FROM MOLECULAR TO COLLECTIVE THERMOPHYSICAL PROPERTIES UNDER RESERVOIR CONDITIONS

G. Galliero

LFCR, UMR 5150 CNRS-TOTALENERGIES-UPPA

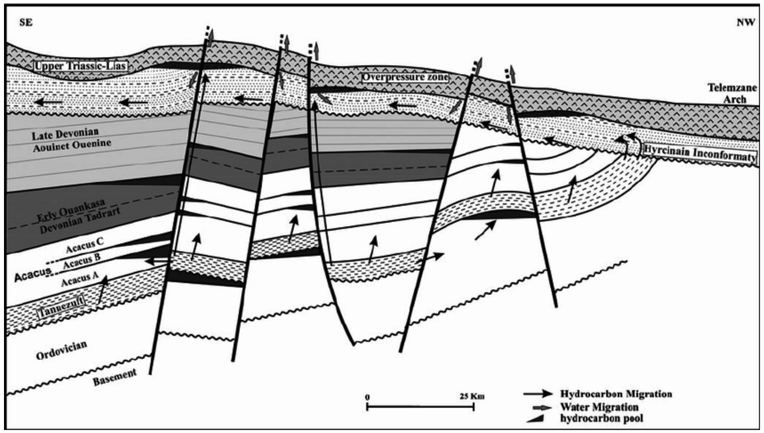
July 2022
Journée Thermodynamique du sous-sol

MOTIVATIONS OF OUR WORKS

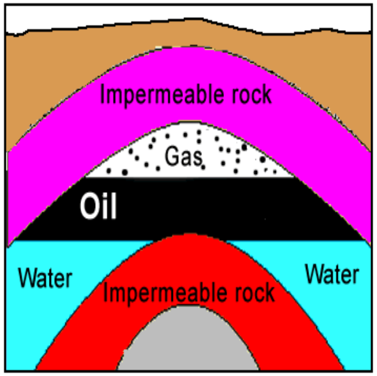
Motivations

Improving the management of geo-resources and the underground storage is crucial for the energy mix

Fluid Origins/Migration



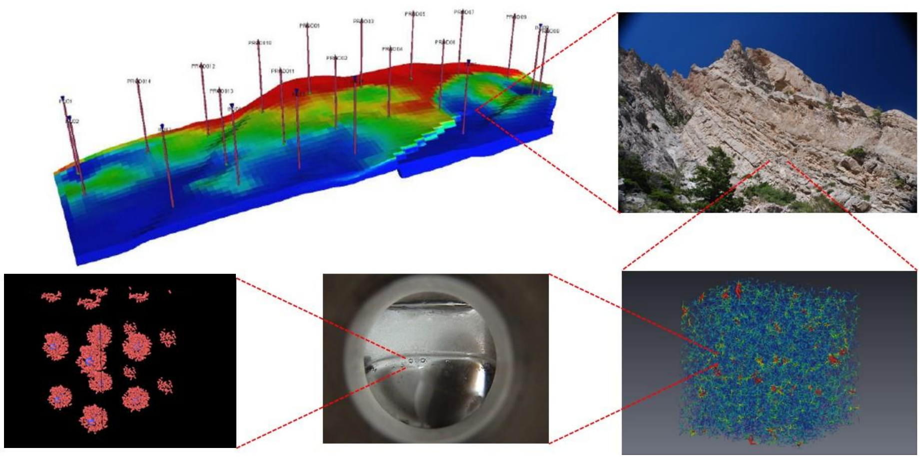
Reservoir Initial state



Gas Storage Monitoring

Fluid properties and behaviors in porous medium under reservoir conditions are required at all stages

METHODOLOGY



The tools: Molecular Simulations

Molecular Model
Force Fields

Molecular Simulations

Monte-Carlo, Molecular Dynamics

“Exact” emerging properties/fields

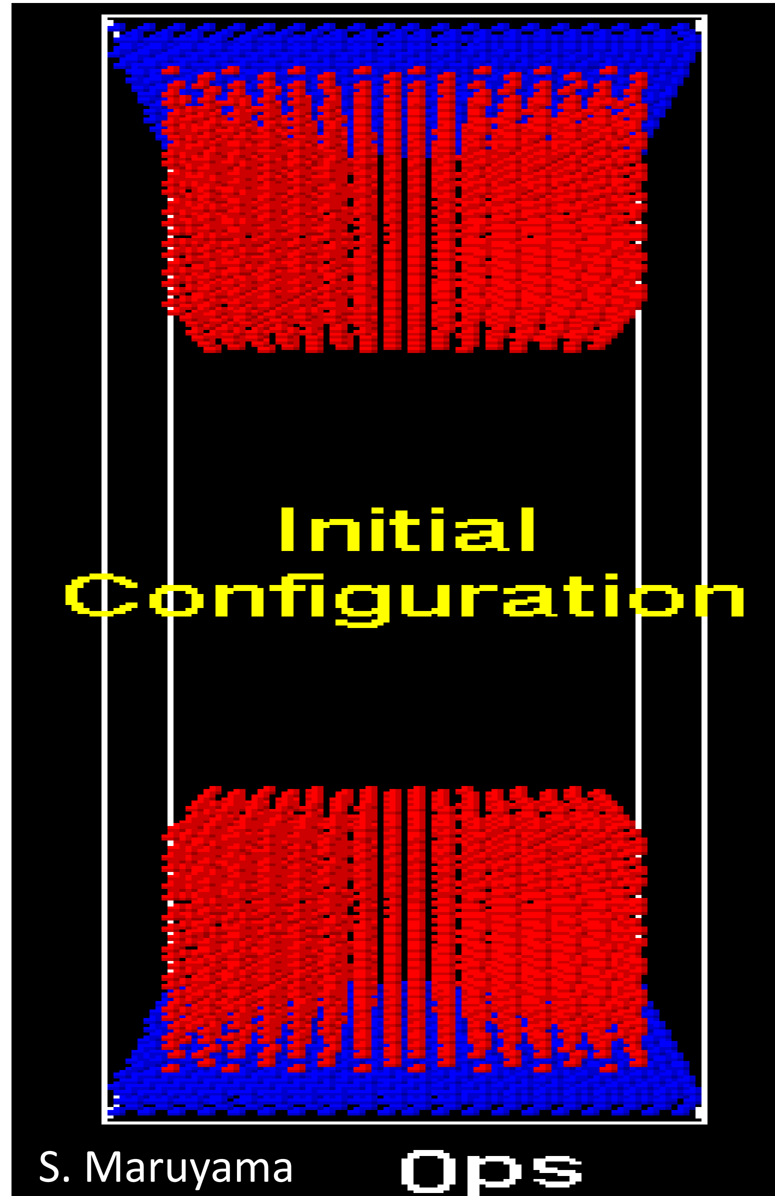
PVT, γ, η, *D*, *k* …

Test/Development of Models/Theories

- ✓ *Equation of State*
- ✓ *Excess entropy*
- ✓ *Boundary conditions…*

Pseudo-experimental Data

- ✓ *Viscosity*
- ✓ *Diffusion coefficients*
- ✓ *Slip length …*



The strategy : From the nano to the macro scale

Develop/use simulations codes to study/model finely fluid properties/behaviors and transport

Properties

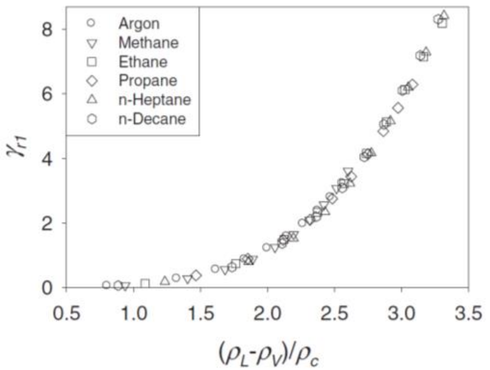
Coarse grain, entropy scaling …

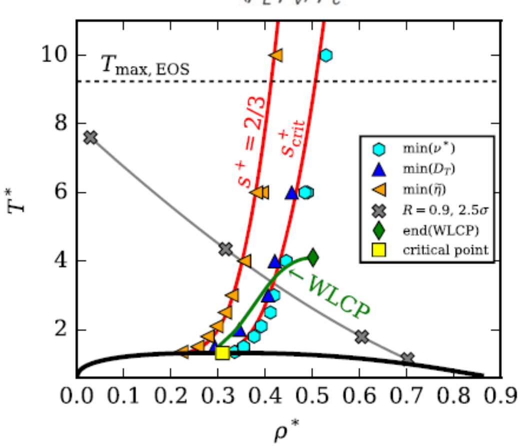
Physical mechanisms

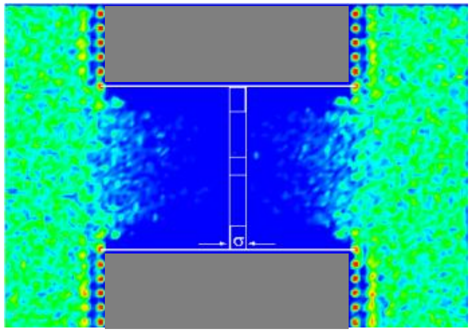
Transport, Osmosis …

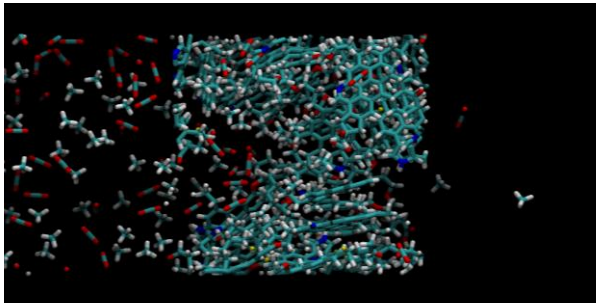
Direct/indirect upscaling

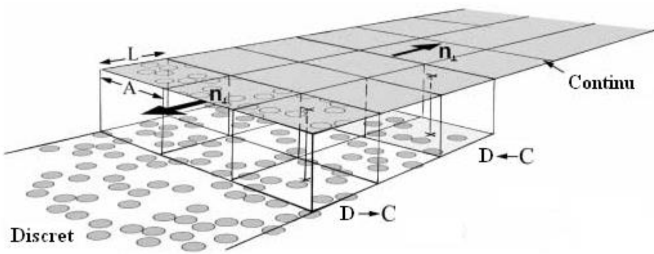
Boundary conditions …

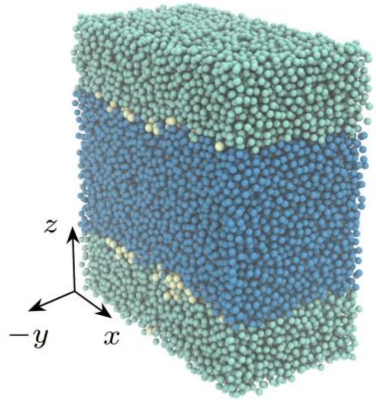








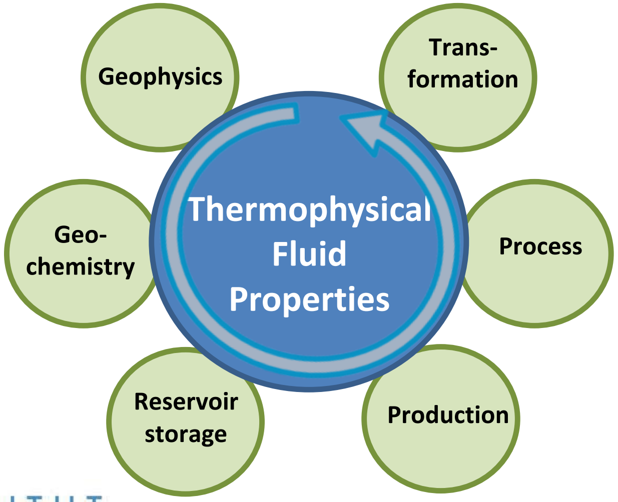




COLLÈGE STEE
SCIENCES ET TECHNOLOGIES
POUR L'ÉNERGIE ET L'ENVIRONNEMENT

SOME RESULTS

I. FROM THE MOLECULAR SCALE…



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

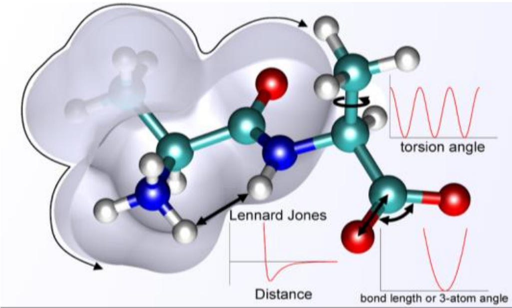
FLUID PROPERTIES: TOWARDS A COARSE GRAINED MODEL

A.W.S. HAMANI, S. KHENNACHE, H. HOANG, J.L. DARIDON (LFCR)
S. DELAGE (LMAP)

Delage et al., JCP (2015), Hoang et al., IECR (2017), Saley Hamani et al., JSF (2019, 2020) …

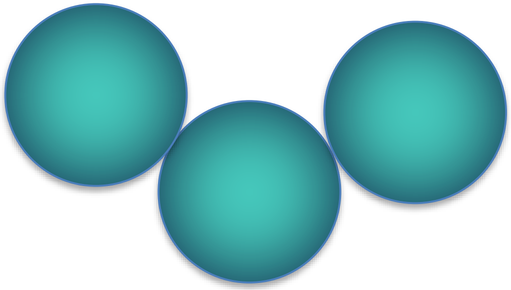
Is it possible to build an efficient coarse grained molecular model to describe fluid properties ?

Detailed molecular model



Dozens of parameters
Hours to Days

Coarse Grained model



4 parameters
Milliseconds to hours

$$U_{Mie} = C\varepsilon\left[\left(\frac{\sigma}{r}\right)^{\lambda} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

Mie potential
+ freely jointed chain

Compatible with SAFT EoS

Top-Down strategy for parameterization

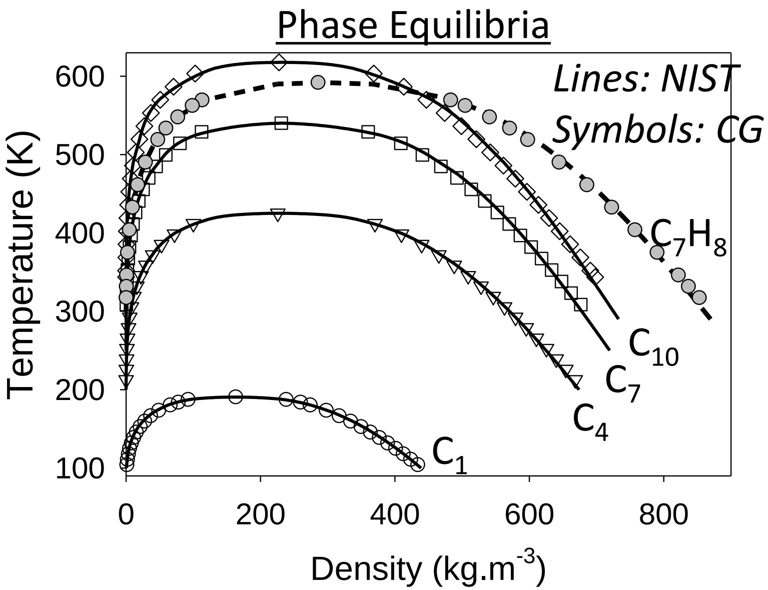
Phase equi. + Viscosity
T_c, $\rho_{Tr=0.7}$, ω, $\mu_{Tr=0.7}$

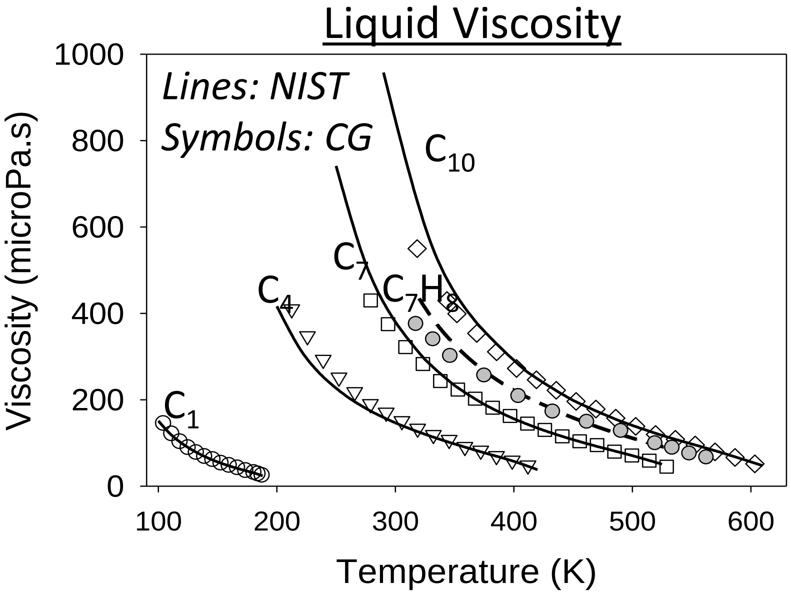
Corresponding States

Mie Coarse Grained model
ε, σ, N, λ

What about its accuracy?

Coarse Grained Model: What can be expected ?





Exact T_c, deviations on P_c ~5 % and on ρ_l ~0.5 %

Interfacial tensions, diffusions, mixtures properties are equally good

Simulations time is roughly one order shorter than an all-atoms model

Bulk thermophysical properties are very well estimated !

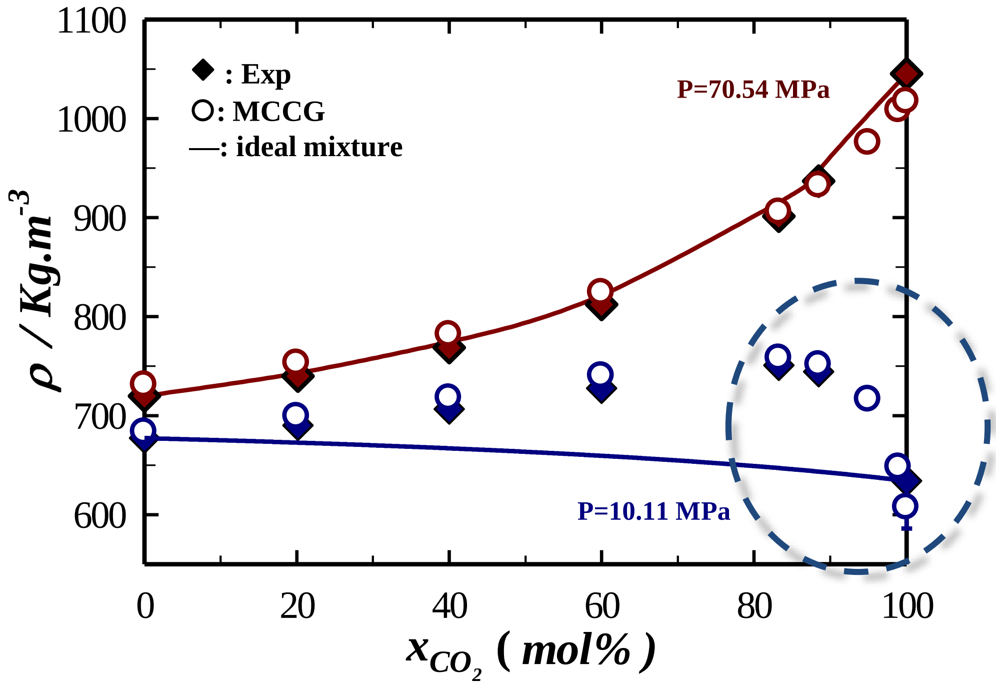
How to deal with more complex molecules, i.e. H-bonding ones ?

How to include internal rigidity in SAFT EoS *(PhD Samy Khennache)*?

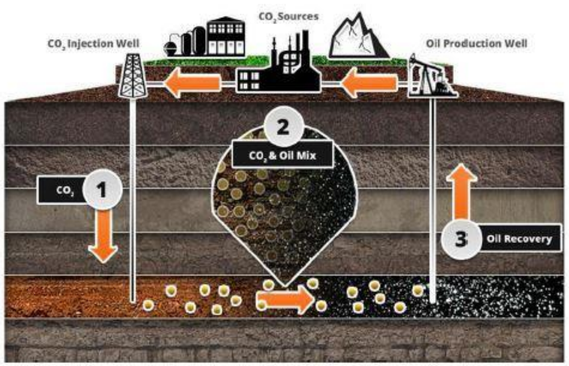
APPLICATION: CLUSTERING EFFECT

Study the non ideal behavior of CO_2+n-C7 close to CO_2 critical point

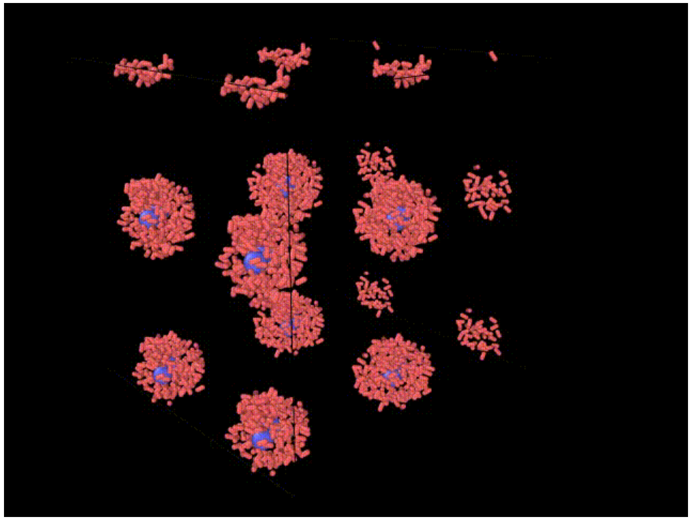
CO2-nC7 density at 313.25 K



CO_2-Enhanced Oil Recovery



Clusters of CO_2 around n-heptane



Non ideality can appears at infinite dilution !

These CG simulations can help to characterize clustering effects

II. … TO THE MACROSCOPIC SCALE

ELEMENTAL FRACTIONATION OF NOBLE GASES: THINGS ARE NOT ALWAYS COMPLEX …

H. HOANG, A. BATTANI (LFCR)

J. SCOTT, M. PUJOL (TOTALENERGIES)

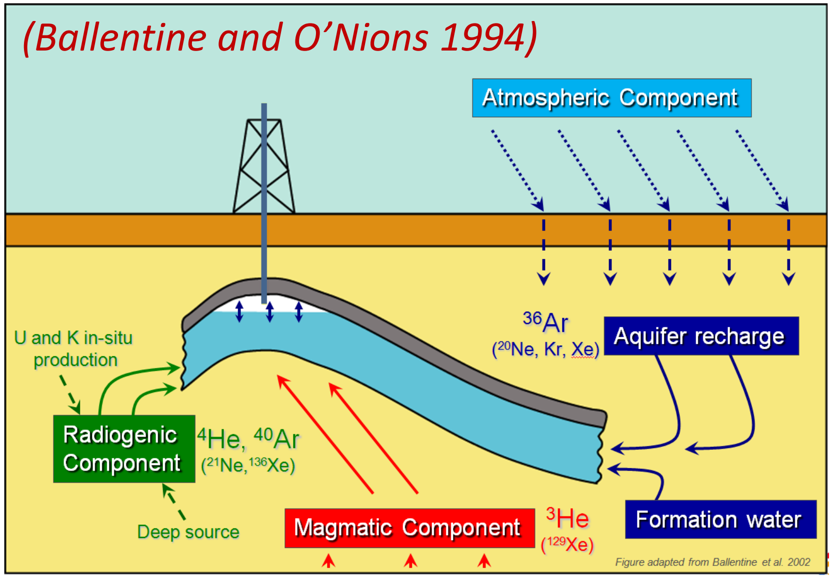
Hoang et al., EPJE (2019), Hoang et al., GCA (2021)

TotalEnergies

ISSUES

Fluid tracers relative contents ("Fractionation") are useful to manage reservoir (gas/CO2 storage, fluid origins …)

Noble gases as tracers?
Chemically inert & Ubiquist



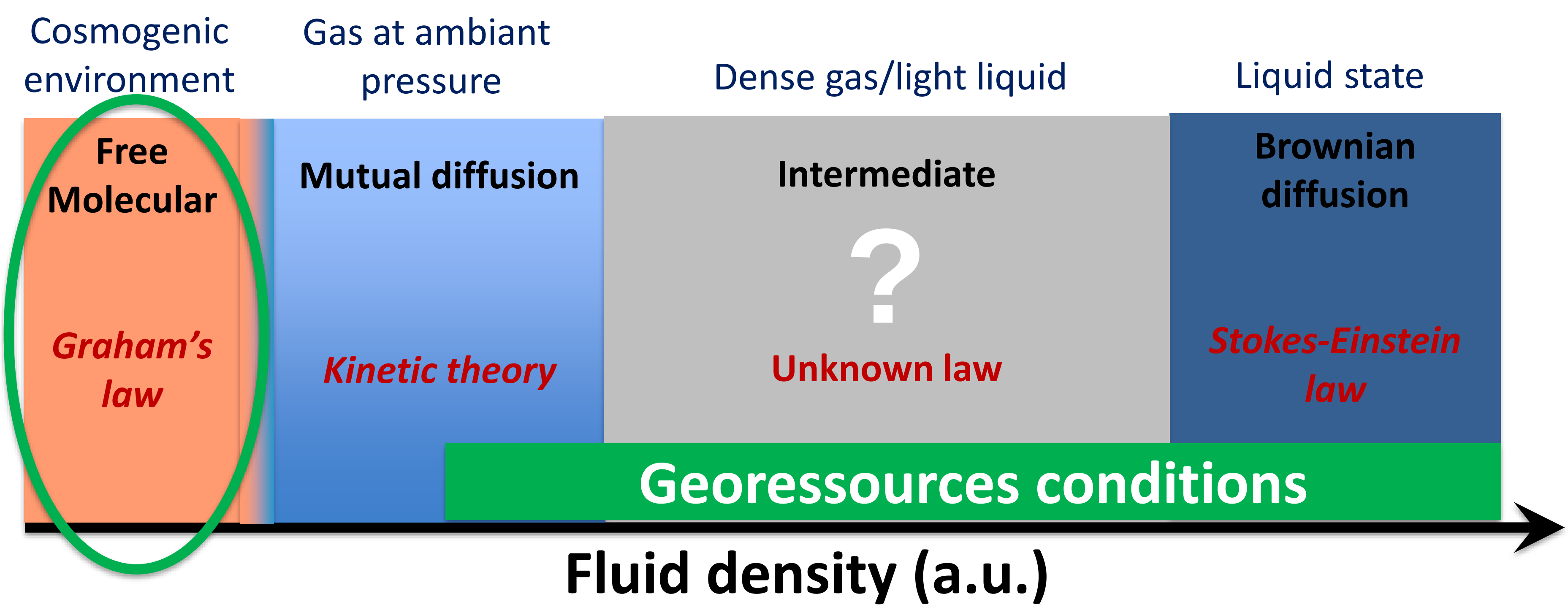
Fractionation by physical phenomena only :

- ✓ Thermodynamic
- ✓ Kinetic (Diffusion)
- ✗ ~~*Reactions*~~

But there is a lack of data and models are questionable …

MODELING ISSUES

Tracers are used to assess fluid migration, origins …
but are their (diffusive) fractionation well modeled ?

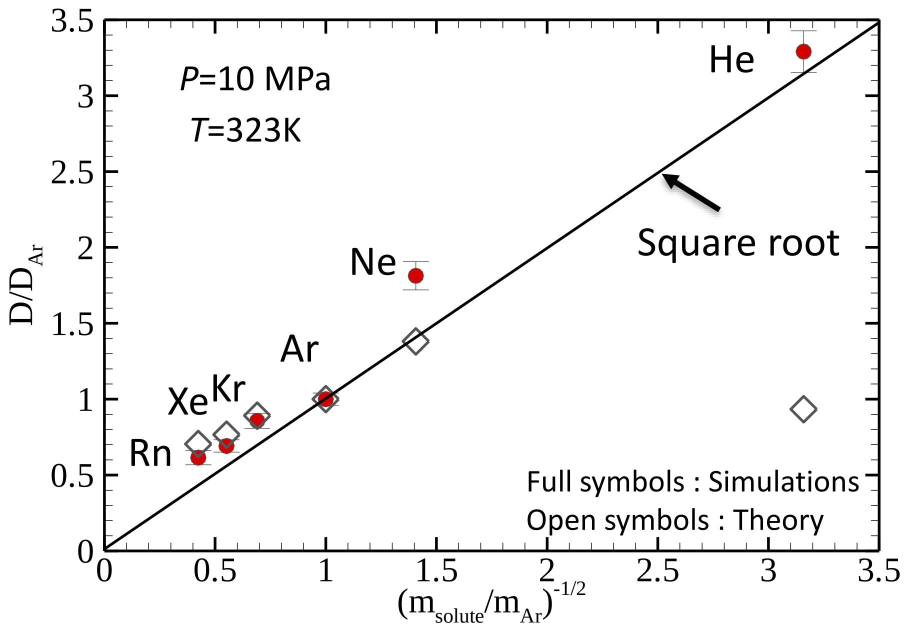


Often used in the
Geo-chemistry community
(Square root of mass)

No law a priori **valid to model appropriately element & isotopic fractionation**

Elemental Fractionation by Mass diffusion

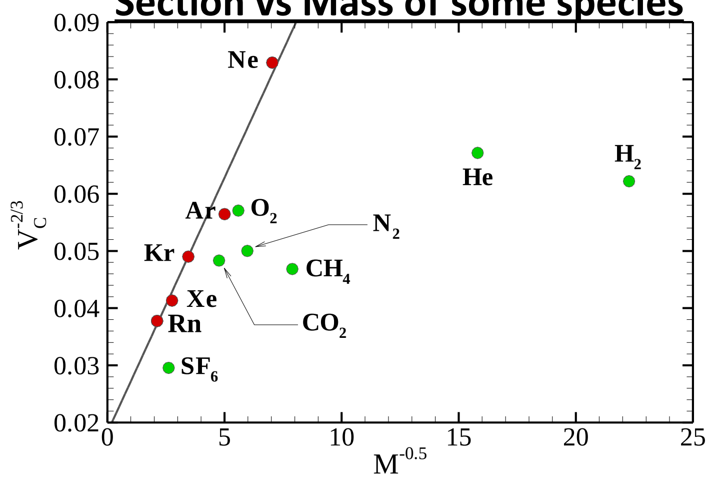
Elemental diffusion in n-hexane



Similar result in gas (and in water)

The $M^{-1/2}$ rule holds because of equivalence between mass/size effects ($r^{-2} \propto M^{-1/2}$), but that is size which matters ...

Section vs Mass of some species



The $M^{-1/2}$ rule holds well for Noble Gases fractionation in gas and liquids but does not work for isotope fractionation !

Similar results on C and H isotopes (BTEX in aquifers)

Initial State of A Reservoir: Impact of Thermodiffusion ?

F. Montel(LFCR), V. Vesovic (ICL), B. Rousseau (UPS), S. Xu (CAS), K. Zhang (RIPED)

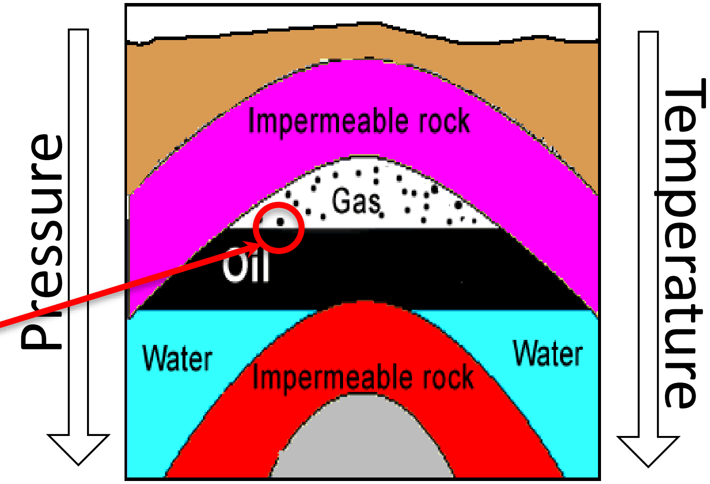
Galliero et al., NPJ Micrograviity, 2017, Braibanti et al. EPJE 2019, Hoang et al., EPJE 2019, 2022 …

RIPED TotalEnergies esa

ISSUES

Modeling pressure and compositional gradient in reservoir is essential to avoid errors in OIP/GIP

- More sampling/PVT operations are needed otherwise
- Gas Oil Contact location can be inferred from **compositional gradient**



Main "forces" shaping the compositional gradient:

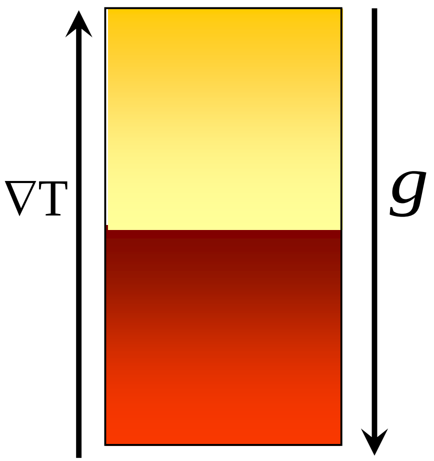
Gravity and geothermal gradient

(Segregation + thermodiffusion/Soret effect)

But data are scarce and models are complex …

Could MD simulations help in modeling contributions of gravity and thermodiffusion/Soret to species distribution ?

How to mimic a fluid column (of ~100m) at the nanoscale (of ~10 nm) ?



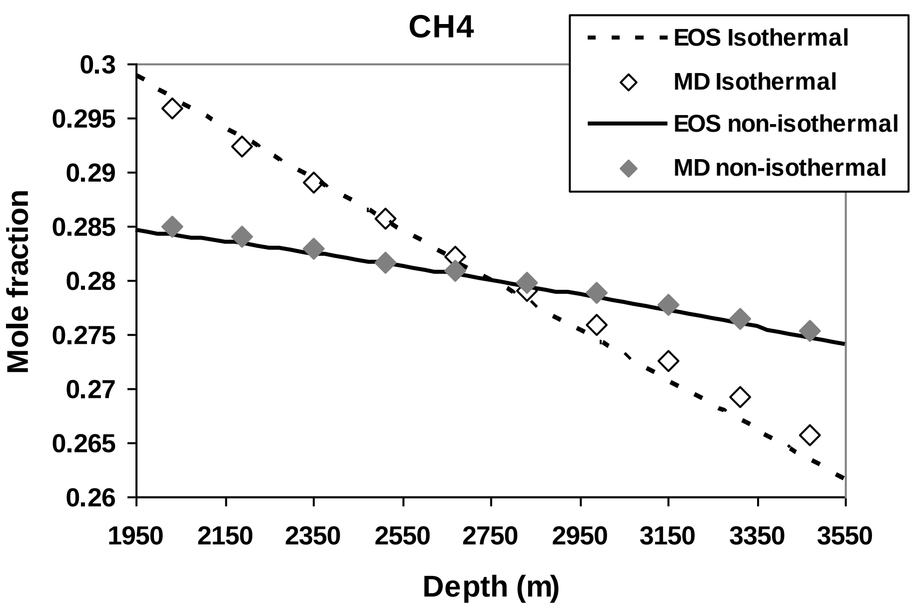
Mol. Sim. with *g* and *∇T* amplified by a factor ~10^{10} (still linear response !)

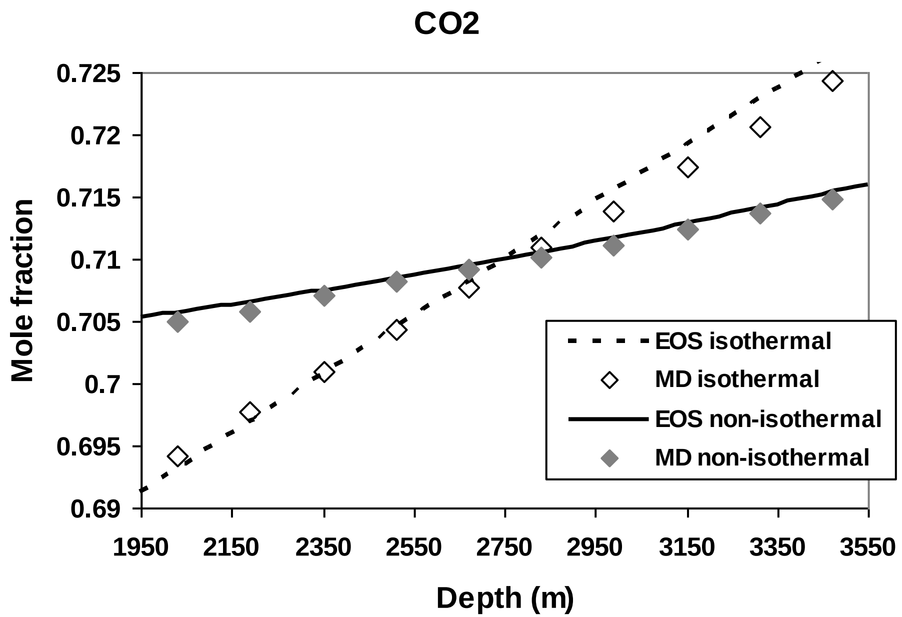
Usual modeling: cubic EoS + empirical laws for thermodiffusion

This scheme has been validated on ideal mixtures

THERMOGRAVITATION OF ACID GAS: NOT THAT SIMPLE !

Mole fraction: C_1 = 0.28, CO_2 = 0.71 and H_2S = 0.01, 443.15 K and 40 MPa, h = 1600 m

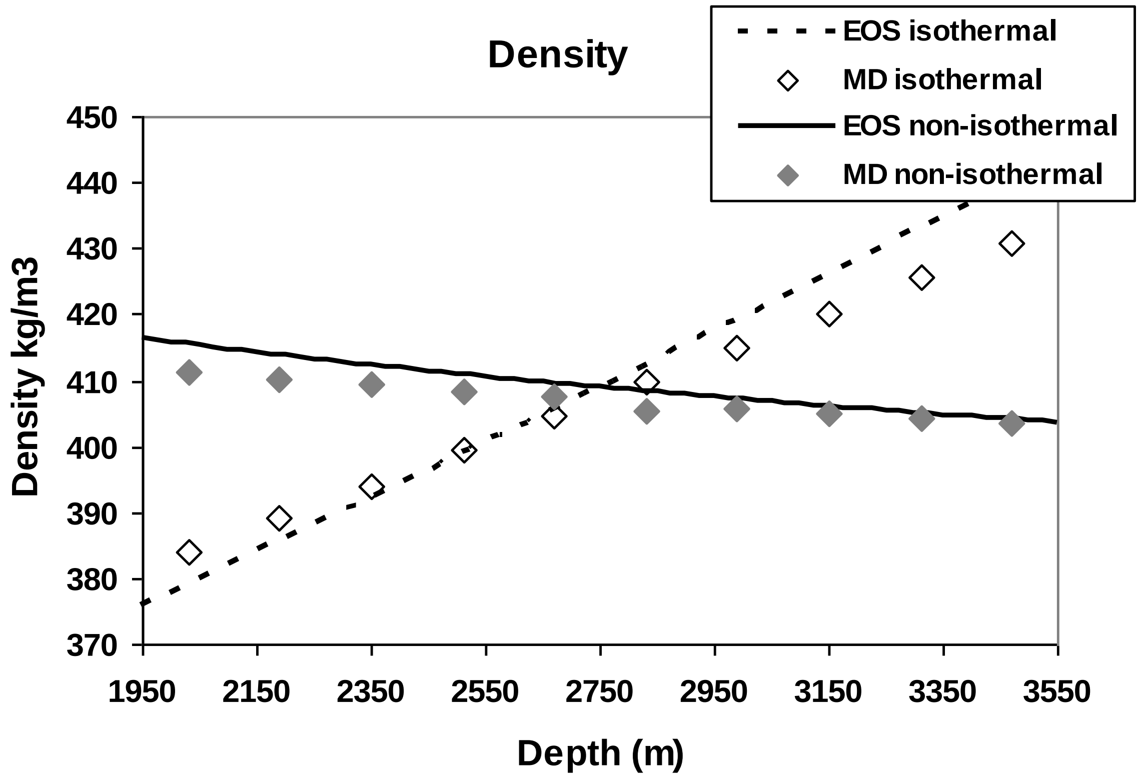




Good agreement with EoS combined with MD data on Soret

Thermodiffusion reduces significantly the CO_2 gradient!

THERMOGRAVITATION OF ACID GAS: UNSTABLE ?



In some cases the fluid column can be unstable !

In some oil & gas reservoirs thermodiffusion is as important as segregation

One problem is to evaluate thermodiffusion coefficients (Models limitations)

Hoang et al., EPJE 2022

OUTCOMES

TAKE HOME MESSAGES

MS gives access to information inaccessible by experiments and/or behaviors not well tackled by continuum approaches

Help in further developing thermodynamics models

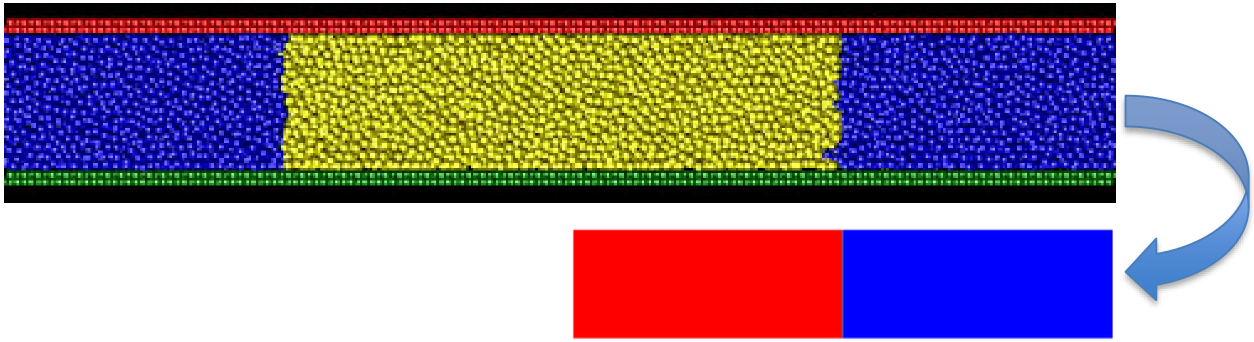
✓ *Immediately applicable for a lot of systems (but not all!)*
✓ ***Allow to check/enhance some (macro)physical concepts***

but

❑ *Based on "molecular models" with intrinsic limitations*
❑ ***Upscaling not always easy for heterogeneous systems***

Molecular Dynamics

Computational Fluid Dynamics



Si Hadj Mohand et al., JCP 2019

THANKS TO ALL COLLABORATORS


Samy Khennache


Dr. Aboul Hamani


Dr. Hai Hoang

PhD & PDRA


Dr. François Montel

Prof.


Dr. Romain Vermorel


Prof. J.L. Daridon


Dr. Magali Pujol


Dr. Julien Collell

TotalEnergies

And Dr. S. Delage, Dr. A. Battani, Prof. V. Vesovic …

AND THANK YOU FOR YOUR ATTENTION !

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

TotalEnergies

cnrs

e2s UPPA energy environment solutions

Extra Slides

NANOPOROUS FRACTIONATION:
ON THE INFLUENCE OF CLAY INTERLAYER

B. BENAZZOUZ, H. HOANG, A. BATTANI (LFCR)

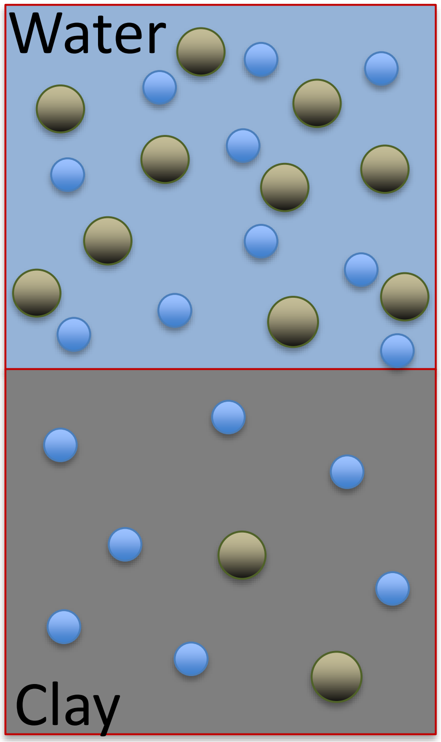
J. SCOTT, M. PUJOL (TOTALENERGIES)

Benazzouz et al., JNGSE (2021)

TotalEnergies

INSTITUT CARNOT ISIFoR

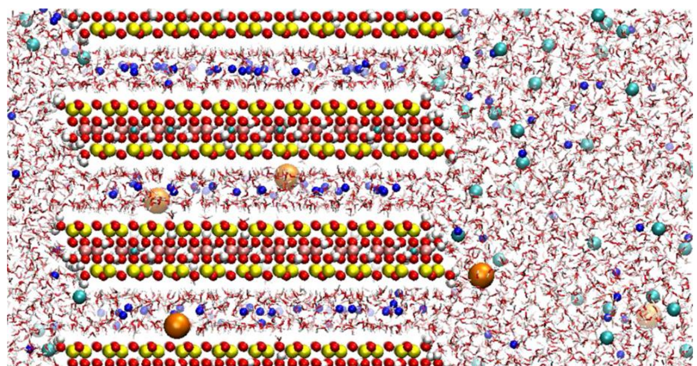
Issues on Fractionation due to Clay



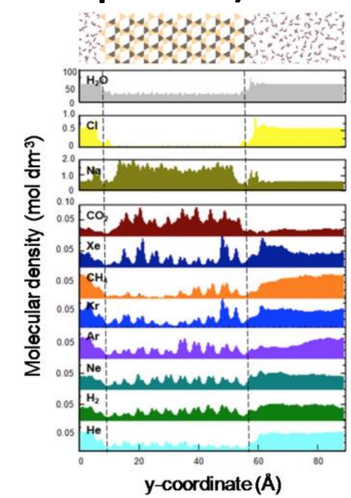
Nanoporous fractionation :

Isotopes: negligible, elements: ?

Fractionation in clay interlayer due to sieving effect + oversolubility (absorption) ?



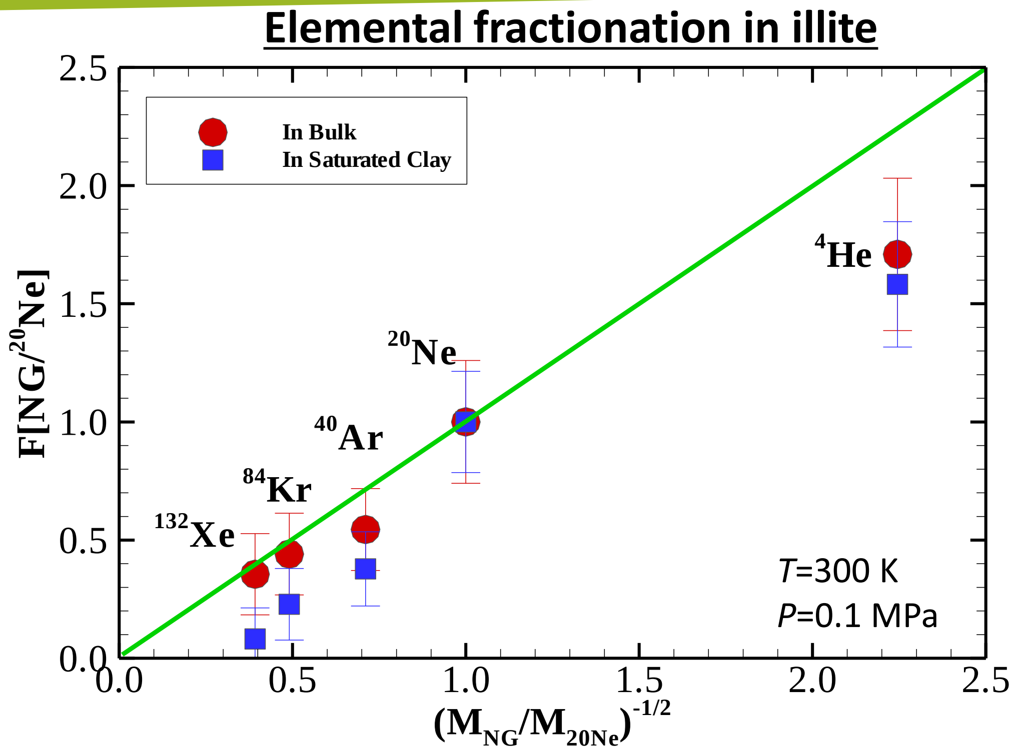
Gadikota et al., 2017



Could clay interlayers induce fractionation of elements ?

Evaluation of solubility + diffusion of NG in saturated clay interlayers

Issues on Fractionation due to Clay



Extreme confinement (not the surface) can lead to "fractionation" of Noble Gases

Results are (too?) extremely sensitive to molecular models details …

Impact on quantification of leakage through caprocks!