UNIVERSITÉ DE PAU ET DES PAYS DE L'ADOUR | COLLÈGE STEE SCIENCES ET TECHNOLOGIES POUR L'ÉNERGIE ET L'ENVIRONNEMENT

cnrs TotalEnergies

GDR CNRS HydroGEMM 2023

SOLUBILITY AND DIFFUSIVITY OF H_2-RICH GAS MIXTURES IN BRINE UNDER SUBSURFACE STORAGE CONDITIONS: MOLECULAR SIMULATIONS AND THERMODYNAMIC MODELING

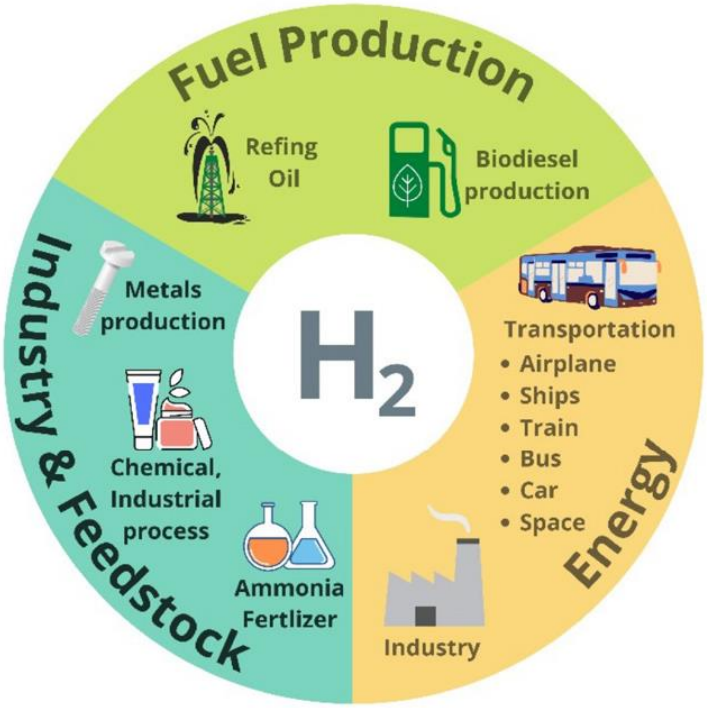
Halla KERKACHE

e2s UPPA energy environment solutions

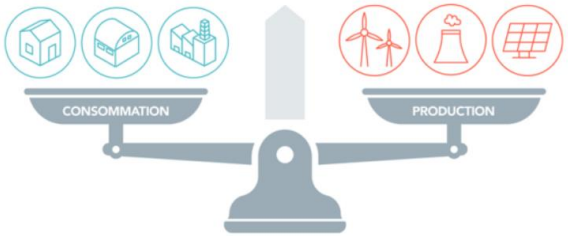
INSTITUT CARNOT ISIFoR

Director: Guillaume Galliero
Co-director: Salaheddine Chabab
Followed by (TE): Sabine Delahaye and Magali Pujol

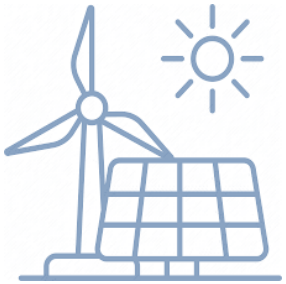
Context and goals



Strategic reserve



Offer/Demand



Renewable energy intermittence

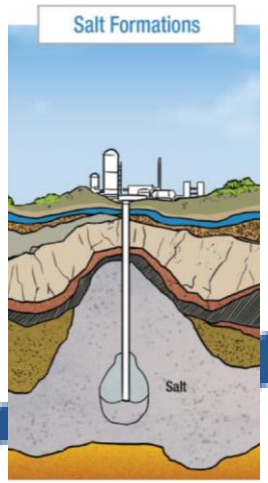
Need for MASSIVE storage capacity!

H_2 STORAGE FACILITIES (FOR ENERGY PURPOSES)

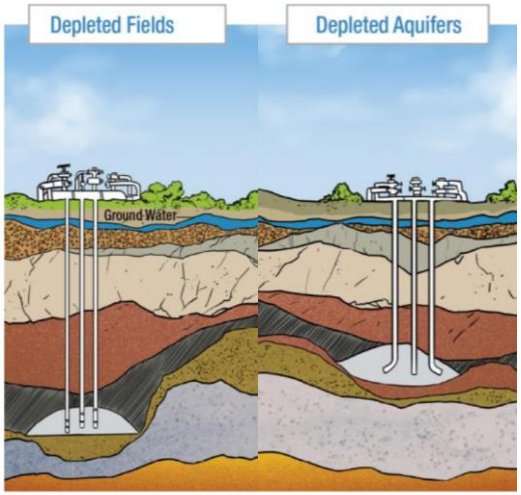
TWh

TRL 9

TRL 9



Low TRL



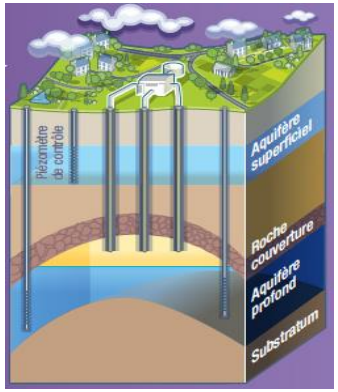
✓Large storage capacity
✓Geographical availability

2020

2030

2050

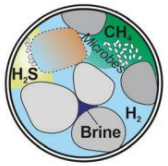
UNDERGROUND HYDROGEN STORAGE : INFLUENCING FACTORS



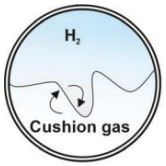
Underground hydrogen storage in aquifers

Influencing factors

Rock properties	Fluid properties	Rock-fluid interactions
Absolute permeability (k_a);	Density (ρ);	Wettability;
Effective porosity ($\phi_{effective}$);	Viscosity (μ);	Solid-fluid interfacial tension (γ_{SF});
Effective stress ($\sigma_{effective}$).	Fluid-fluid interfacial tension (γ_{FF});	Capillary pressure (P_c);
	Solubility;	Relative permeability (k_r);
	Diffusivity.	Mobility ratio (M);
		Saturation (S);
		Adsorption-desorption;
		Chemical reactions;
		Biology/bacteria.



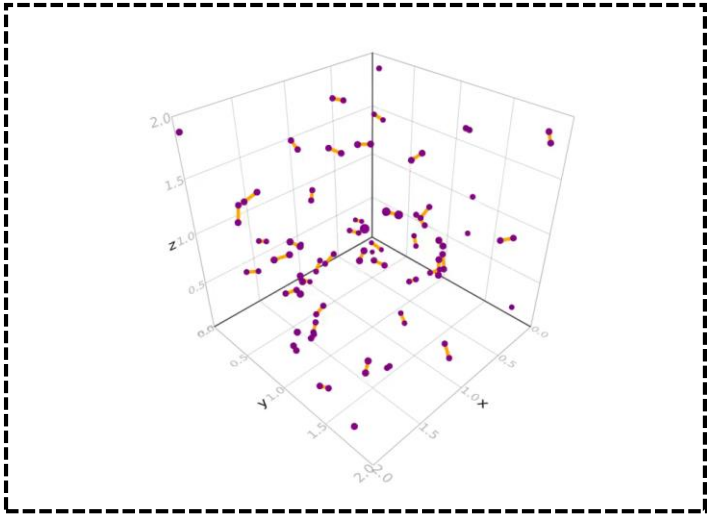
- Loss through H_2 dissolution and reactivity
- Sealing capacity of caprock

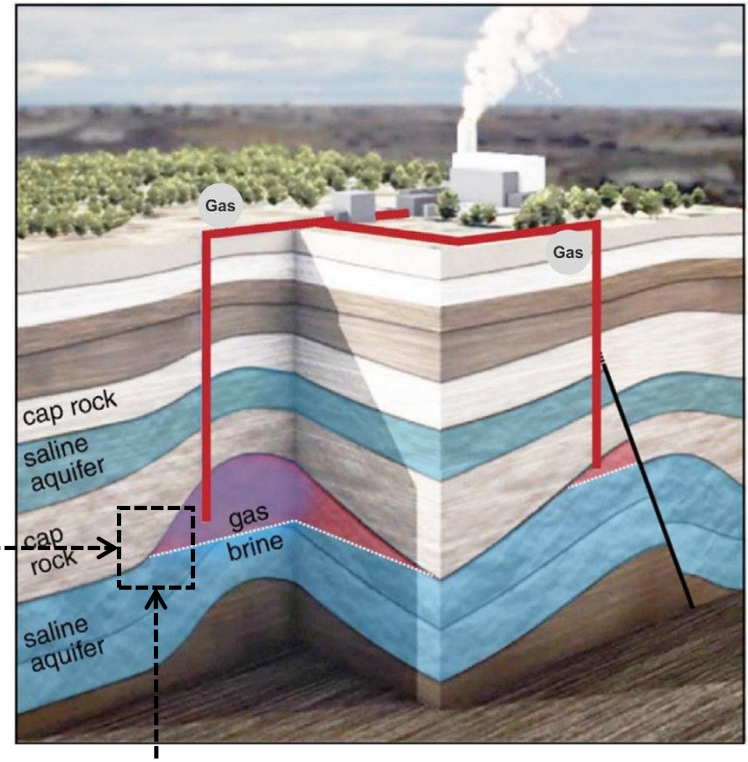


- Potential mixing between H_2 and cushion gas (if other than H_2)
- Gas humidification

THESIS PURPOSES

- ✓ Molecular Simulations (MS) of Equilib. Prop.
- ✓ Development of thermodynamic models
- Estimation of the diffusion coefficient



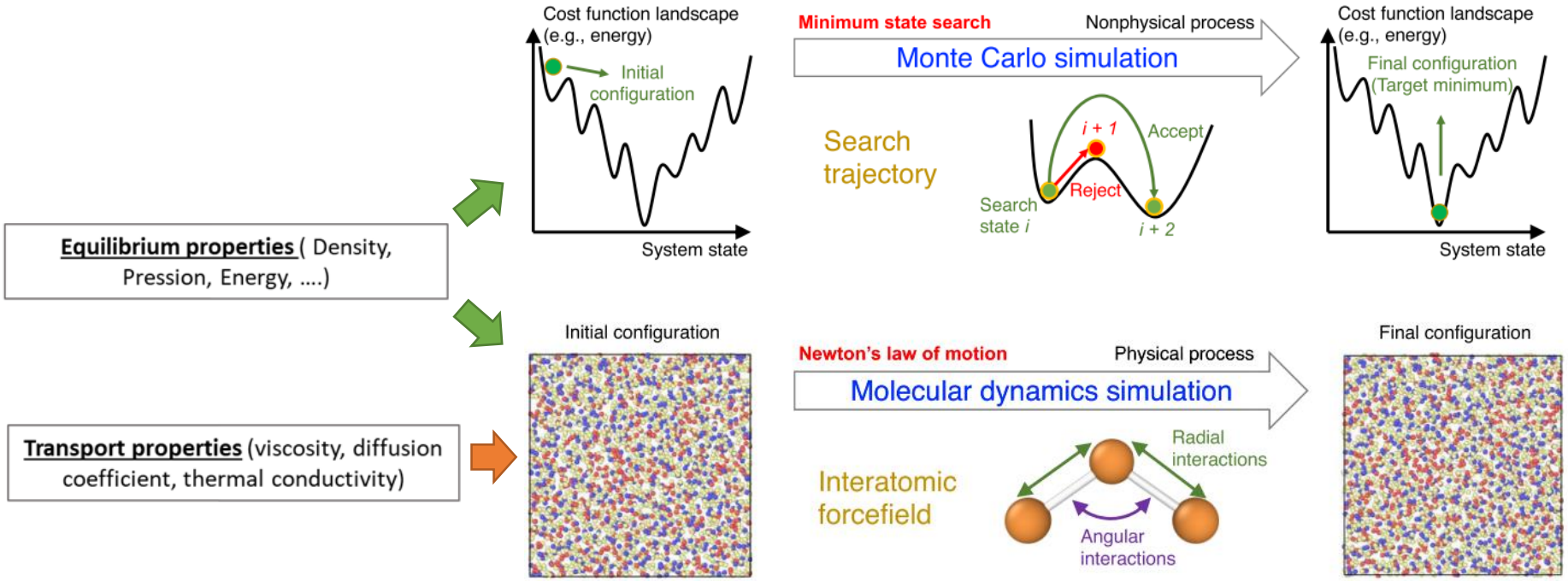


Considered gases: H_2, CH_4, CO_2

Field of study: Material exchange in “gas/brine” and “gas/brine/rock media”

WHAT IS AND WHY MOLECULAR SIMULATION?

- High-performance computing (HPC)
- Force field
- Statistical method (Monte Carlo)
- Newton's law of motion (Molecular Dynamics)



Ref: Lachet, Véronique. "La simulation moléculaire: un outil au service de l'industrie." *l'actualité chimique* 340 (2010): 22.

Some results: H_2 solubility in NaCl brine

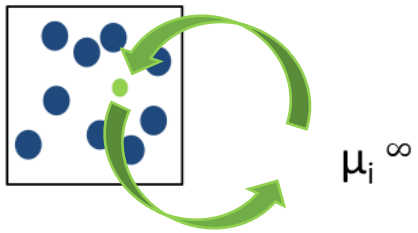
THE DIFFERENT METHODS FOR THE CALCULATION OF SOLUBILITY

✓ **Method 1: Henry constant (H_i)**: The solubility of hydrogen in water/brine can be calculated using the Henry constant, which is related to the residual chemical potential of the solute i at infinite dilution μi∞ :

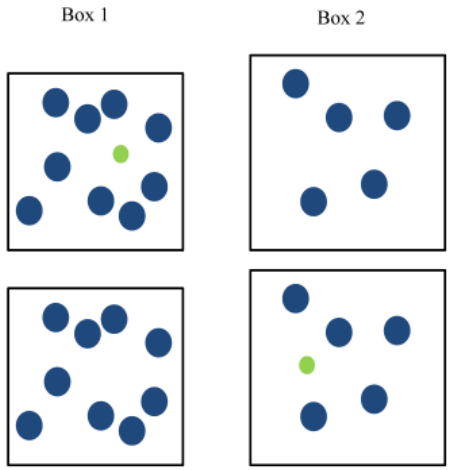
$$H_i = \rho k_B T \exp(\mu_i^{\infty} / k_B T)$$

k_B : Boltzmann constant, T: temperature, ρ: solvent density.

μ_i^{∞} : from molecular simulation



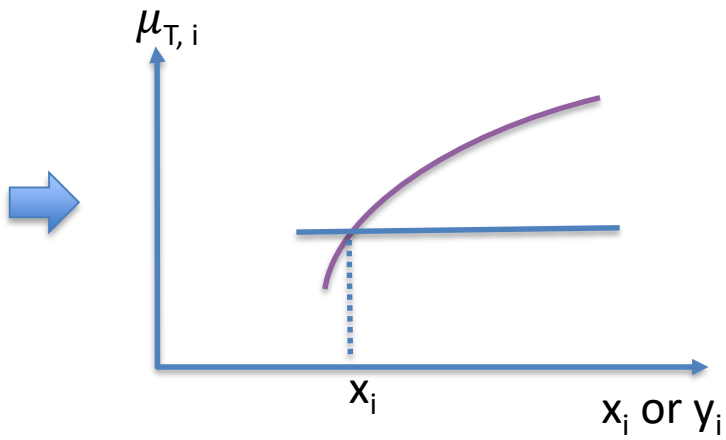
✓ **Method 2: Using Gibbs ensemble** (2boxes -NPT ensemble) => x_i and y_i (molar composition)



THE DIFFERENT METHODS FOR THE CALCULATION OF SOLUBILITY

- **<u>Method 3</u>: Equality of chemical potentials:** Independent NPT simulations => x_i and y_i

	Vapor phase (H_2+H_2O) NPT ensemble		Liquid phase (H_2+H_2O) NPT ensemble	
N simulations	**H_2**	**H_2O**	**H_2O**	**H_2**
1	600	1	730	1
2	600	2	730	2
3	600	…	730	…
4	600	…	730	…
…	…	…	…	…

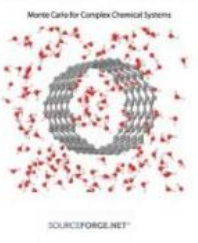


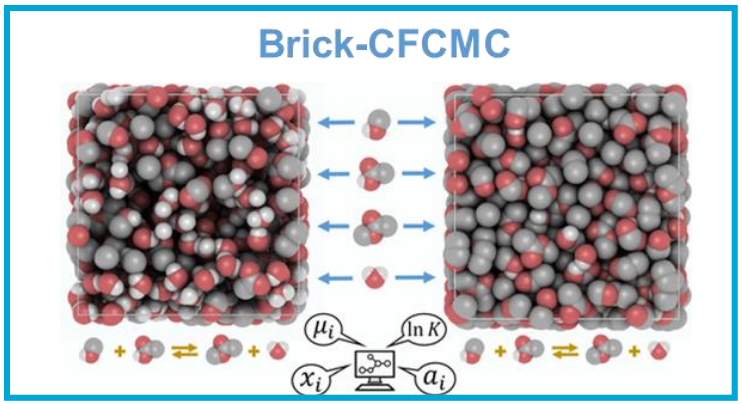
Internship from 02 May to 29 sept 2023: Molecular simulation of the thermodynamic properties of H_2 in NaCl brine at high pressure and temperature for a native hydrogen production application

MOLECULAR SIMULATIONS: TOOLS

✓ 2 tools were used for the calculation of H_2 solubility by performing Monte Carlo simulations : **Towhee-CBMC** and **Brick-CFCMC**

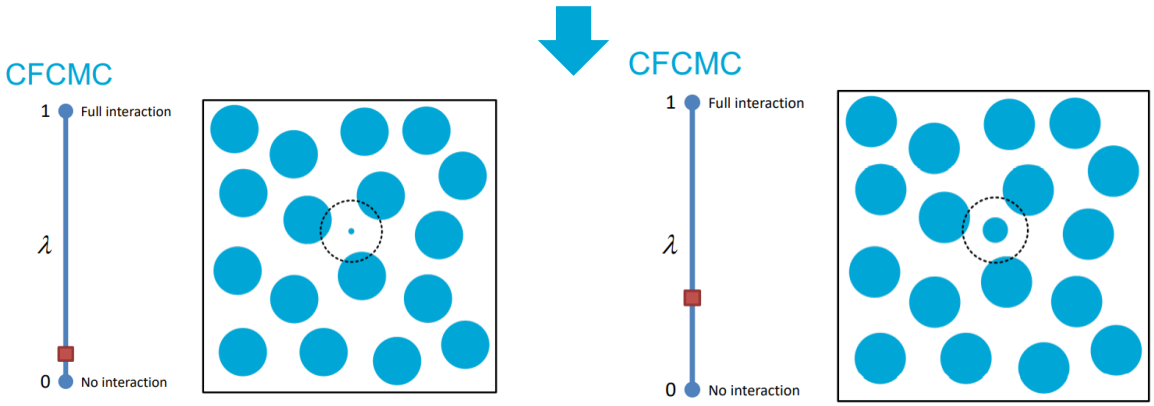
MCCCS Towhee





CPU time:

Brick-CFCMC= 3-6days vs Towhee=23 days-1 month!

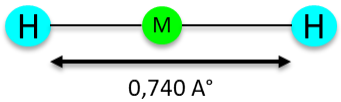


- *N* whole molecules, 1 fractional molecule
- Fractional molecule has scaled interactions (λ)
  - λ=0: no interactions with surrounding molecules
  - λ=1: full interactions with surrounding molecules

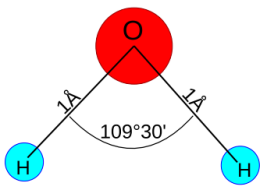
Ref :Hens, R., Rahbari, A., Caro-Ortiz, S., Dawass, N., Erdős, M., Poursaeidesfahani, A., ... & Vlugt, T. J. (2020). Brick-CFCMC: Open source software for Monte Carlo simulations of phase and reaction equilibria using the Continuous Fractional Component Method. *Journal of chemical information and modeling*, *60*(6), 2678-2682.

MOLECULAR SIMULATIONS: MODELS

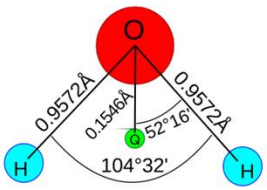
✓ **Pure H_2 model:** Alavi, Marx



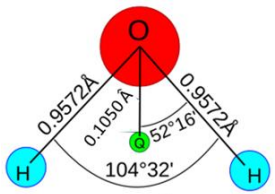
✓ **Pure H_2O model:** SPC/E, TIP4P/2005, TIP4P/EP



SPC/E



TIP4P/2005



TIP4P/EP

✓ **Na^+, Cl^- model:** KBF, Madrid2017, OPLS

✓ **Cross-interaction:** Lorentez-Berthelot (LB)

Cross energy: $\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$ cross diameter: $\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}$

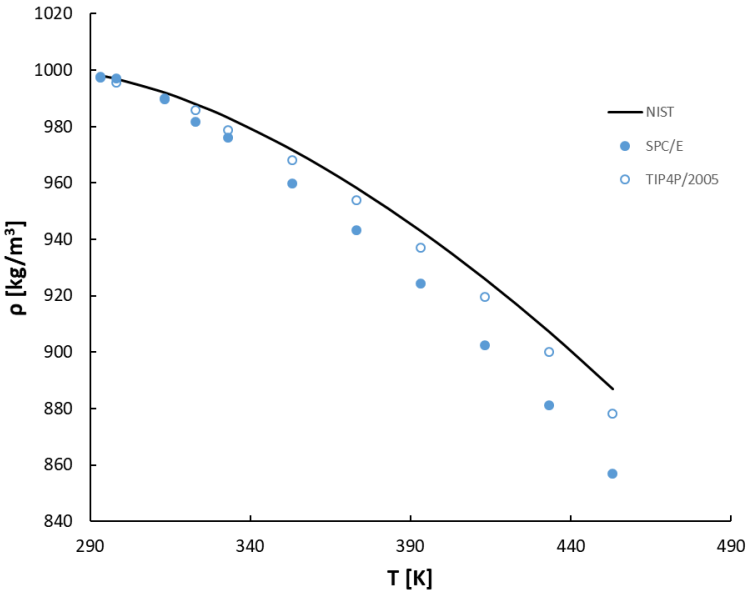
Solubility of H_2 in water

HENRY COEFFICIENT FOR H_2-H_2O SYSTEM

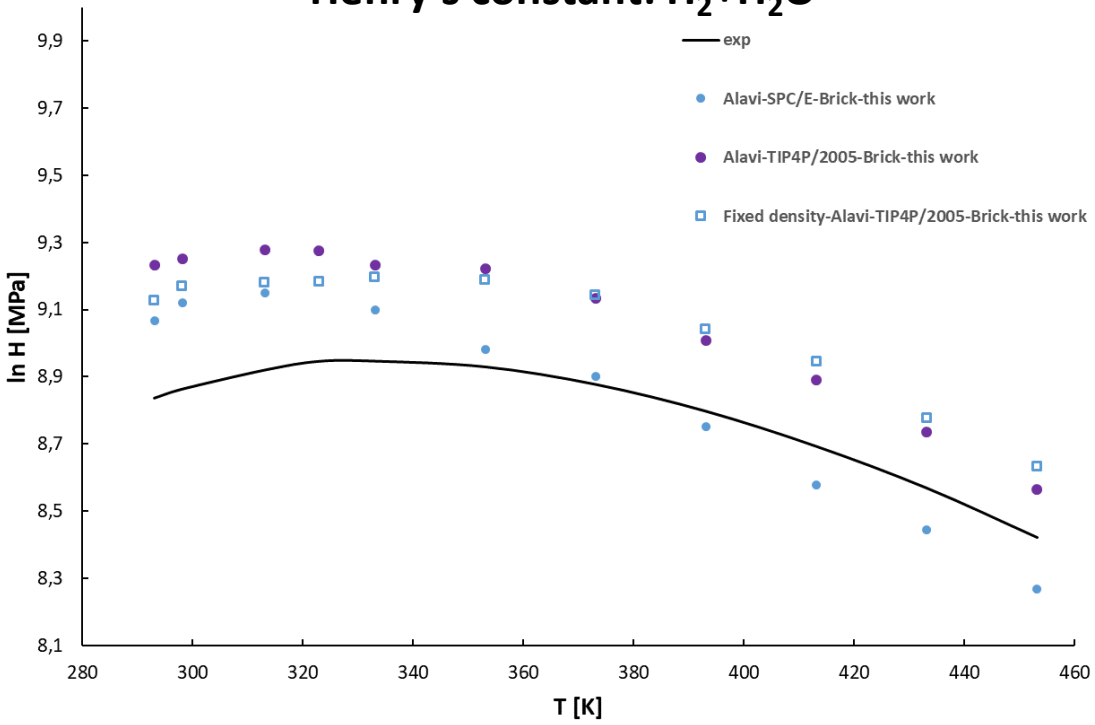
Effect of density on the qualitative representation of H vs. T

$$Hi = \rho k_B T \exp(\mu_i^{ex}/k_B T)$$

Solvent (H_2O) density



Henry's constant: H_2+H_2O

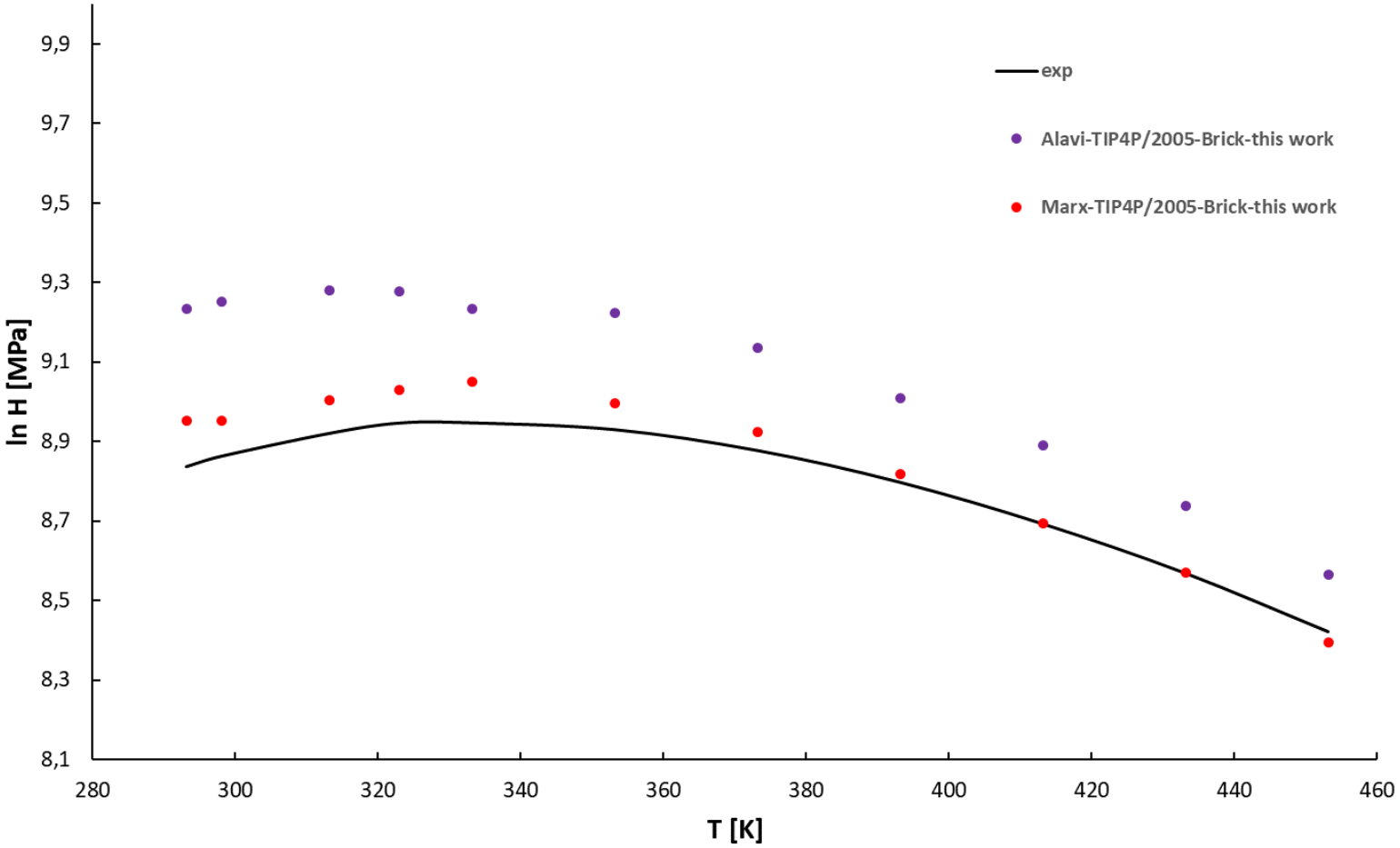


By **fixing the density** (exp) or by **using a suitable model for water density** (TIP4P/2005), the results are **qualitatively** much **improved** (H vs. T)

What can be done to quantitatively improve predictions?

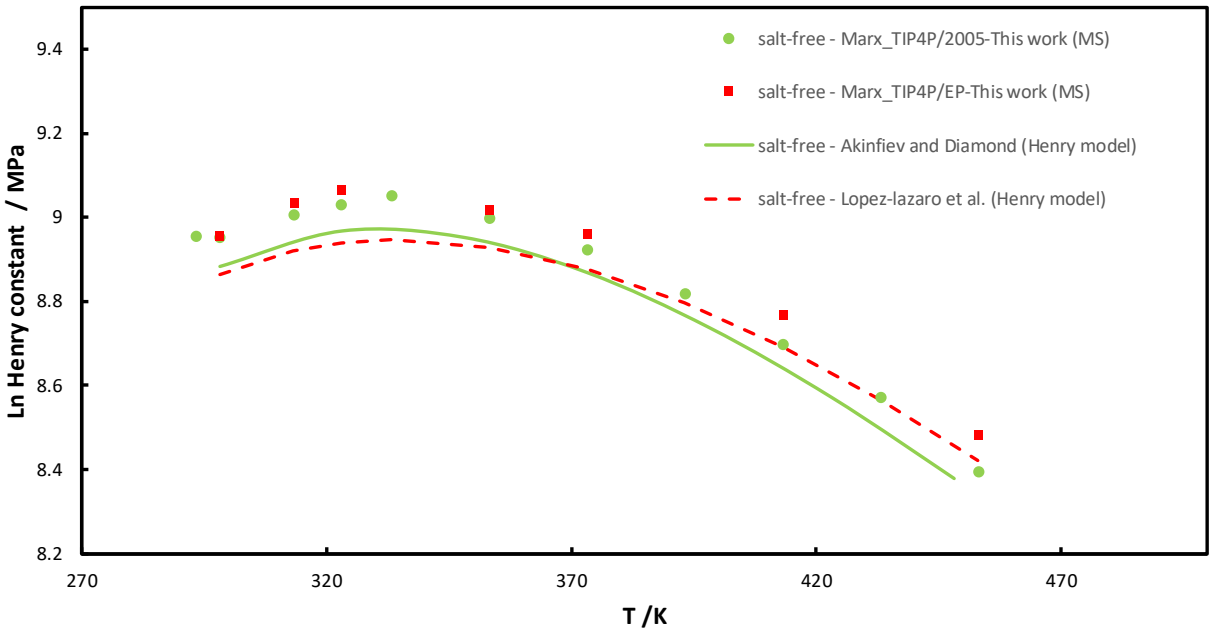
HENRY COEFFICIENT- H=F(T)

Effect of the excess chemical potential on the quantitative representation of H vs. T



✓ Using the **Marx** model for H_2 significantly **improves** the predictions.

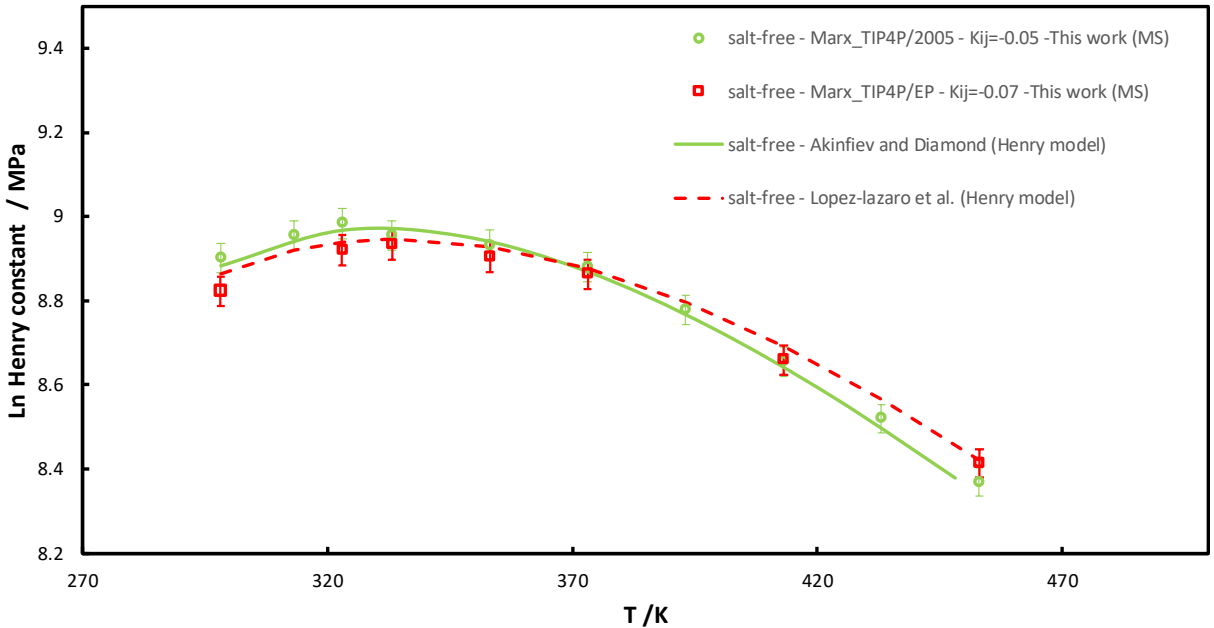
HENRY COEFFICIENT FOR H_2-H_2O SYSTEM



Models used:

- Marx_TIP4P/2005
- Marx_TIP4P/EP

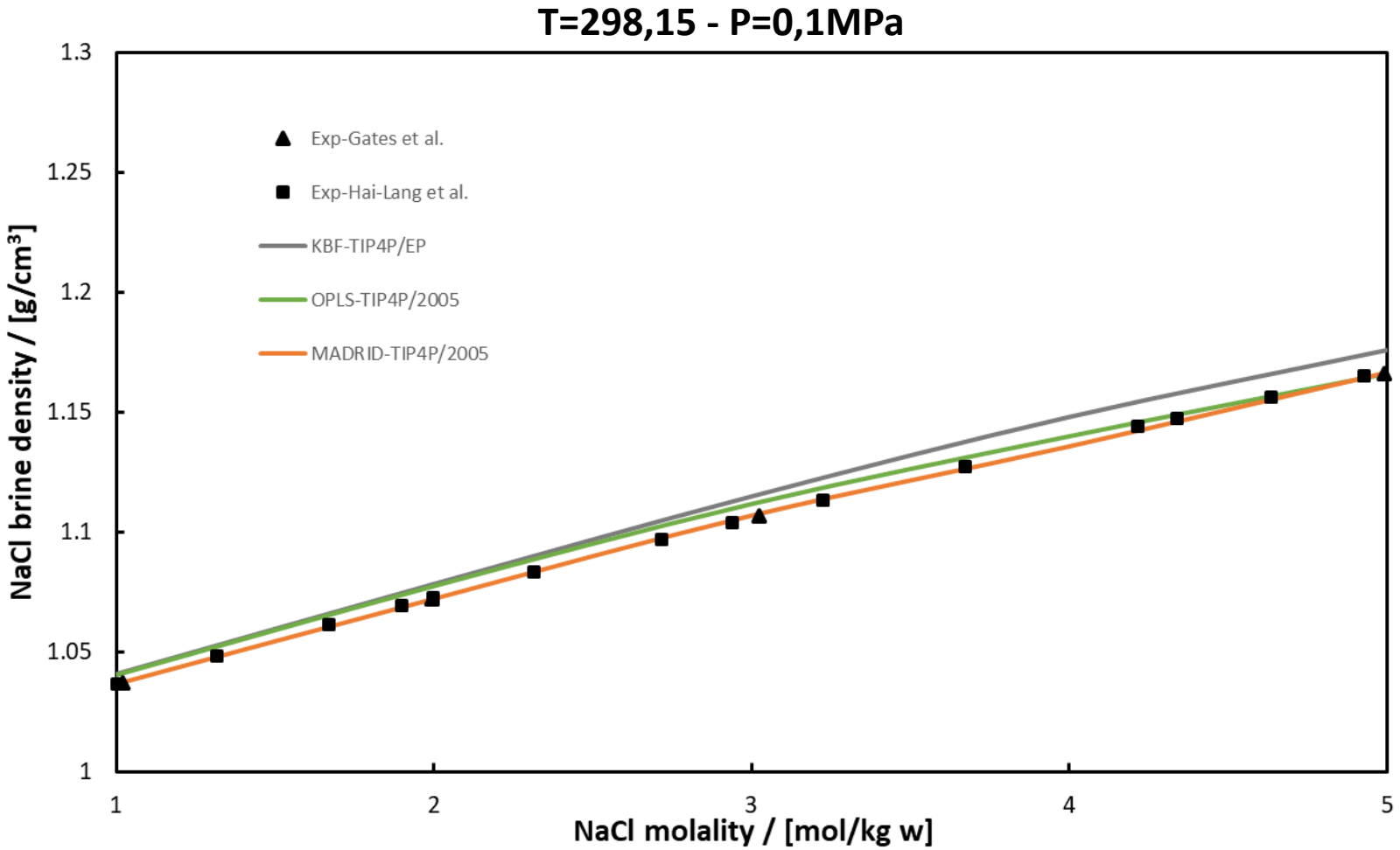
✓ **A constant BIP** on energy for H_2-H_2O are used to improve the quantification of the H_2 solubility in pure water.



BIP: Binary interaction parameters

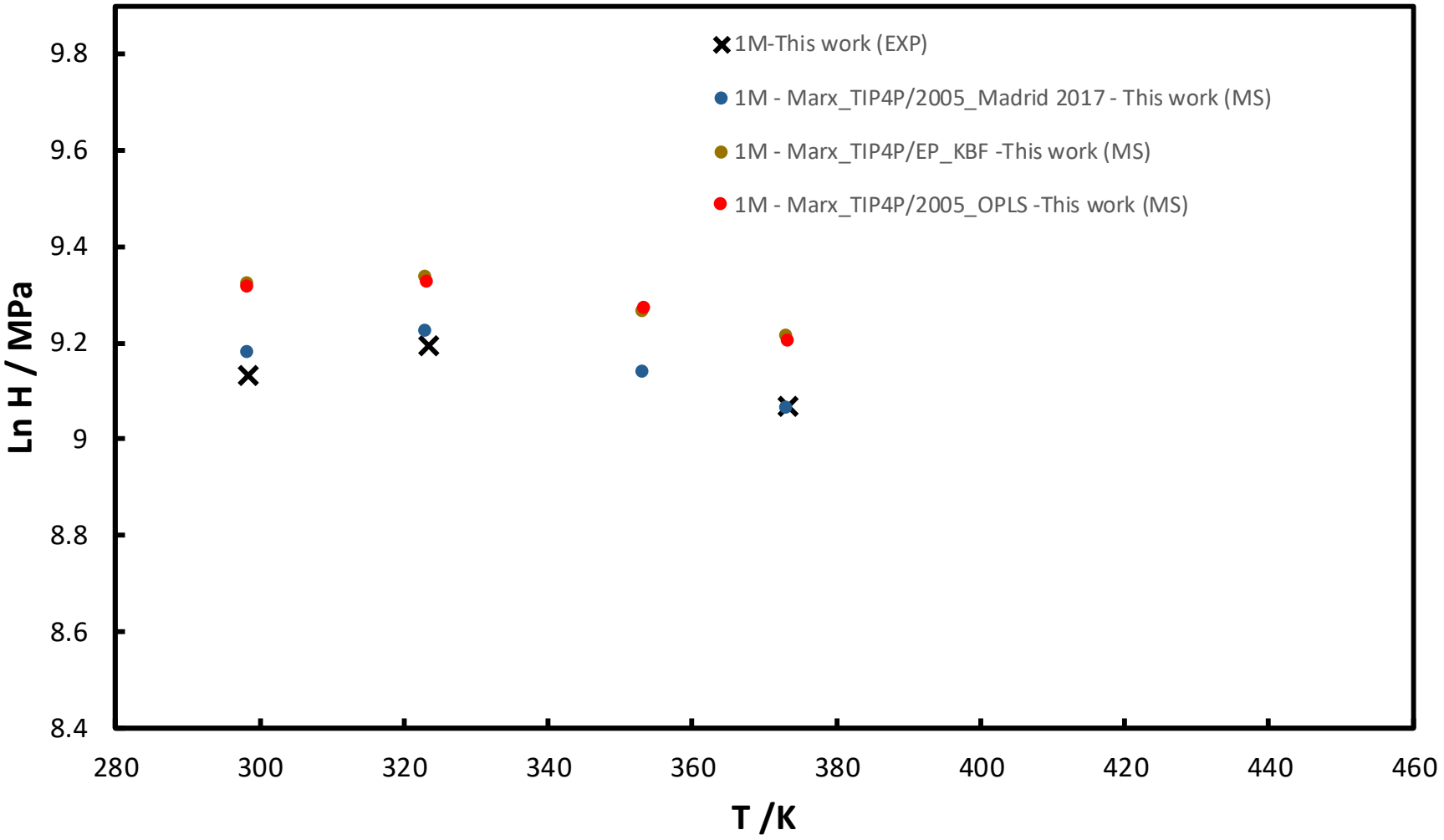
Solubility of H_2 in NaCl brine

Brine (H_2O+NaCl) density



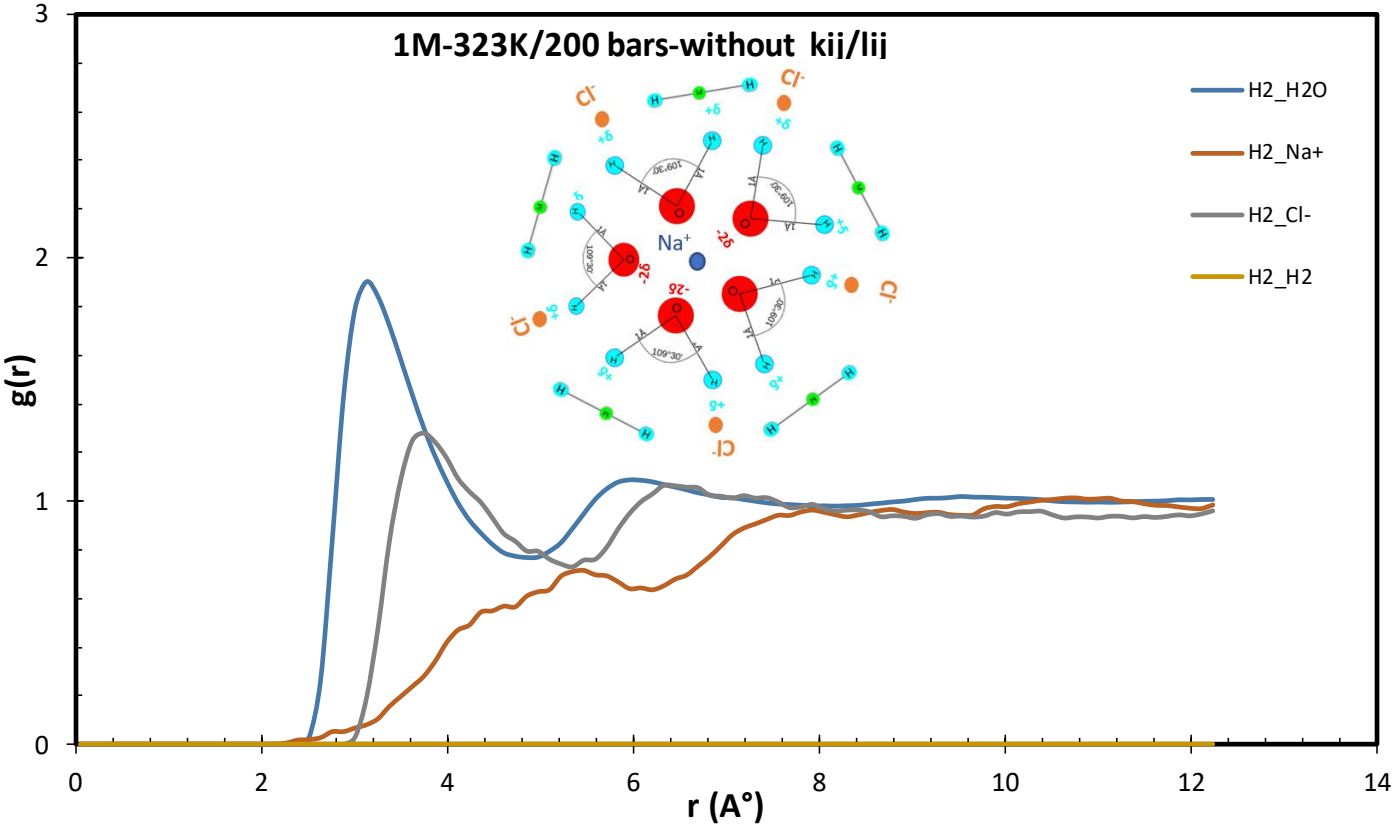
✓ The **TIP4P/2005-OPLS**, **TIP4P/2005-Madrid 2017** and **TIP4P/EP-KBF** models were selected for the calculation of H_2 solubilities in brine.

HENRY COEFFICIENT FOR H_2-H_2O-NACL SYSTEM



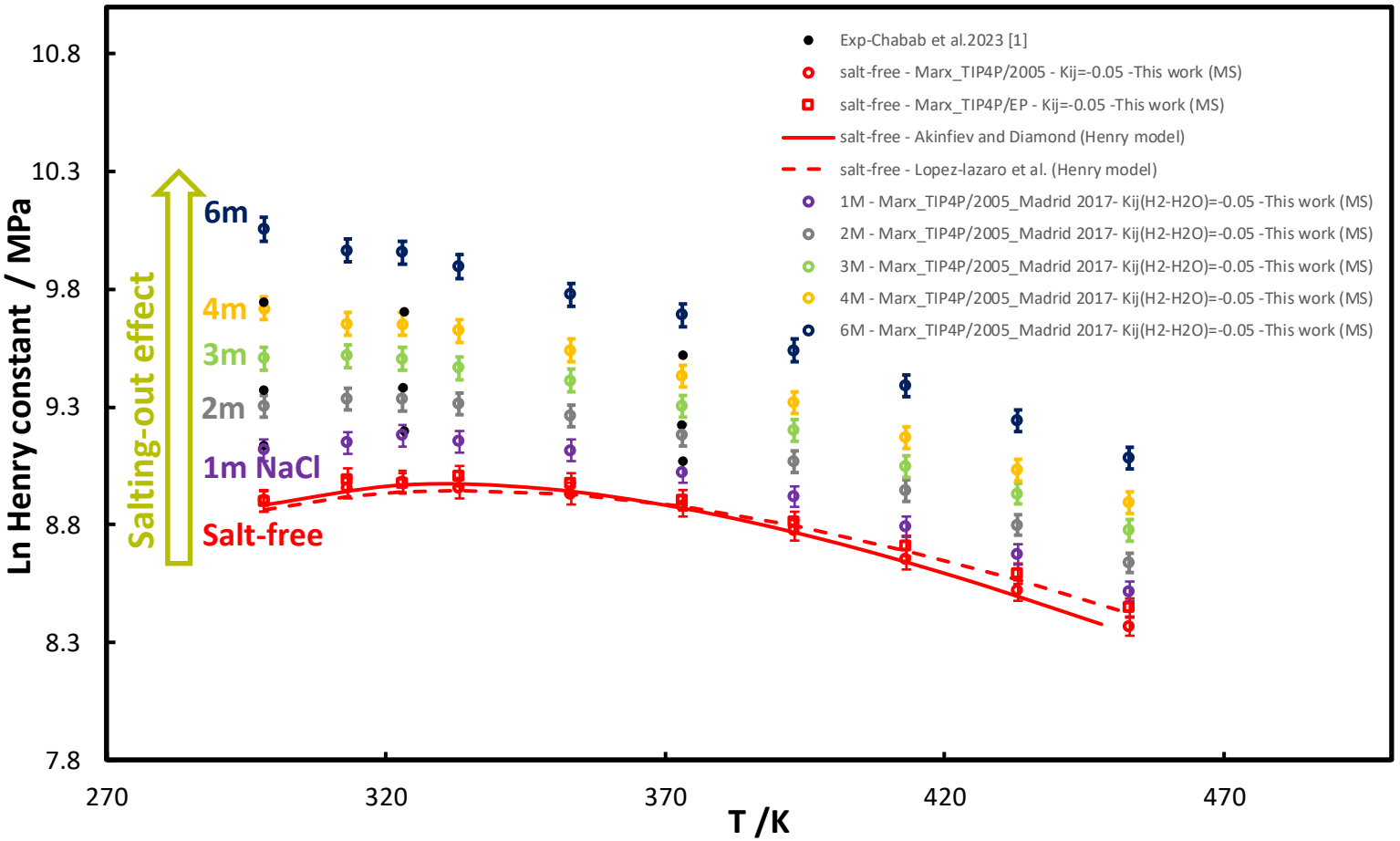
Radial distribution function (RDF) of H_2+H_2O+NaCl system

Solvation structure of H_2/NaCl brine mixtures



- ✓ **The radial distribution function (RDF)** is used to evaluate the solvation structure of the H_2/brine mixtures which is shown to be **dominated** by the **H_2-H_2O** and **H_2-Cl^-** interactions
- ✓ **According to the RDF results, H_2-H_2O and H_2-Cl^- interactions are dominant!**

HENRY COEFFICIENT FOR H_2-H_2O-NACL SYSTEM



✓**Excellent** representation of **H_2 solubility in NaCl brine** using three different models (Marx_TIP4P/2005_OPLS – Marx_TIP4P/EP_KBF-Marx_TIP4P/2005_Madrid).

Thermodynamic modeling

THERMODYNAMIC MODELING : GAMMA/PHI APPROACH

At phase equilibrium, $\mu^{l}_{H_2} = \mu^{v}_{H_2}$

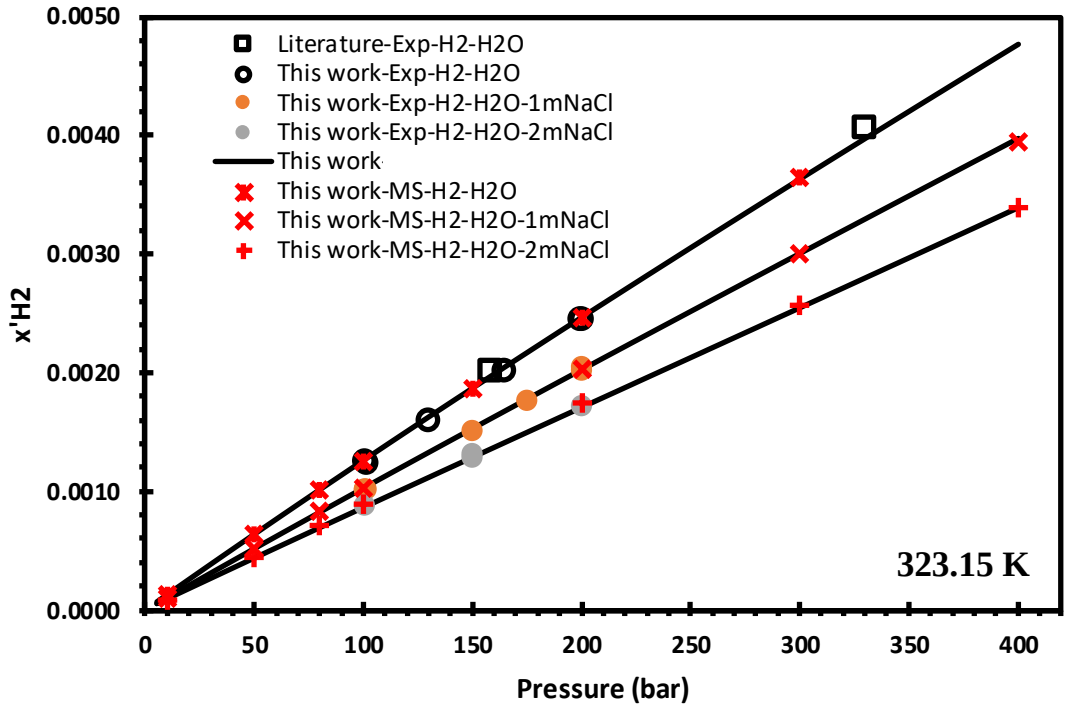
PR EoS

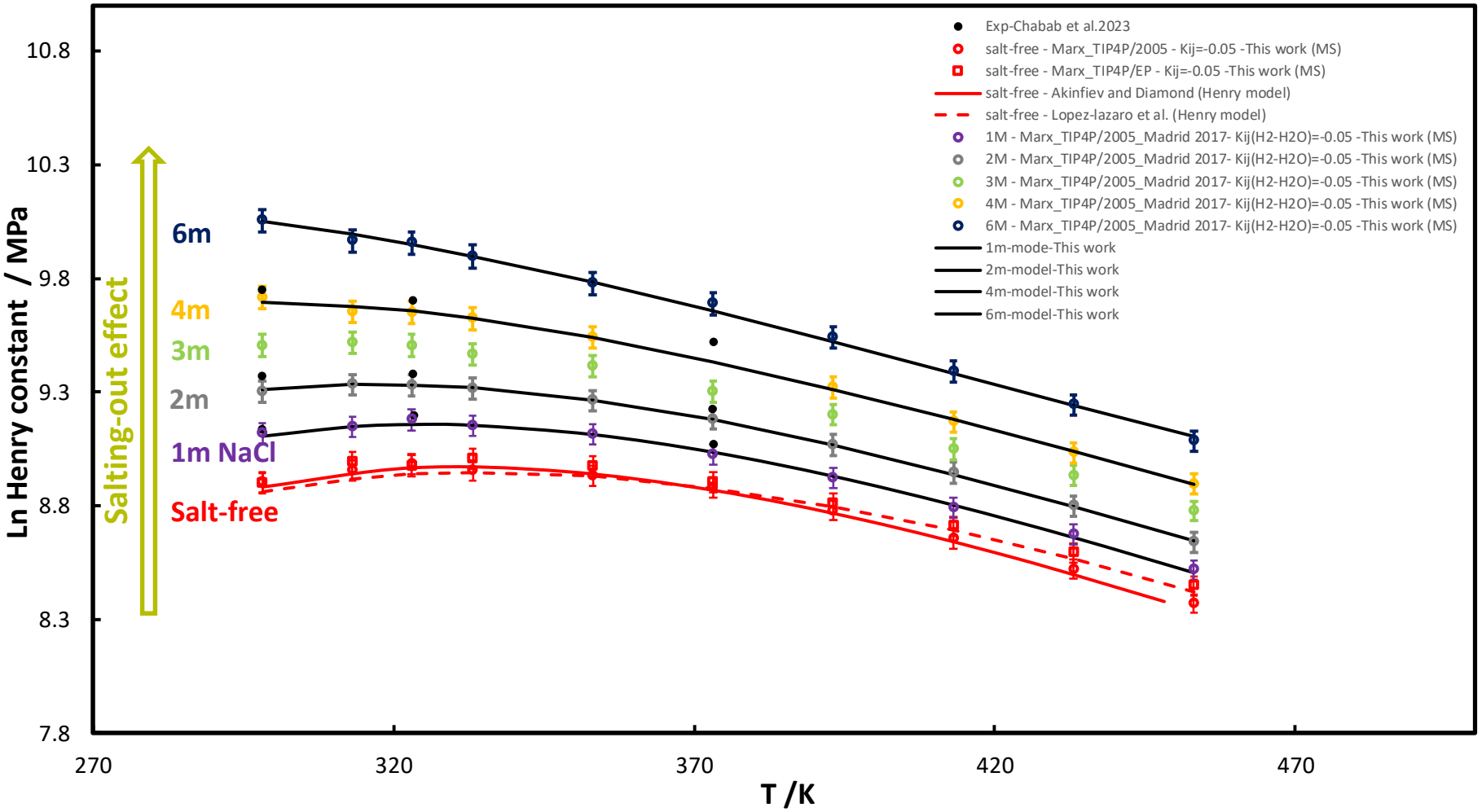
$$x_{H2}(\mathrm{T},\mathrm{P},m_s) = \frac{y_{H2} \cdot P \cdot \varphi_{H2}}{H_{H2}(T,P_w^{sat}) \cdot \gamma_{H2} \cdot \exp\left(\frac{\vartheta^{\infty}_{H2,w}}{RT}(P - P_w^{sat})\right)}$$

Henry H_2/H_2O

Henry $H_2/H_2O/NaCl$

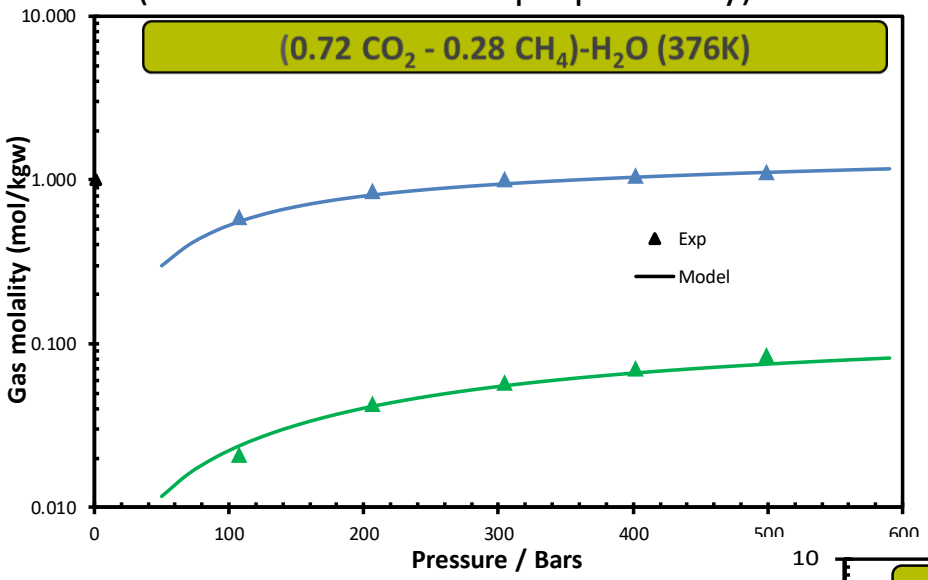
Poynting correction




Exp-Chabab et al.2023
salt-free - Marx_TIP4P/2005 - Kij=-0.05 -This work (MS)
salt-free - Marx_TIP4P/EP - Kij=-0.05 -This work (MS)
salt-free - Akinfiev and Diamond (Henry model)
salt-free - Lopez-lazaro et al. (Henry model)
1M - Marx_TIP4P/2005_Madrid 2017- Kij(H2-H2O)=-0.05 -This work (MS)
2M - Marx_TIP4P/2005_Madrid 2017- Kij(H2-H2O)=-0.05 -This work (MS)
3M - Marx_TIP4P/2005_Madrid 2017- Kij(H2-H2O)=-0.05 -This work (MS)
4M - Marx_TIP4P/2005_Madrid 2017- Kij(H2-H2O)=-0.05 -This work (MS)
6M - Marx_TIP4P/2005_Madrid 2017- Kij(H2-H2O)=-0.05 -This work (MS)
1m-mode-This work
2m-model-This work
4m-model-This work
6m-model-This work
Salting-out effect
6m
4m
3m
2m
1m NaCl
Salt-free
Ln Henry constant / MPa
T /K
10.8
10.3
9.8
9.3
8.8
8.3
7.8
270
320
370
420
470

AN EXAMPLE OF APPLICATION : UNDERGROUND BIO-METHANATION

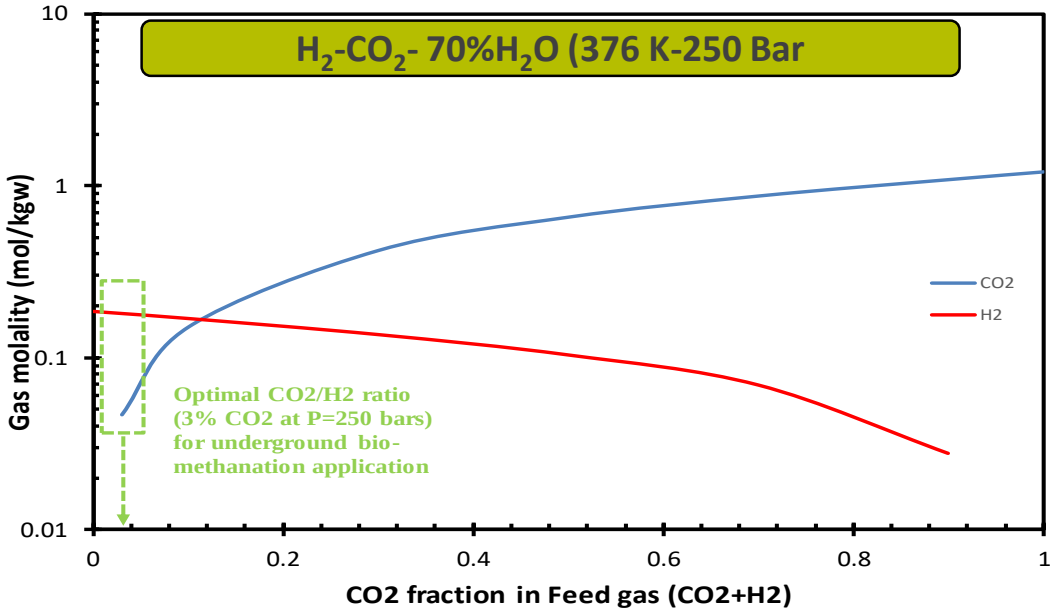
(For model validation purpose only)



✓ The models **predict** the ternary **CO_2-CH_4-H_2O** system very well when **compared** with **literature experimental data**.

✓ The ternary **H_2-CO_2-H_2O** system was also modeled to estimate the **optimal H_2/CO_2 ratio** for **underground bio-methanation** application.

$$4\,H_2 + CO_2 \rightarrow CH_4 + 2\,H_2O$$



Transport properties

Self-diffusion coefficient (SDC) of H_2 in Water and Brine

EMD vs NEMD

There exist two main techniques used in the MD simulations to estimate the SDC

✓ Equilibrium molecular dynamics (EMD):

The Kubo-Green formula

$$D_{\text{Gas}}^{\text{EMD}} = \lim_{t\to\infty} \frac{1}{6t} \int_0^t \langle \boldsymbol{v}_i(t) \cdot \boldsymbol{v}_i(0) \rangle dt$$

$\boldsymbol{v}i\ (t)$ is the velocity of gas molecule i th at the time t, and ⟨… ⟩ is the average over molecules

Einstein's relation

$$D_{\text{Gas}}^{\text{EMD}} = \lim_{t\to\infty} \frac{1}{6t} \langle [\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2 \rangle$$

$\mathbf{r}i\ (t)$ is the position of gas molecule i th at the time t.

☹ **Slow convergence and a low signal-noise ratio => Large statistical uncertainties especially for highly diluted gases**

✓ Non-Equilibrium molecular dynamics (NEMD)

☺ **High-noise ratio => good statistical uncertainties**

External field non-equilibrium molecular dynamics (EF-NEMD) is used in this work

$$D_{\text{Gas}}^{\text{NEMD}} = \frac{\boldsymbol{u}_{\text{Gas}} \times RT}{\boldsymbol{F}_{\text{Gas}}^{\text{Ext}}}$$

SDC : Self-diffusion coefficient

H_2-H_2O	Approaches	T [K]	P [bar]	D x 10^9 [m^2/s]	σ
Marx + TIP4P/2005 [1]	EMD	298.15	1	5.90	1.8
	EMD				
Vrabec + TIP4P/2005 [1]	EMD	298.15	1	4.90	0.3
Vrabec + TIP4P/2005 [2]	EMD	298.15	1	4.40	0.6
Marx + TIP4P/2005 –This work	**NEMD**	**298.15**	**1**	**5.20**	**0.28**

H_2-H_2O-NaCl (m_{NaCl}=1 mol_{NaCl}/kg_w)	Approaches	T [K]	P [bar]	D x 10^9 [m^2/s]	σ
Vrabec + TIP4P/2005+Madrid Transport [2]	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_2 in pure water and NaCl brine** are within the order of magnitude and **very similar to literature results**, with a better (lower) uncertainty.
- ✓ H_2 Diffusion tends **to decrease** in brine relatively to pure water

[1]: Tsimpanogiannis et al. 2021
[2]: Van Rooijen et al. 2023

CONCLUSION

- ✓ **New equilibrium data of H_2/brine system** are predicted using Monte Carlo simulation while studying **the effect of bulk and excess properties** representation on solubility
- ✓ MS data for H_2/brine in addition to those from the literature for other gases (CH_4 and CO_2) were used to **optimize** the parameters of **the thermodynamic models.**
- ✓ First coherent **diffusivity** results with **better uncertainties**
- ✓ The results obtained can be used to **assess dissolution losses** and **caprock integrity**, in addition to the **other properties (diffusivity, clay effect)** currently being studied.
- ✓ Finally, for **underground bio-methanation application, the thermodynamic modeling** showed that **the optimal H_2/CO_2 ratio is around 3% CO_2 (97% H_2)** to be injected (to have a stochiometric ratio of 1:4).

Molecular simulation is a practical tool to:

- ✓ Predict pseudo-experimental data and **reduce** the number of experimental **measurements**
- ✓ Explore **extreme T and P conditions** that are difficult to measure.
- ✓ Investigate **physical phenomena** at the molecular scale.

Thank you for your intention

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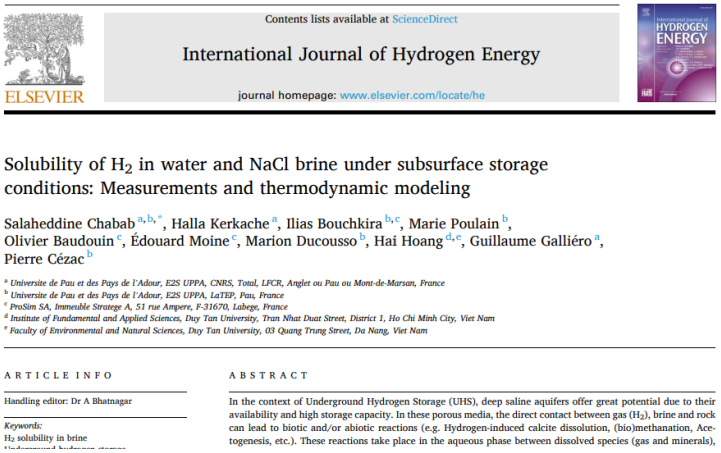

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Solubility of H_2 in water and NaCl brine under subsurface storage conditions: Measurements and thermodynamic modeling

Salaheddine Chabab [a,b,*], Halla Kerkache [a], Ilias Bouchkira [b,c], Marie Poulain [b], Olivier Baudouin [c], Édouard Moine [c], Marion Ducousso [b], Hai Hoang [d,e], Guillaume Galliéro [a], Pierre Cézac [b]

[a] Université de Pau et des Pays de l'Adour, E2S UPPA, CNRS, Total, LFCR, Anglet ou Pau ou Mont-de-Marsan, France
[b] Université de Pau et des Pays de l'Adour, E2S UPPA, LaTEP, Pau, France
[c] ProSim SA, Immeuble Stratege A, 51 rue Ampere, F-31670, Labege, France
[d] Institute of Fundamental and Applied Sciences, Duy Tan University, Tran Nhat Duat Street, District 1, Ho Chi Minh City, Viet Nam
[e] Faculty of Environmental and Natural Sciences, Duy Tan University, 03 Quang Trung Street, Da Nang, Viet Nam

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ABSTRACT

In the context of Underground Hydrogen Storage (UHS), deep saline aquifers offer great potential due to their availability and high storage capacity. In these porous media, the direct contact between gas (H_2), brine and rock can lead to biotic and/or abiotic reactions (e.g. Hydrogen-induced calcite dissolution, (bio)methanation, Acetogenesis, etc.). These reactions take place in the aqueous phase between dissolved species (gas and minerals),