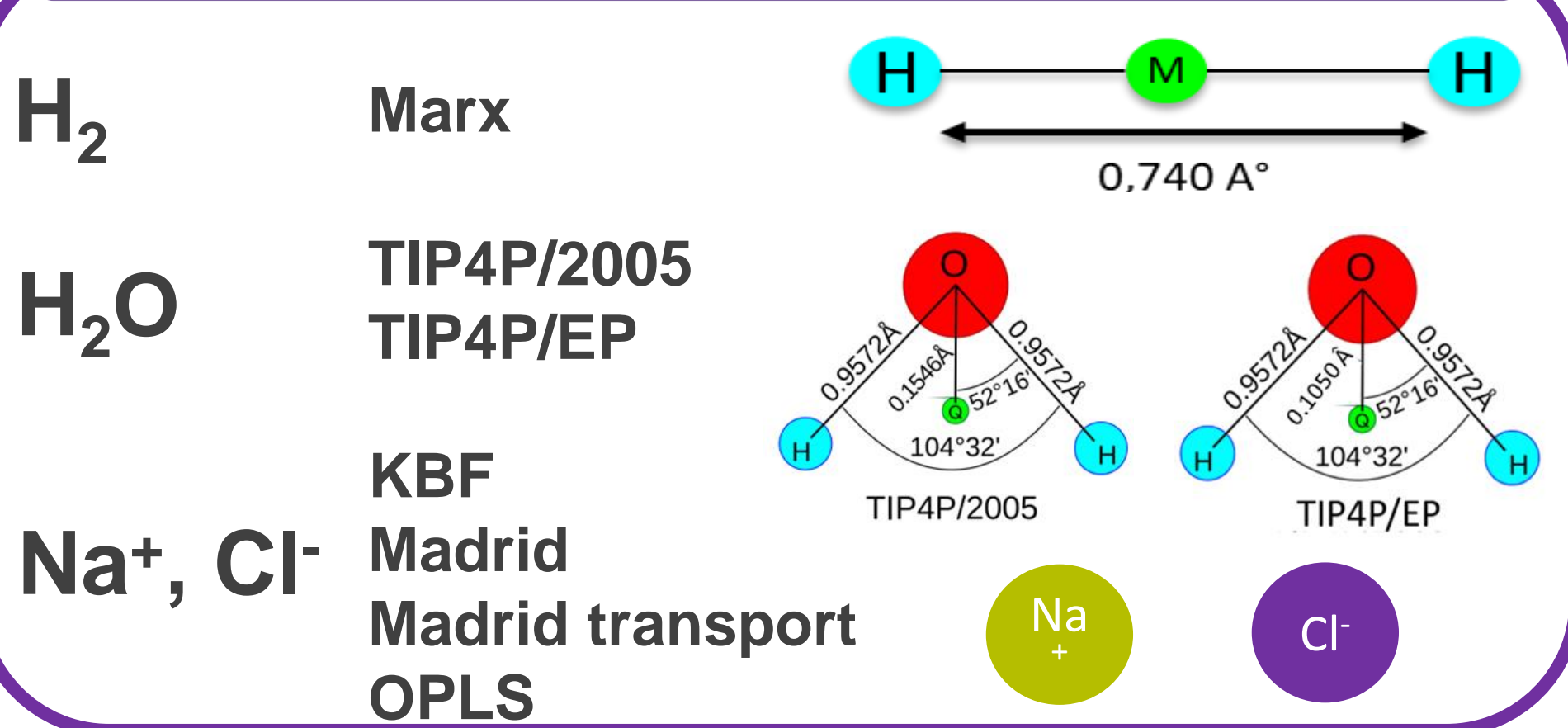
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## Context & Motivations

The storage of hydrogen in deep saline aquifers offer a great capacity and geographical availability for large-scale renewable energy storage. However, the contact between gas, brine, and rock can affect the mobility and stability of hydrogen and is not sufficiently documented at the time being. In the first part of this work, by using Monte Carlo simulation, new equilibrium data for H<sub>2</sub>/brine systems are generated. Then, by using non-equilibrium molecular dynamics, new data on self-diffusivity for H<sub>2</sub>/NaCl brine systems are predicted for a wide range of conditions relevant to underground hydrogen storage in porous media. Finally, the co-solubility of gases in the ternary systems CO<sub>2</sub>-CH<sub>4</sub>-H<sub>2</sub>O and CO<sub>2</sub>-H<sub>2</sub>-H<sub>2</sub>O was modeled. An example of the application of this model is given by the prediction of optimal conditions (CO<sub>2</sub>/H<sub>2</sub> ratio) at equilibrium to ensure the stoichiometry of the in-situ methanation reaction.

### Selected Force Fields



### Monte Carlo Simulation details

Sampling method: Continuous Fractional Component Monte Carlo (CFCMC)/NPT ensemble

Henry constant from molecular simulation

$$H_i = \rho k_B T \exp(\mu_i^{excess} / k_B T)$$

Molar composition

$$x_i(P, T, m_s) = \frac{\gamma_i P \varphi_i}{H_i \gamma_i \exp\left(\frac{\vartheta_i^\infty P - p_{sat,solvent}}{RT}\right)}$$

### Dynamics Simulation details

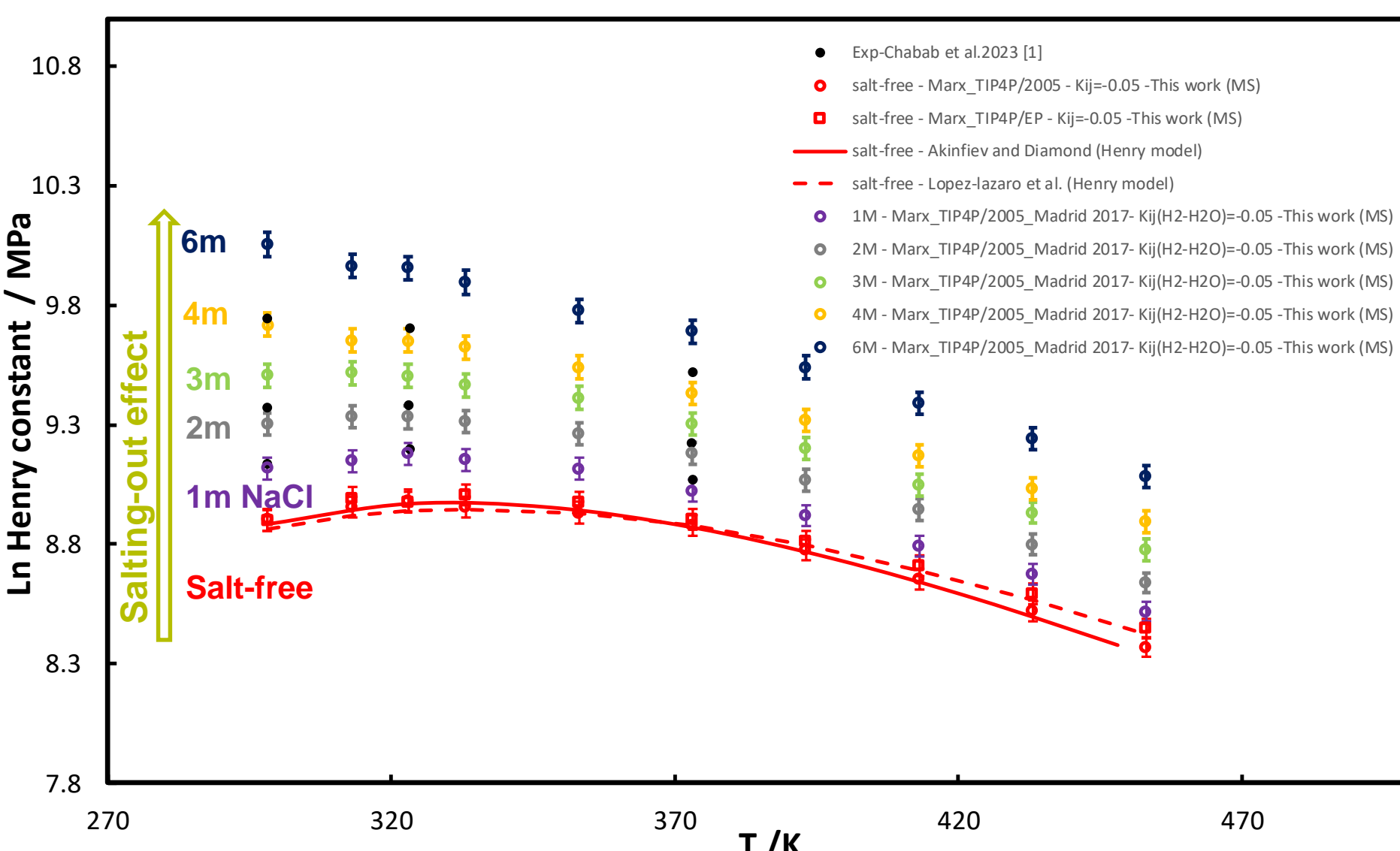
Method: External field non-equilibrium molecular dynamics (EF-NEMD).

Estimation of the Self-diffusion coefficient (SDC)

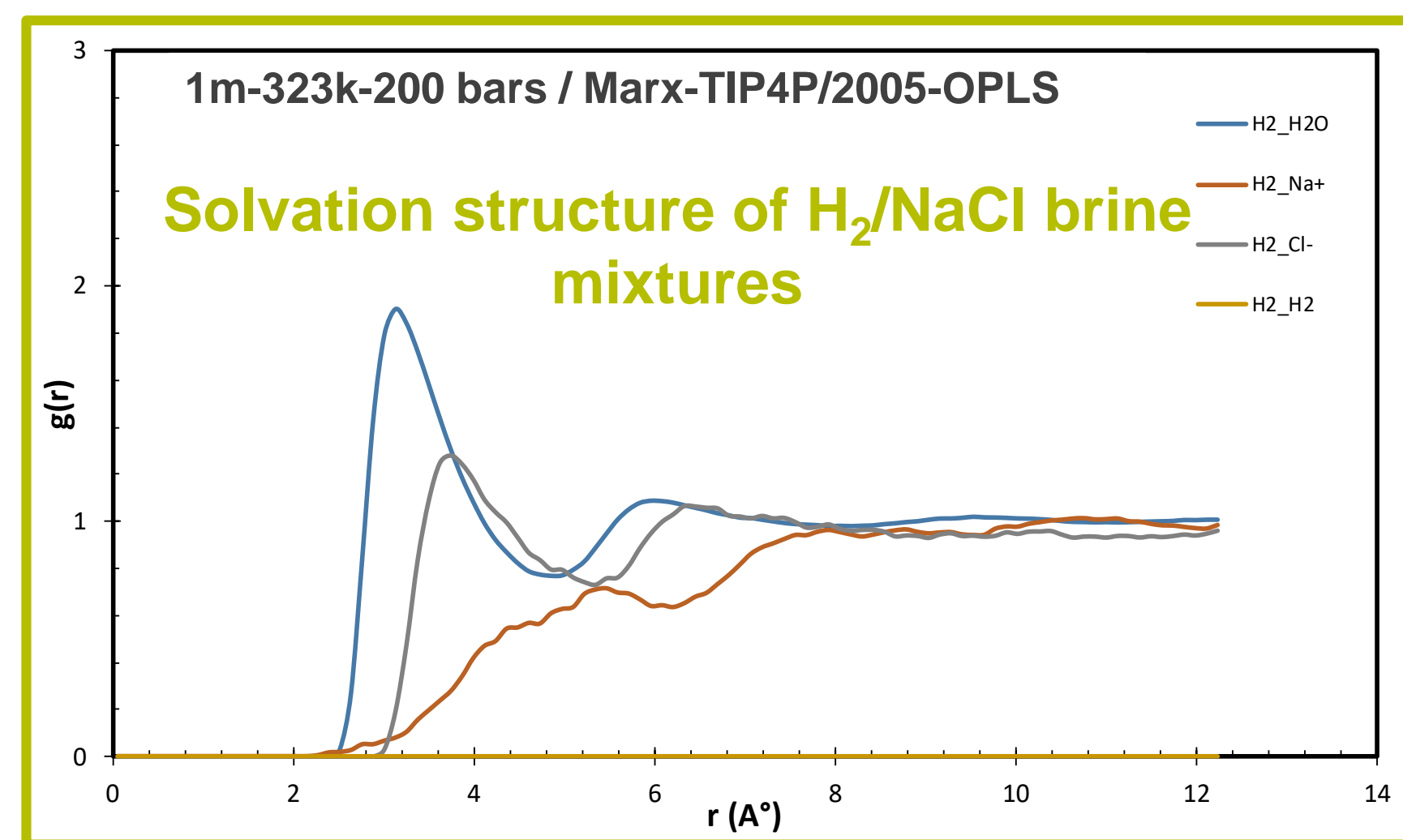
$$D_{Gas}^{NEMD} = \frac{\mu_{Gas} RT}{F_{Gas}^{Ext}}$$

## Monte Carlo Simulation

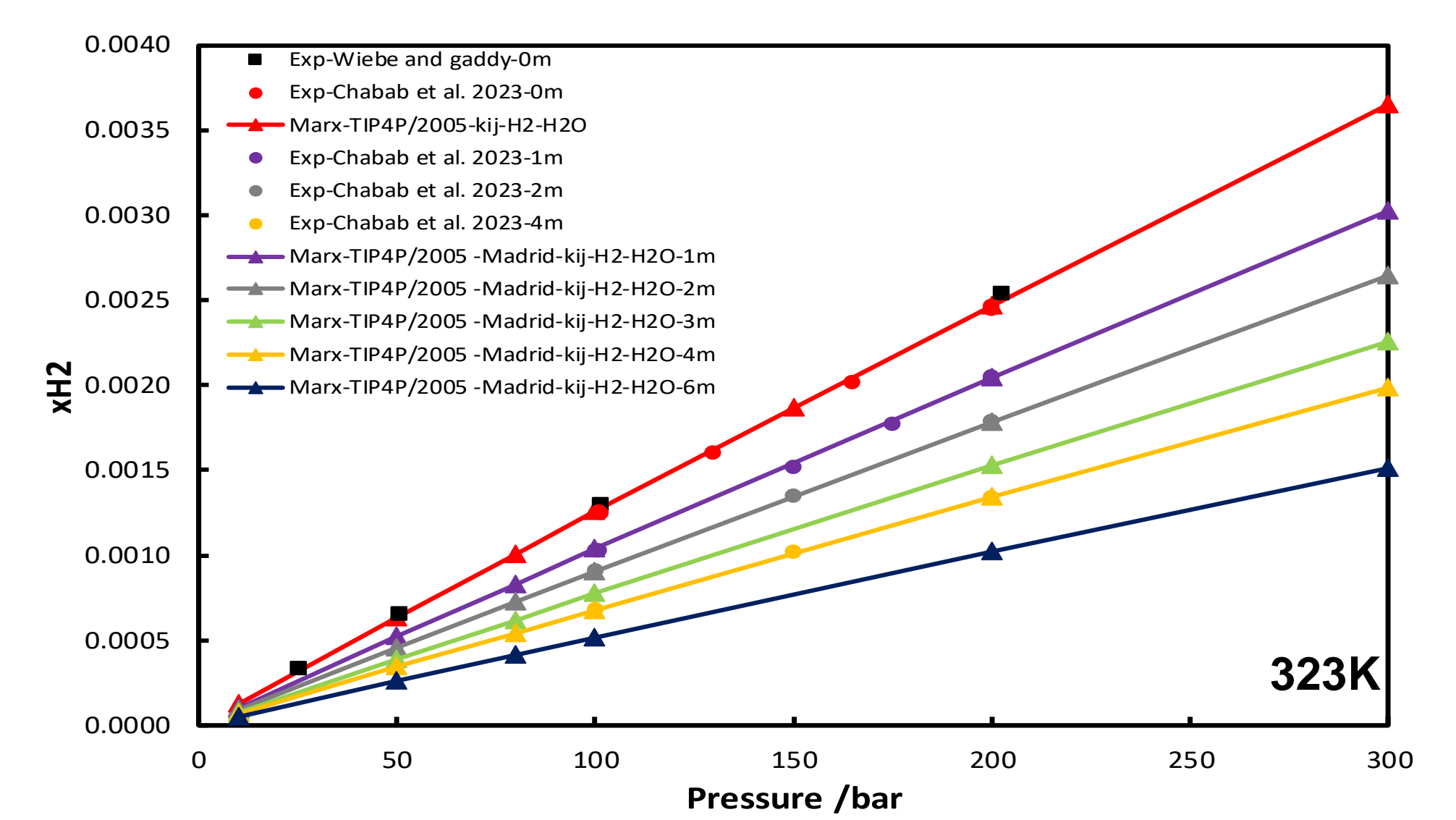
### Henry constant of H<sub>2</sub> in NaCl brine



### Radial distribution function



### Molar composition of H<sub>2</sub> in NaCl brine



- ✓ Excellent representation of H<sub>2</sub> solubility in NaCl brine using three different models (Marx\_TIP4P/2005\_OPLS – Marx\_TIP4P/EP\_KBF-Marx\_TIP4P/2005\_Madrid).
- ✓ The radial distribution function (RDF) is used to evaluate the solvation structure of the H<sub>2</sub>/brine mixtures which is shown to be dominated by the H<sub>2</sub>-H<sub>2</sub>O and H<sub>2</sub>-Cl interactions. A constant BIP on energy for H<sub>2</sub>-H<sub>2</sub>O and on volume for H<sub>2</sub>-Cl are used to improve the quantification of the H<sub>2</sub> solubility in brine.

## Non-Equilibrium molecular dynamics

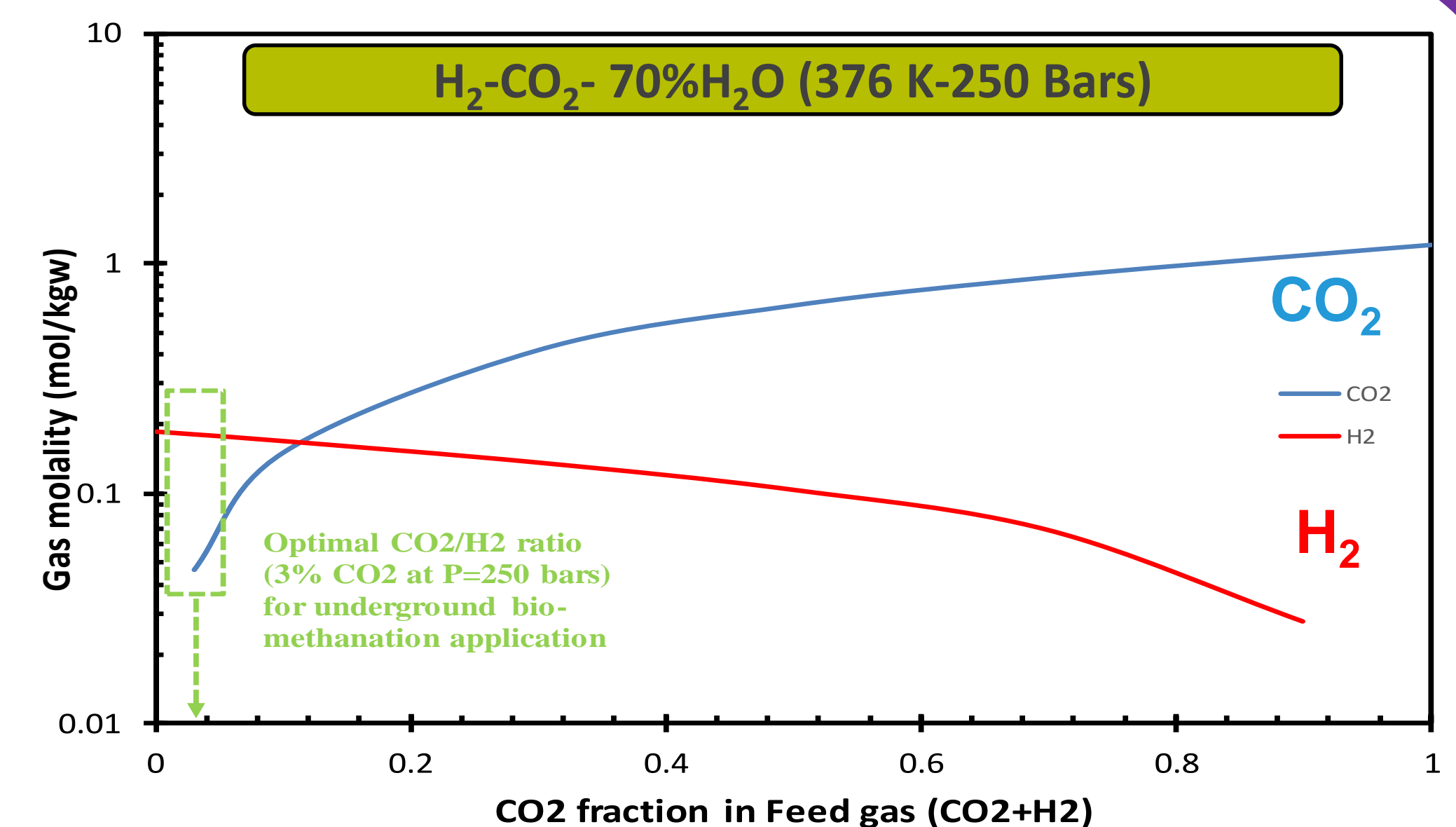
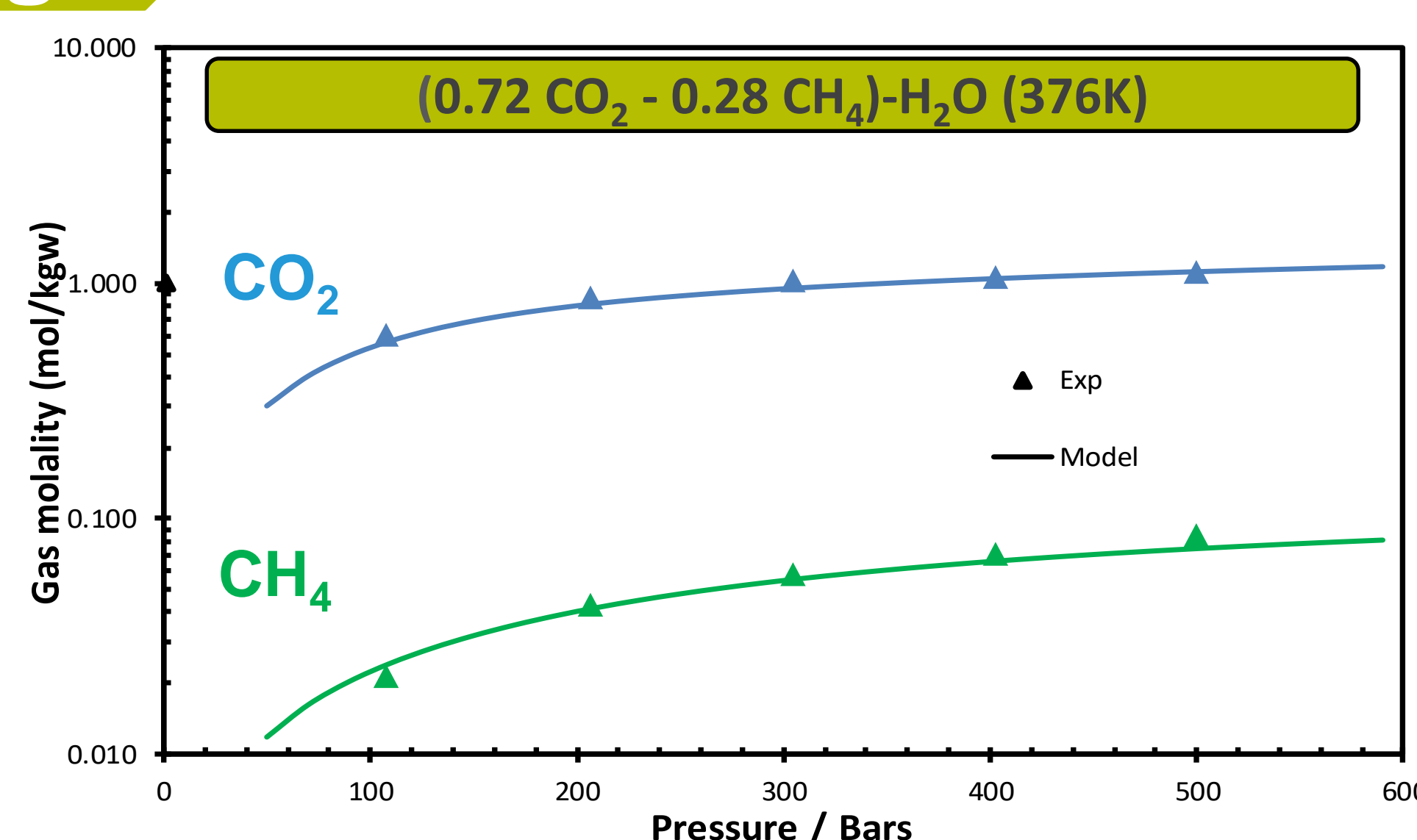
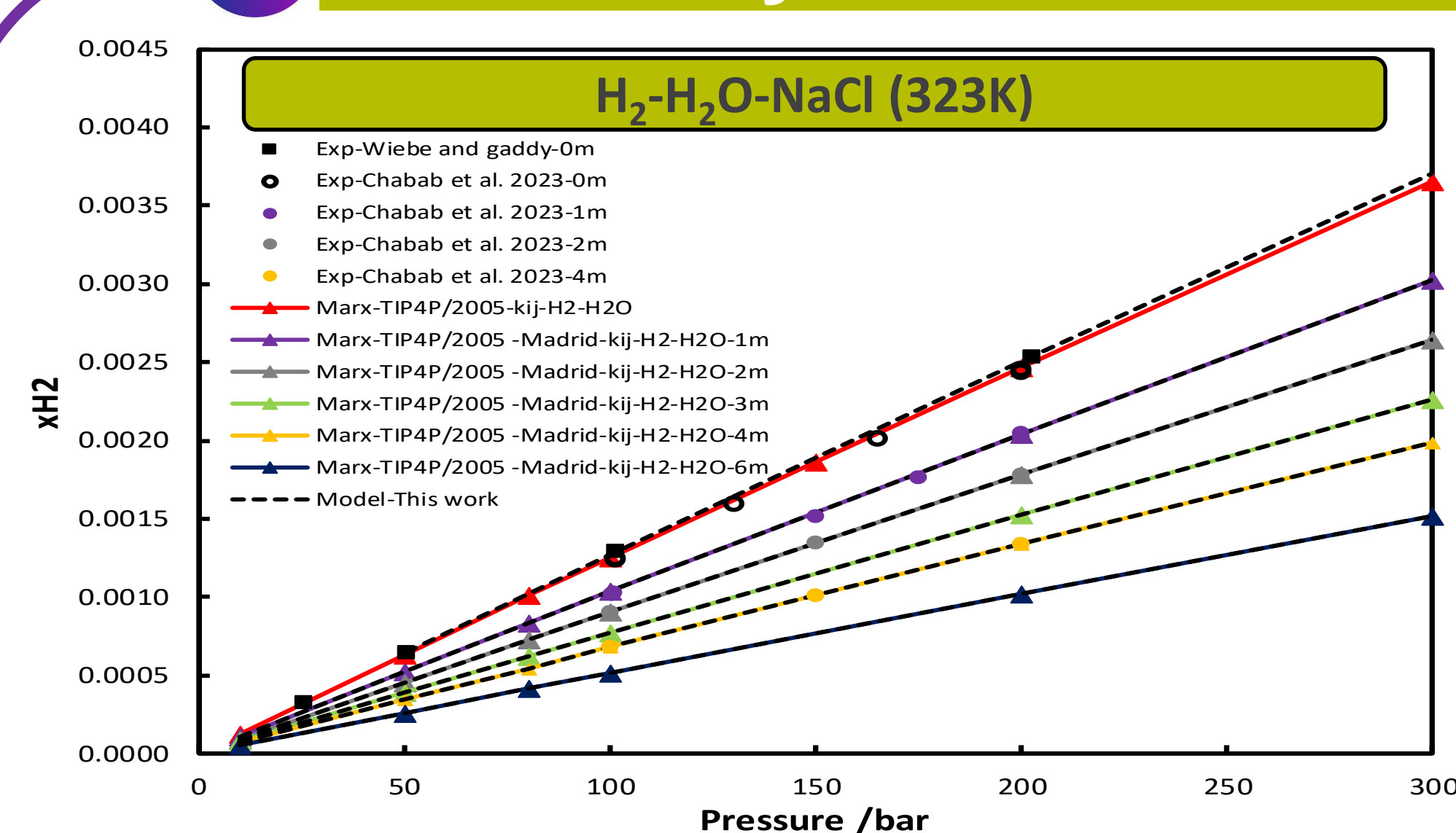
H <sub>2</sub> -H <sub>2</sub> O	Approaches	T [K]	P [bar]	D x 10 <sup>9</sup> [m <sup>2</sup> /s]	σ
Marx + TIP4P/2005 [2]	EMD	298.15	1	5.90	1.8
Vrabec + TIP4P/2005 [3]	EMD	298.15	1	4.40	0.6
Marx + TIP4P/2005 –This work	NEMD	298.15	1	5.20	0.28
H <sub>2</sub> -H <sub>2</sub> O-NaCl (m <sub>NaCl</sub> =1 mol <sub>NaCl</sub> /kg <sub>w</sub> )	Approaches	T [K]	P [bar]	D x 10 <sup>9</sup> [m <sup>2</sup> /s]	σ
Vrabec + TIP4P/2005+Madrid Transport [3]	EMD	298.15	1	3.70	0.6
Marx + TIP4P/2005 +Madrid –This work	NEMD	298.15	1	4.14	0.13
Marx + TIP4P/2005 +Madrid Transport –This work	NEMD	298.15	1	4.45	0.22

- ✓ The predicted self-diffusion coefficients for H<sub>2</sub> in pure water and NaCl brine are within the order of magnitude and very similar to literature results, with a better (lower) uncertainty.

- ✓ H<sub>2</sub> Diffusion tends to decrease in brine relatively to pure water

EMD: Equilibrium molecular dynamics  
 NEMD: Non-Equilibrium molecular dynamics

## Thermodynamic Modeling



### Selected models

Henry+γ/EoS model

- ✓ The parameters of both models are fitted on binary (gas/water) solubility data.
- ✓ The models predict the ternary CO<sub>2</sub>-CH<sub>4</sub>-H<sub>2</sub>O system very well when compared with literature experimental data.
- ✓ The ternary H<sub>2</sub>-CO<sub>2</sub>-H<sub>2</sub>O system was also modeled to estimate the optimal H<sub>2</sub>/CO<sub>2</sub> ratio for underground bio-methanation application.

## Conclusions & Perspectives

- Molecular simulation models were validated and used to provide "pseudo-experimental" data. These data in addition to those from the literature for other gases (CH<sub>4</sub> and CO<sub>2</sub>) were used to optimize the parameters of the thermodynamic models (phi-phi and gamma-phi approaches).
- The thermodynamic modeling showed that the optimal H<sub>2</sub>/CO<sub>2</sub> ratio for underground bio-methanation application is around 3% CO<sub>2</sub> (97% H<sub>2</sub>) to be injected (to have a stoichiometric ratio of 1:4).
- A good representation of H<sub>2</sub> self-diffusion coefficient in water and brine are obtained using External Forces Non-equilibrium Molecular Dynamics.
- The possible influence of the clay interlayer on solubilities and diffusivities will be explored.

### References

