APPORT DE LA MODÉLISATION MOLÉCULAIRE À LA COMPRÉHENSION DU COMPORTEMENT THERMODYNAMIQUE DES FLUIDES CONFINÉS

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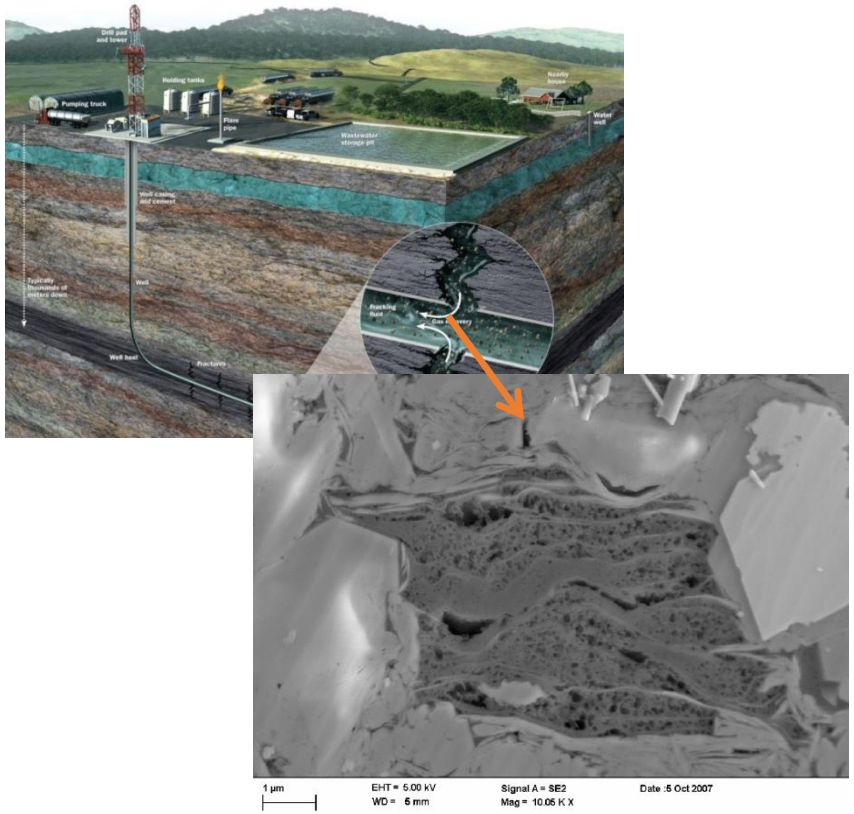
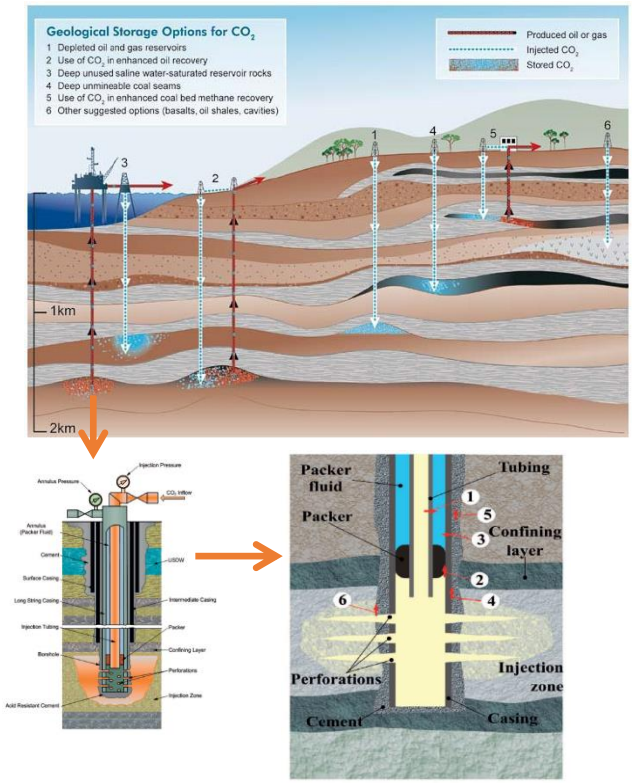
CONTEXT OF APPLICATIONS (I)

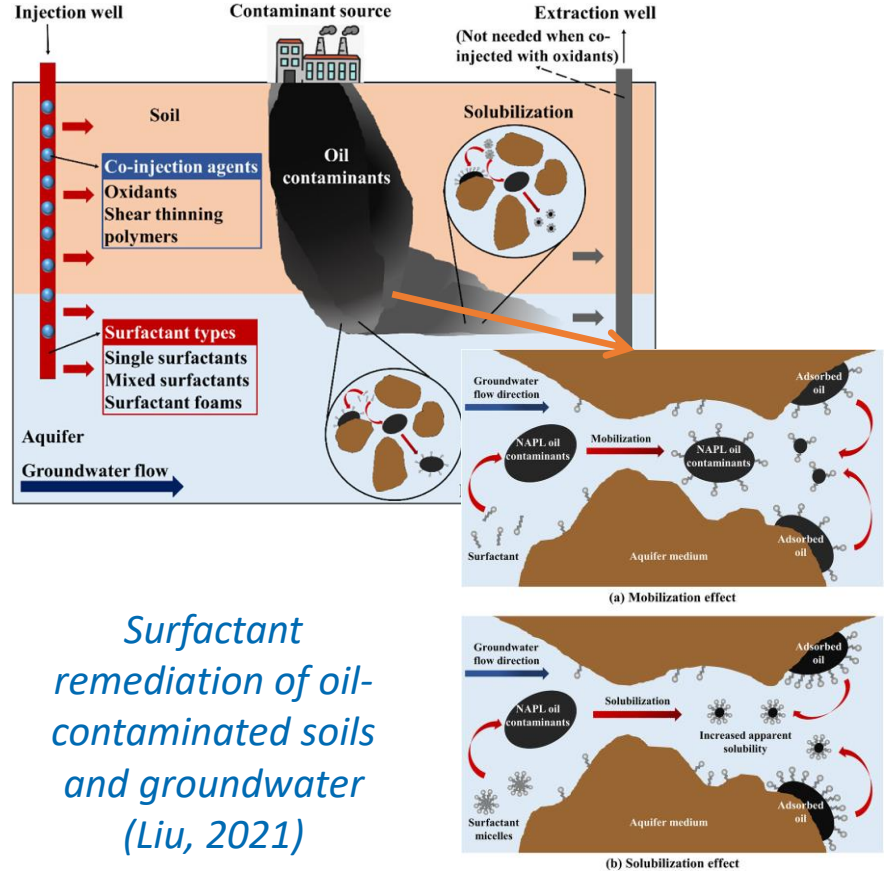
- Understand the phase behavior of fluids under confinement or adsorbed at mineral surfaces
- Problem can be present in different applications: Shale reservoirs, CCS, soil decontamination



Scanning electron microimage of Barnett Shale (Wang, 2009)



Integrity of wells for CO_2 injection at reservoir conditions (Pasic, 2011)



Surfactant remediation of oil-contaminated soils and groundwater (Liu, 2021)

CONTEXT OF APPLICATIONS, LENGTH SCALES VS CONFINEMENT & STATISTICAL MECHANICS

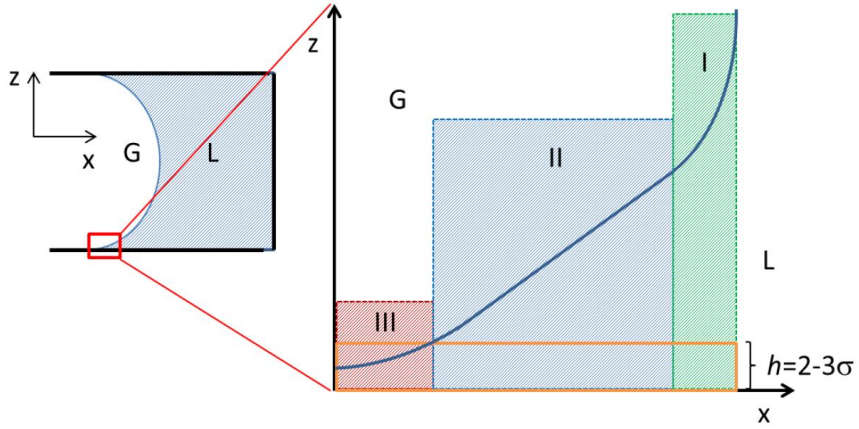
- Strong rock-fluid interaction within nano-pores at reservoir thermodynamic conditions
- Very heterogenous pore size distribution (PSD)
- Nanoscale confinement changes the PVT behavior of the fluid at small scale
- Impact on reservoir/injection/production monitoring at large scale

Consider materials of different porosity size (crystalline or not)
IUPAC: microporous (<2 nm), mesoporous (2-50 nm) and macroporous (>50 nm)

I. Capillary zone → Classically handled by Laplace-Young (L-Y)
II. Transition zone → Extension of L-Y by including the adsorbed layer though $\Pi(h)$ (disjoining pressure vdW+elec)
III. Molecular zone→ Governed by the relative strength of adsorbate-wall vs adsorbate-adsorbate interactions

Representation of a capillary rise in contact with bulk @ LV equilibrium

In macropores in contact to a LV bulk system



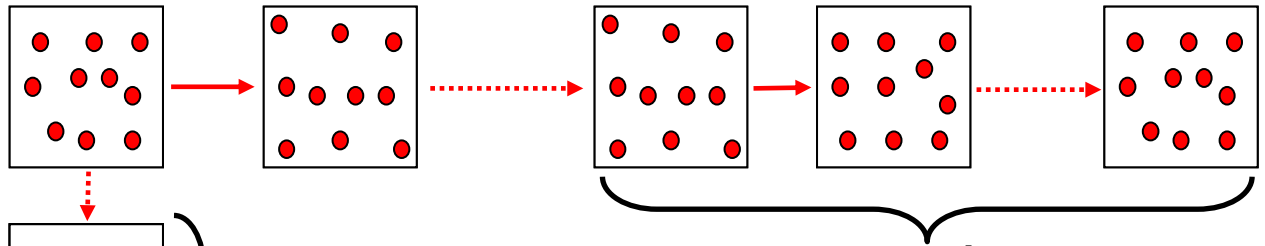
Molecular simulation techniques are at the appropriate length scale

Thermodynamics ←→ Statistical mechanics

[1] Gelb & Gubbins Rep. Prog. Phys. 1999, 62, 1573-1659
[2] Gubbins et al. J. Chem. Therm. 2014, 74, 169-183

MOLECULAR SIMULATION TECHNIQUES

Monte Carlo: Statistical method (Markov chain + Metropolis algorithm) ensuring occurrence of configuration $i \sim \exp(-U_i/kT)$



Representative array of n configurations ($n > 5.0 \times 10^7$)

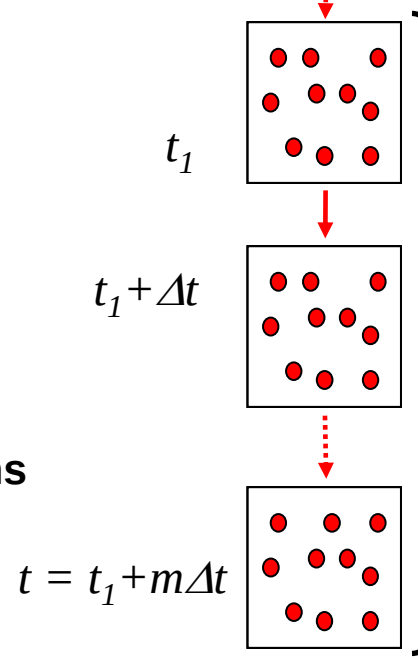
$$\langle X \rangle_{MC} = \frac{1}{n} \sum_{i=1}^{n} (X_i)$$

Molecular Dynamics:

Integration of Newton's equations of motion

Δt = 1 to 2 fs

$m\Delta t$ = 4 to 5 ns



$$\langle X \rangle_{MD} = \frac{1}{t} \int_{t1}^{t} X(t) dt$$

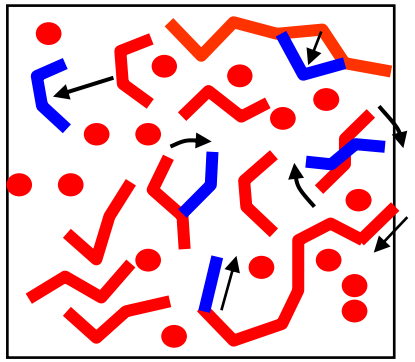
averages for property $X = V, U, \ldots$

Ergodicity theorem: $\langle X \rangle_{MD} = \langle X \rangle_{MC}$

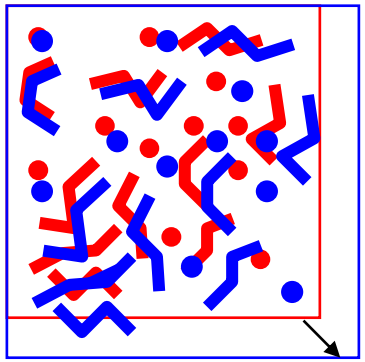
Statistical mechanics ⇔ Thermodynamics

MONTE CARLO SIMULATION AT DIFFERENT ENSEMBLES

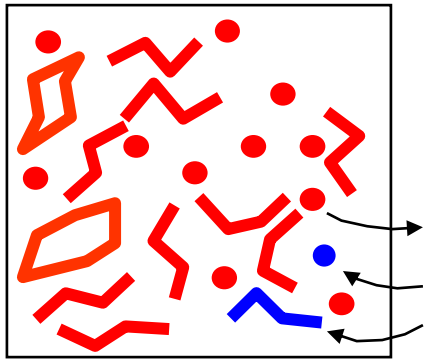
All ensembles (NVT, NPT,…)
Internal moves (thermal equilibrium) :
Translation, rotation, reptation*, flip, regrowth*



NPT ensemble
volume changes (mechanical equilibrium at fixed pressure)



Grand Canonical (μVT) ensemble
Insertions - destructions, particle exchange (chemical equilibrium)*

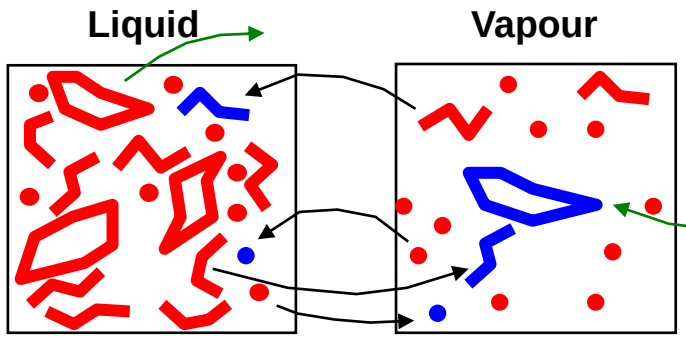


Average properties X= V,U.., from Configurations

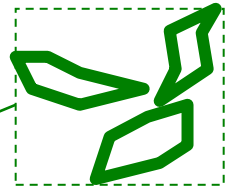
$$\langle X \rangle_{MC} = \frac{1}{n}\sum_{i=1}^{n}(X_i)$$

Gibbs ensemble NVT (phase equilibrium without explicit interface) :
All previous mouvements

Transfers between phases *



reservoir of molecular conformations



Basic ensemble for VLE of bulk fluids

* moves using statistical bias techniques such as Configurational Bias Monte Carlo[1] or reservoir bias [2]

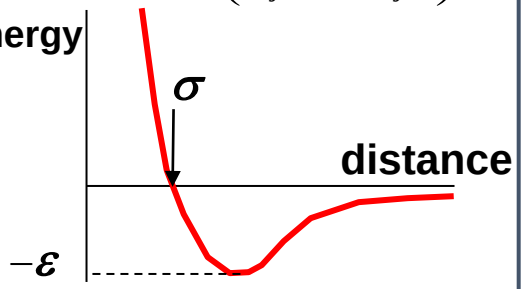
[1] Smit et al., JCP, 1995, 102, 2126
[2] Bourasseau et al. , JPC-B, 2002, 106, 5483

FLUID-FLUID & WALL FLUID INTERACTIONS

Fluid-fluid

Lennard-Jones potentiel

$$U^{disp-rep}{}_{ij} = 4\varepsilon\left(\frac{\sigma^{12}}{r_{ij}{}^{12}} - \frac{\sigma^{6}}{r_{ij}{}^{6}}\right)$$

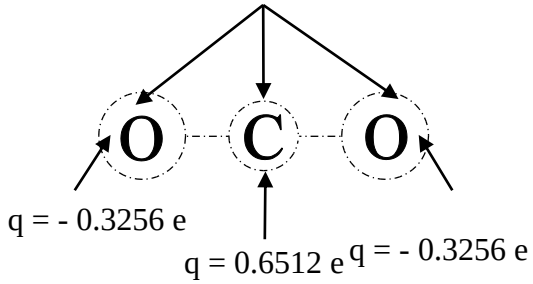


Electrostatic energy

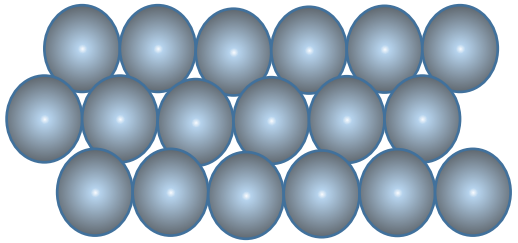
$$U^{el}{}_{ij} = \frac{q_i\, q_j}{4\pi\varepsilon_o r_{ij}}$$

- Rigid molecule [1]
- Three 6-12 Lennard-Jones centers + three-point charges

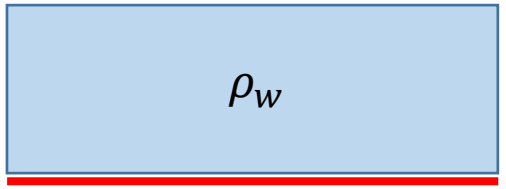
3 Lennard-Jones centers
(σ_O = 3.03 Å and ε_O = 80.507 K)
(σ_C = 2.76 Å and ε_C = 28.129 K)



Wall-fluid [2]



Integral form



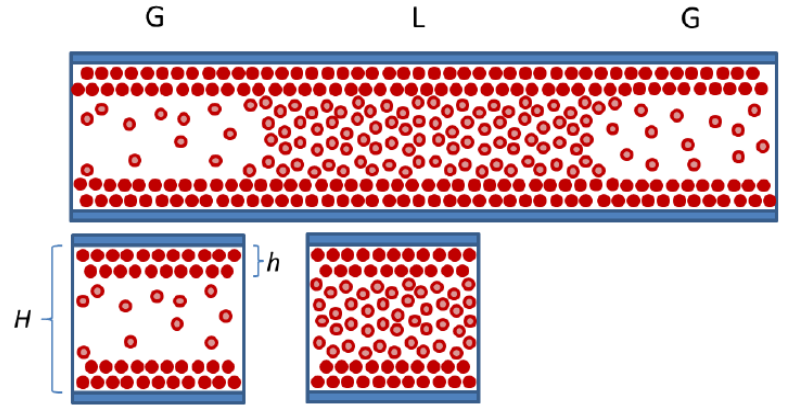
$$U_{wf} = \frac{2}{3}\pi\rho_w\epsilon_{wf}\sigma_{wf}^3\left[\frac{2}{15}\left(\frac{\sigma_{wf}}{z}\right)^9 - \left(\frac{\sigma_{wf}}{z}\right)^3\right]$$

Graphite model [3] → Lorentz-Berthelot → ϵ_{wf} & σ_{wf}

$$U_{\mathrm{Tot}} = U^{disp-rep} + U^{el} + U_{wf}$$

Explicit LV interface

LV without interface

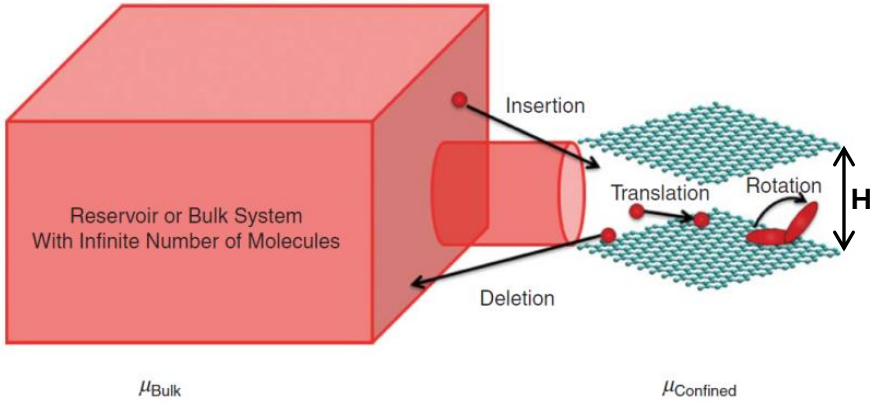


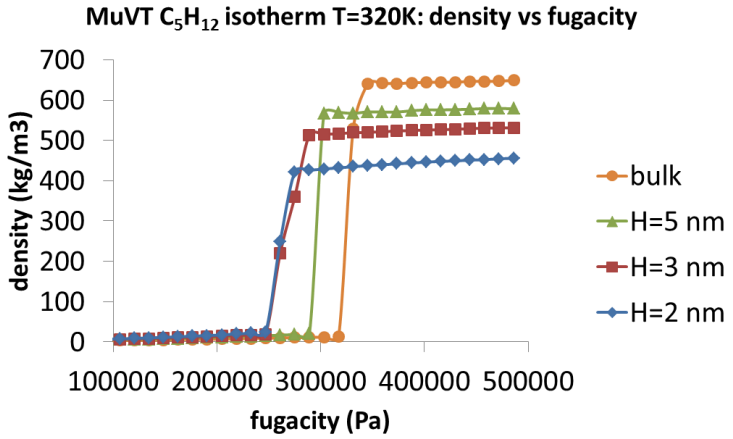
Avoid the explicit description of the interface

[1] Harris & Yung, J. Phys. Chem. 1995, 99, 12021
[2] Gelb & Gubbins Rep. Prog. Phys. 1999, 62, 1573-1659
[3] Porcheron et al. Phys. Chem. Chem. Phys. 1999, 1, 4083-4090

MONTE CARLO SIMULATION OF VLE OF CONFINED FLUIDS

Grand canonical Monte Carlo simulation (µVT)

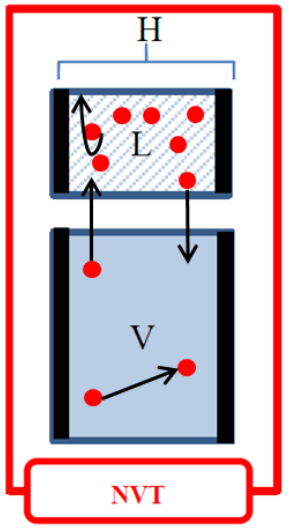


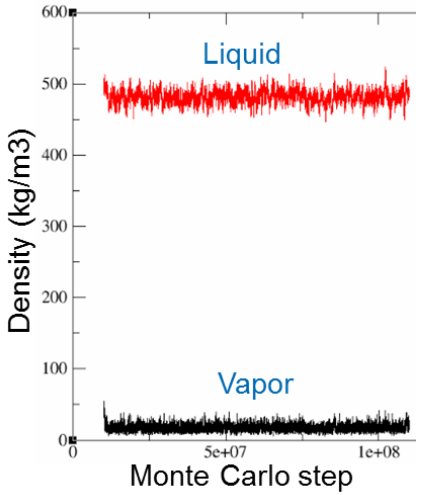


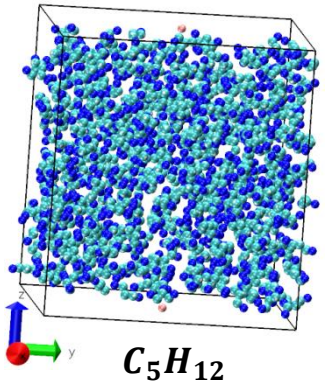
Initialisation

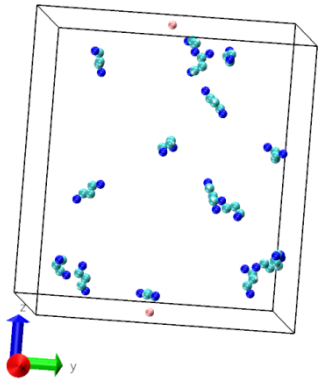
Confined Gibbs ensemble Monte Carlo simulation (NVT) [1]

Anisotropic volume change
of the two boxes







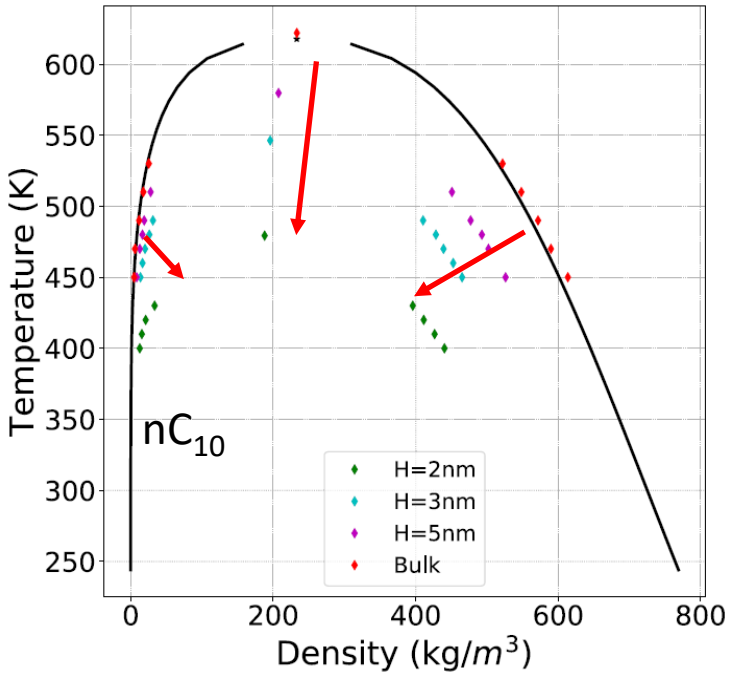


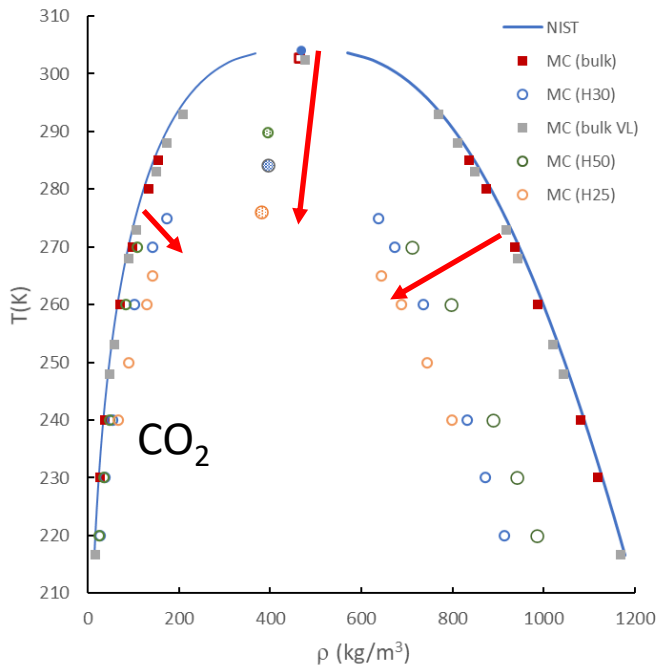
Other approaches are possible:
Configurational-bias grand-canonical transition-matrix Monte Carlo [2]

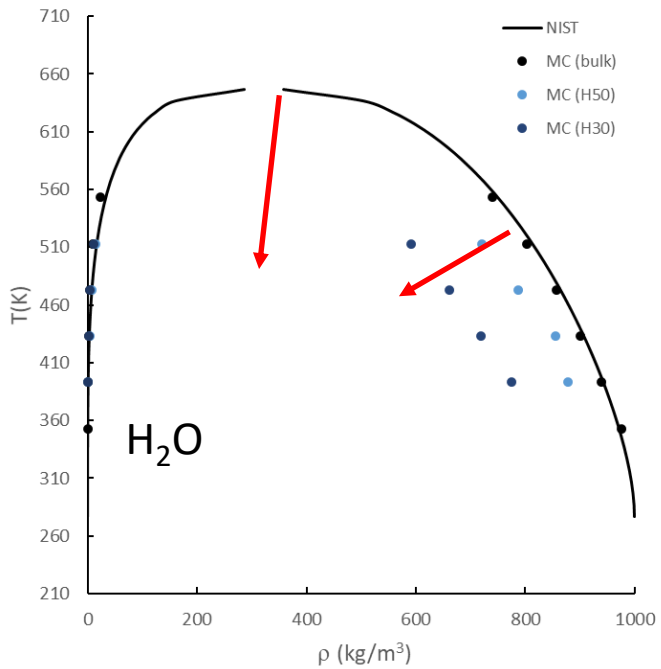
[1] Panagiotopoulos. Mol. Phys. 1987, 61, 813-826
[2] Errinton Phys. Rev. E. 2003, 67, 012102; J. Chem. Phys. 2003, 118, 9915

PURE COMPONENT VLE UNDER CONFIENEMENT

All fluids confined on ideal graphite slit pores





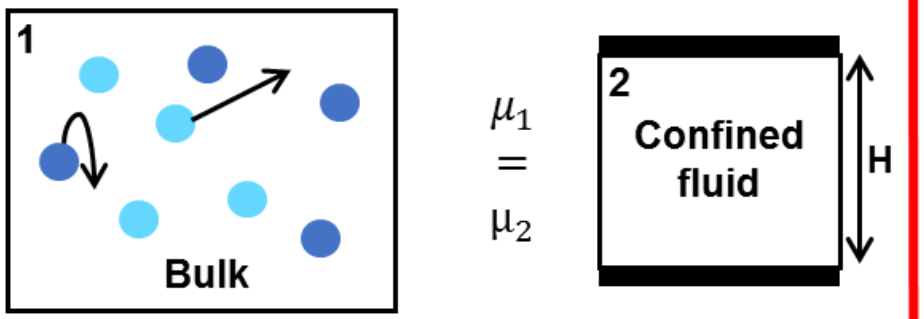


Conclusion: Systematic reduction of the VLE with confinement
→ Tc ↓ & Pc ↓ with reduction of pore size

[1] Sobecki et al. Fluid Phase Equilib. 2019, 497, 104-121

EXTENSION TO MIXTURES: BUBBLE POINT MC SIMULATION

- Gibbs ensemble Monte Carlo simulation (NPT) with BPMC [1]

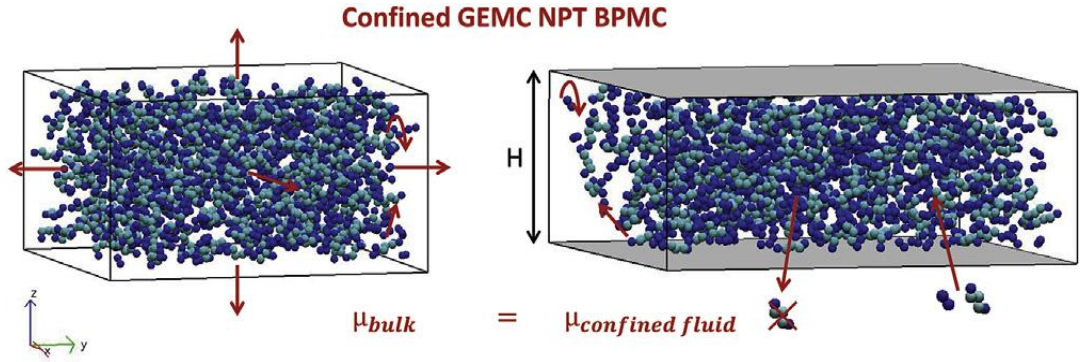


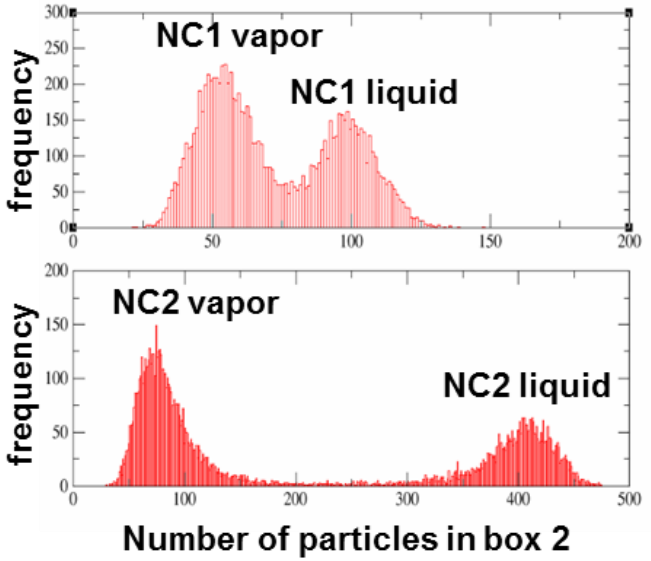
- Constant composition
- Volume change
- Initialized at vapor pressure condition (EOS)

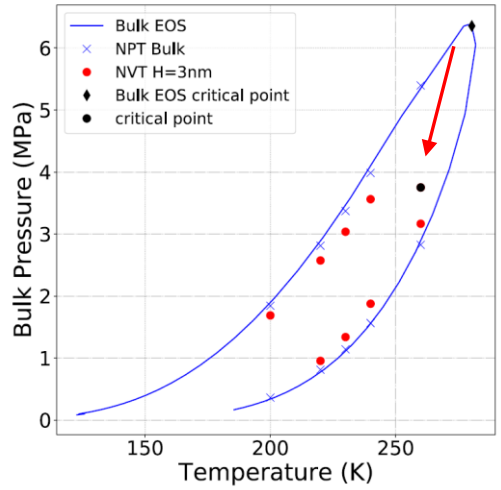
- Constant volume
- Initially empty
- Insertion
- Deletion

NPT BPMC

Bubble Point Monte Carlo





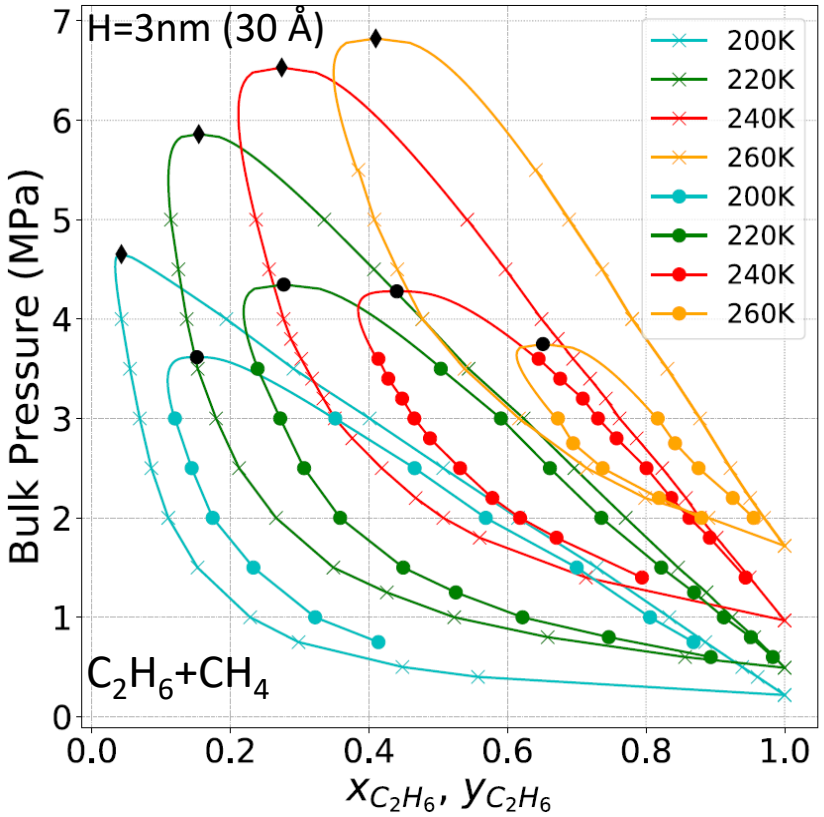


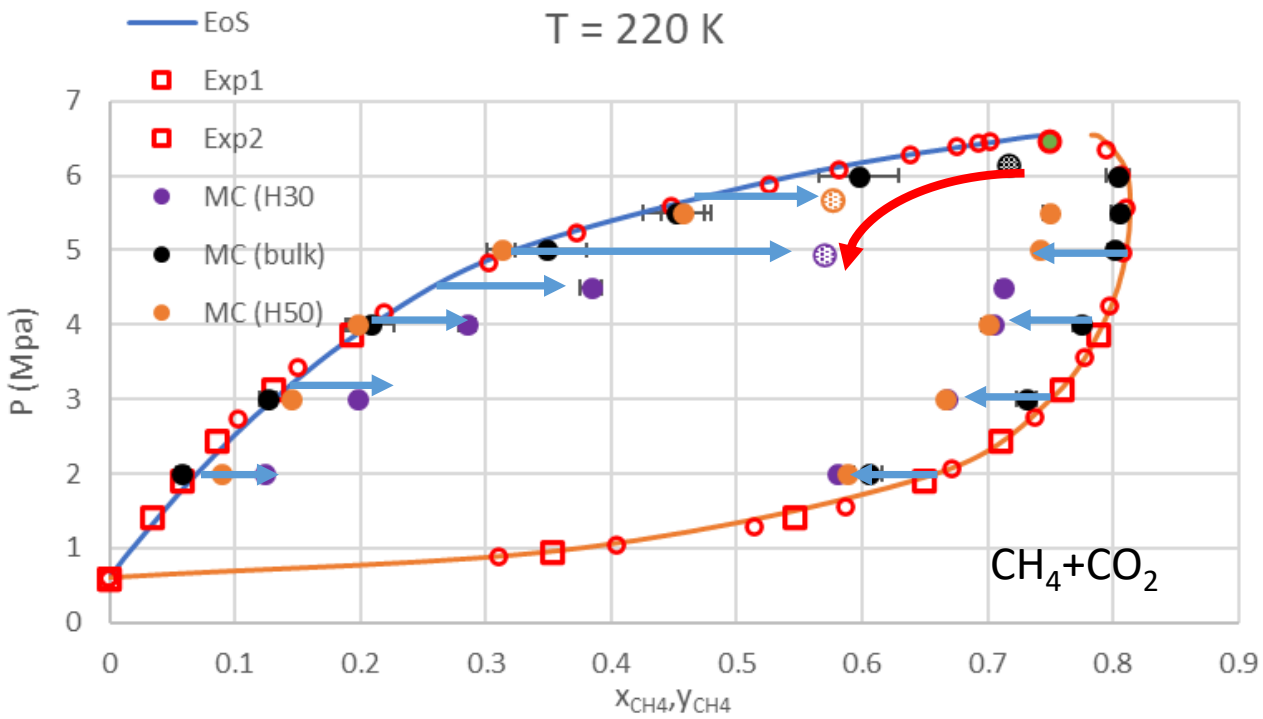
- Confined GEMC NVT → @ high pressures close to Pc

60% nC_2 + 40% nC_5 @ 3 nm graphite pore

[1] Sobecki et al. Fluid Phase Equilib. 2019, 497, 104-121

MIXTURE VLE UNDER CONFINEMENT





Conclusion: Systematic reduction of the VLE with confinement

→ Tc ↓ & Pc ↓ with reduction of pore size

→ Asymmetry between L or V in function of molecular affinity to the surface

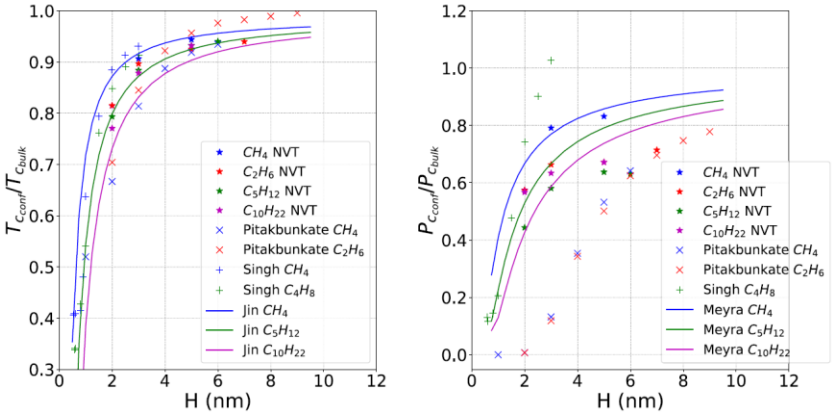
[1] Sobecki et al. Fluid Phase Equilib. 2019, 497, 104-121

EXTENSION TO LARGER LENGTH SCALES

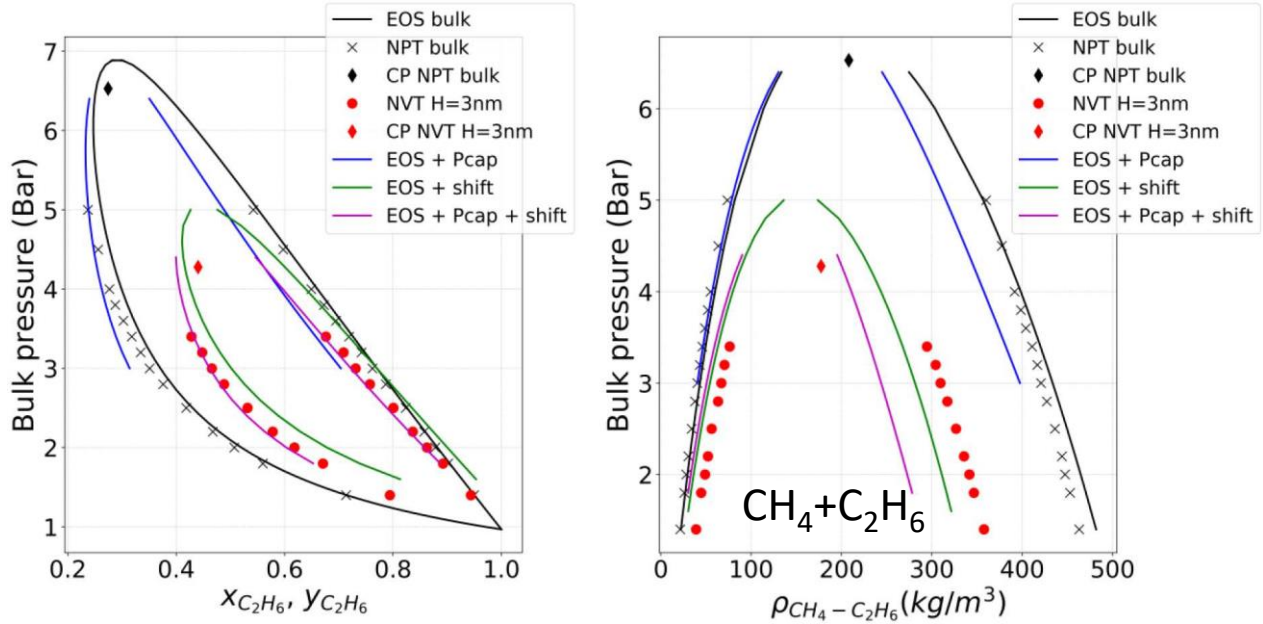
- How the information obtained from MS can be used ?
- To improve EoS (or adsorption models) to better include the confinement effect. Several approaches are possible (or combination of them):
  - Inclusion of capillary pressure (Pc)
  - Scaling of Tc, Pc of pure components
  - Inclusion of the adsorbed phases & the cooperative effect (i.e., surfactants)
- Examples:
- Phase behavior of hydrocarbons in non-conventional reservoirs simulations
  - Indirectly by using more accurate EoS with the effect of pore size (H)
  - Including the possibility to describe the heterogeneity of the medial through local PSD
- Surfactant adsorption modeling on mineral surfaces at mesoscales
  - Coarse grain simulation (DPD) → adsorption models → Lattice Boltzmann (LBM)

IMPROVEMENT OF EOS

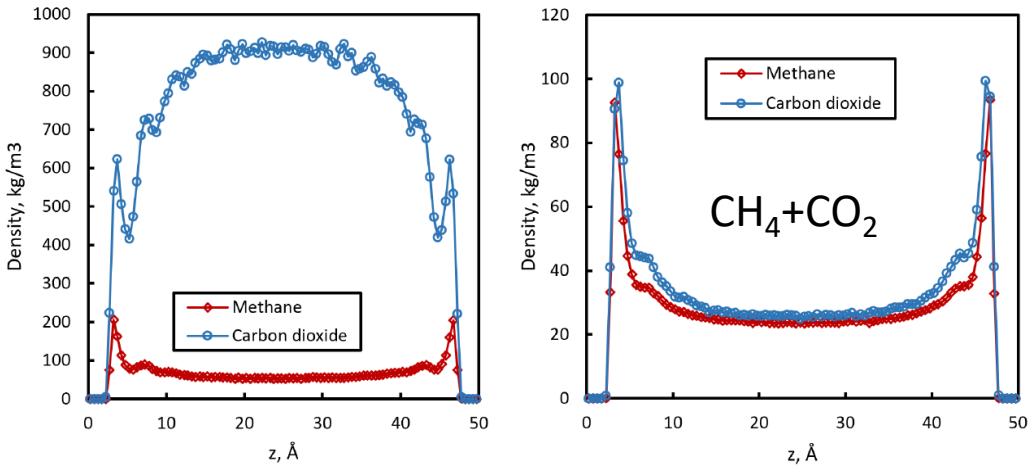
Providing correlations to model the variation of Tc (left) & Pc (right) with pore size



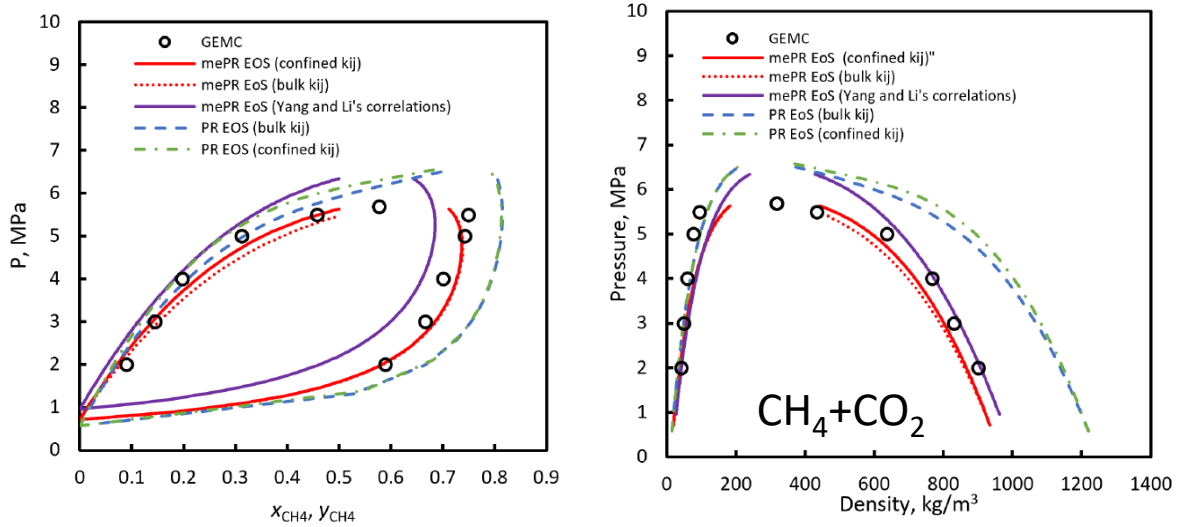
[2]



Providing additional information (local density profiles of pure & mixtures) on different phases



[3]



[1] Sobecki et al. Fluid Phase Equilib. 2019, 497, 104-121
[2] Sobecki et al. SPE-193867; J. Petril. Sci. & Eng. 2020, 193, 107364
[3] Liu et al. J. Sup. Fluids 2022 (submitted)

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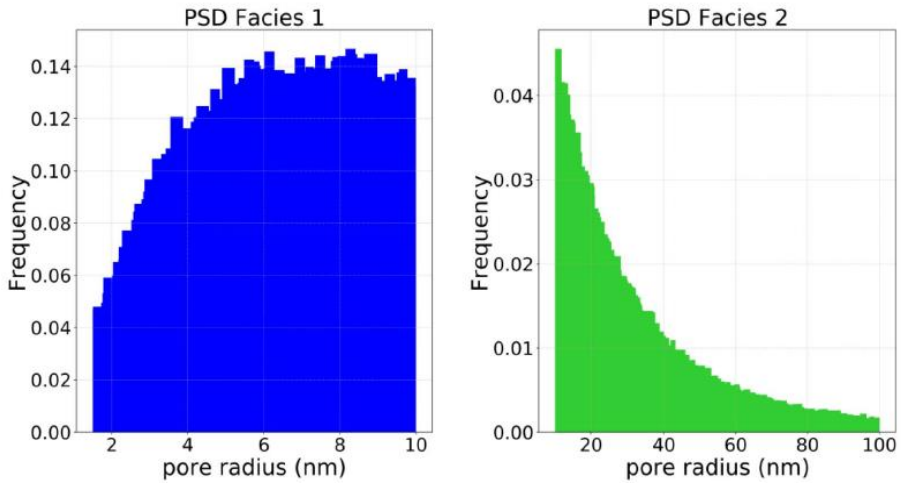
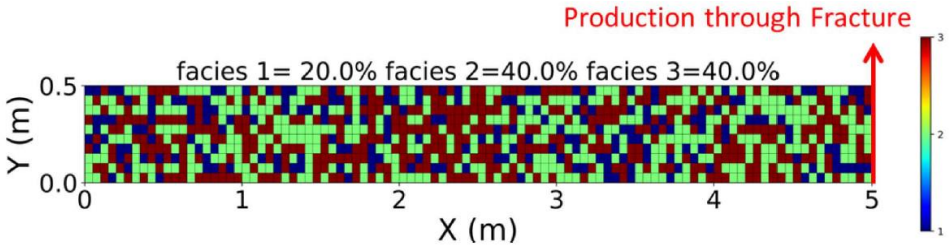
GRID MATRIX/FRACTURE PVT SIMULATION

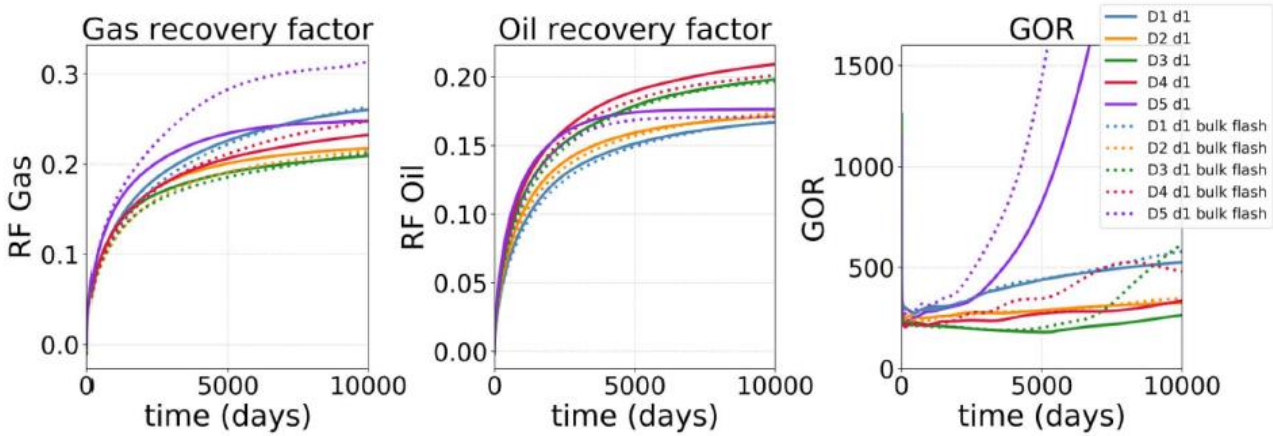
- Simulation of a fine grid including a pore size distribution (PSD) of different facies
- Influence of considering confinement in EoS on the Gas recovery factor, Oil recovery factor and Gas Oil Ratio (GOR)



Histogram of an example of PSD sample for facies 1 & 2



Example of one of the ten facies spatial distribution of D3 in the matrix

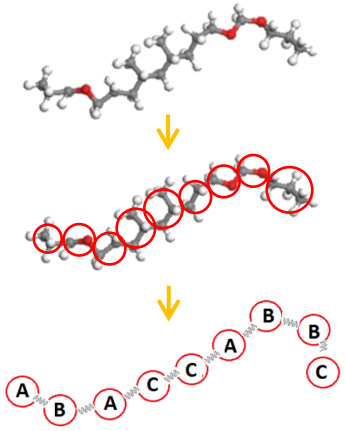


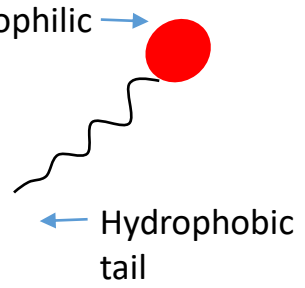
Distributions D1 & D3 have a negligible part of nanopores, modified PVT modelling has no strong impact on production for such distributions. However, D4 & D5 with higher percentage of nanopores, the difference between the two models is significant which mean that pore radius dependent EoS has an important impact on production for these distributions

[1][2] Sobecki et al. SPE-193867; J. Petril. Sci. & Eng. 2020, 193, 107364

DISSIPATIVE PARTICLE DYNAMICS (DPD)

- Developed by Hoogerbrugge et Koelman in 1992. Stochastic simulation technique for simulating the dynamic and rheological properties of simple and complex fluids
- Particles represent whole molecules or fluid regions, rather than single atoms.
  - Particles or beads have the same volume ν_m. In aqueous systems, the amount of water molecules/bead is used as the coarse graining level N_m
- Calculations are done with ***Newton*** code[1] and the Slater screening charge implementation for Ewald sum.[2]
- Implementation of the protonation/deprotonation process through a Morse potential.[3]



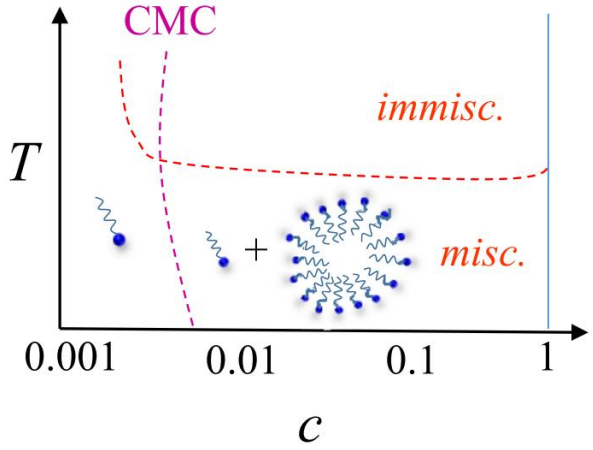


$$\frac{d\mathbf{r}_i}{dt} = \mathbf{v}_i$$

$$m_i \frac{d\mathbf{v_i}}{dt} = \mathbf{f_i}$$

$$\mathbf{f}_i = m\frac{d\mathbf{v}_i}{dt} = \sum_{i\neq j}\left(\mathbf{F}_{ij}^{C} + \mathbf{F}_{ij}^{D} + \mathbf{F}_{ij}^{R} + \mathbf{F}_{ij}^{S} + \mathbf{F}_{ij}^{el} + \mathbf{F}_{ij}^{M} + \mathbf{F}_{i}^{W} + \mathbf{F}_{i}^{EW}\right)$$

Conservative — Dissipative — Random — Spring — Electrostatics — Morse — Wall-bead vdW — Wall-bead Elec



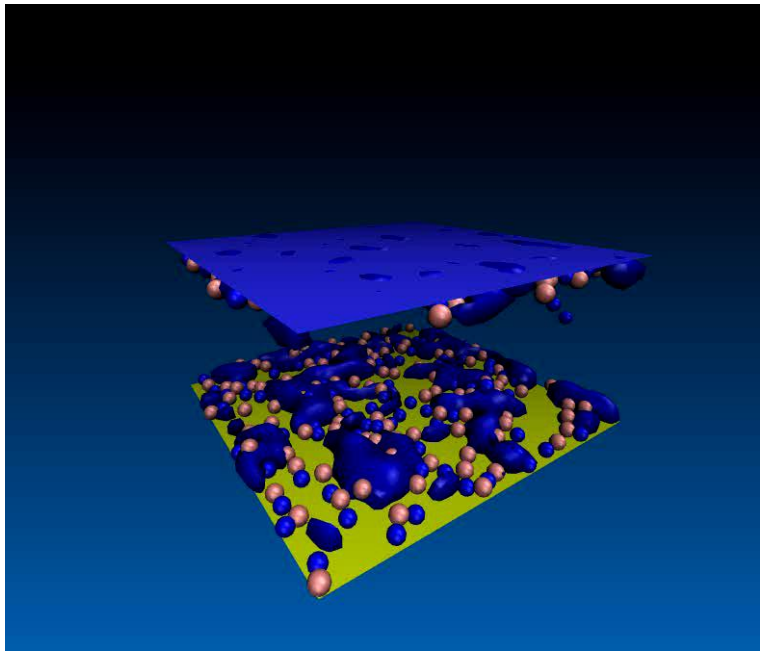
CMC: Critical micellar concentration

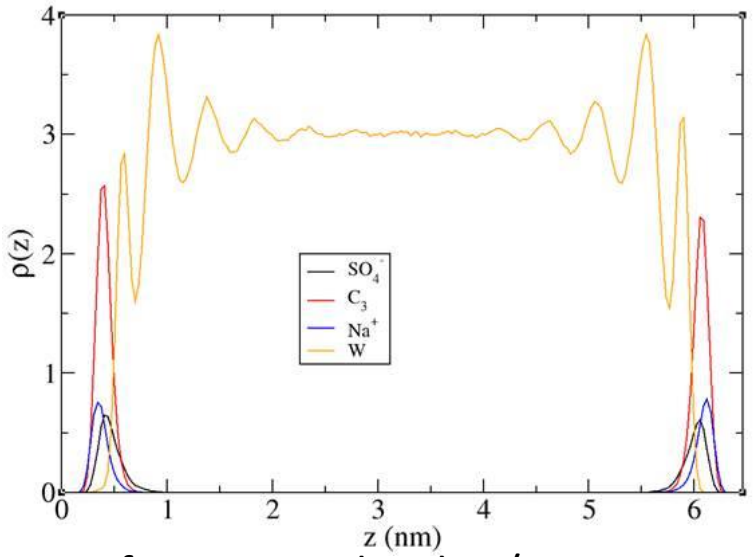
[1] PCCP 2010, 12 930.
[2] Gonzalez-Melchor et al. J. Chem. Phys. 2006, 125, 224107
[3] Lee et al. J. Chem. Theory Comput. 2015, 11, 4395−4403
[4] Alarcon et al. Soft. Matt. 2013, 9, 3777

ADSORPTION OF SURFACTANTS OVER MODEL-MINERAL SURFACES

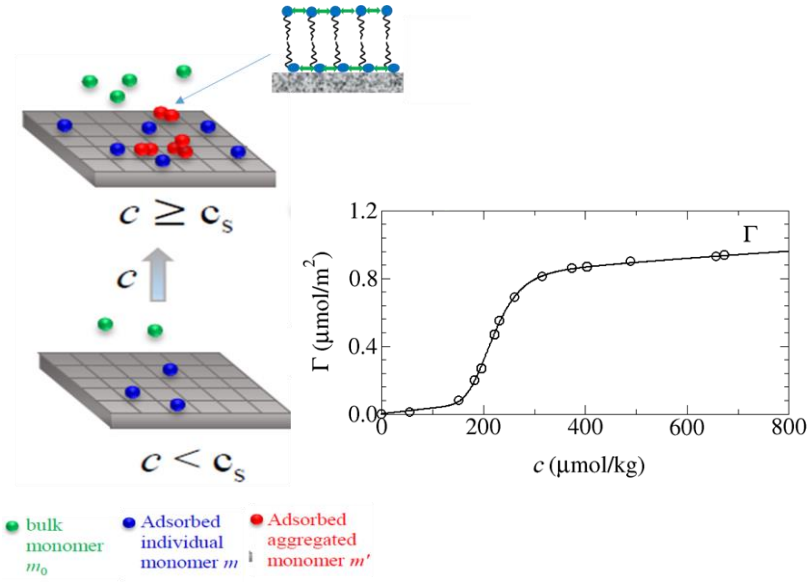
- CG (DPD) model of charged surfactants (SNS = $C_9H_{19}SO_4^-Na^+$) H_1T_3 Bulk [C]=0,308 mol/l
- Hydrophobic SiO_2 charged surface Q=600mC/m² (Slit pore of lx=13 nm, ly=13 nm et lz=6,5 nm)

Surface aggregation of surfactants





Surf. Cs=0,6 molecules / nm² or 9,95x10^{-7} mol/m²



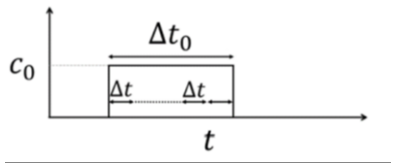
$$\frac{\partial \Gamma_m(c,t)}{\partial t} = k_A c\,[\Gamma^{\infty} - \Gamma_m(c,t)] - k_D \Gamma_m(c,t)$$

Thermodynamic model of surfactant adsorption with surface aggregation and lateral interactions [1]

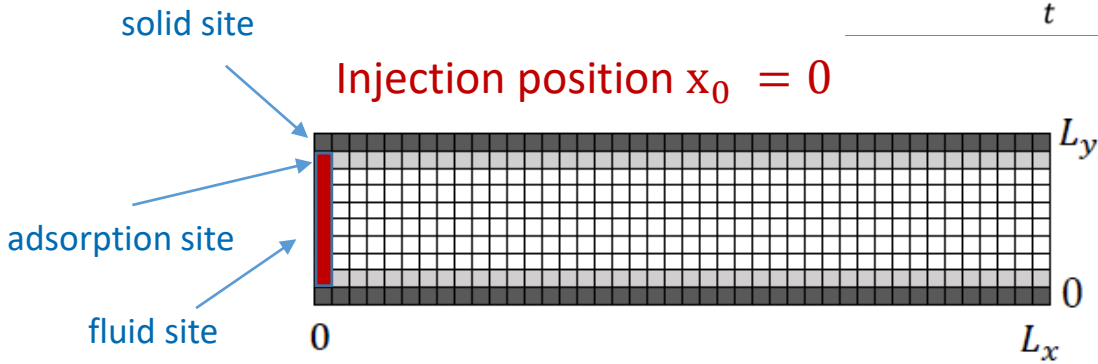
$$\frac{\partial \Gamma_{m'}(c,t)}{\partial t} = k'_A(\Gamma_{m'})\, c \times [\Gamma^{\infty} - \Gamma_m(c,\infty) - \beta \Gamma_{m'}(c,t)] - k'_D(\Gamma_{m'})\, \Gamma_{m'}(c,t)$$

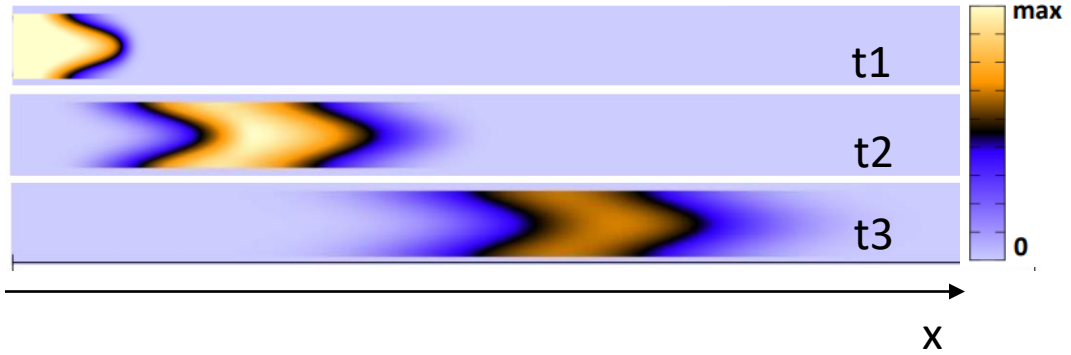
[1] Zaafouri et al. J. Phys. Chem. B 2020, 124, 10841

TRANSPORT AND ADSORPTION MODELING USING LBM
LANGMUIR VS COOPERATIVE MODEL: SLUG INJECTION

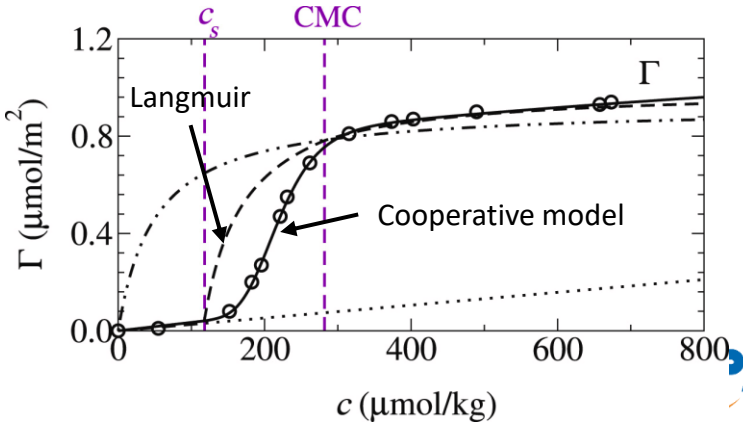


- Lattice Boltzmann, Two-relaxation-Times scheme
- 2D parallel plates geometry
- Two independent simulation steps
  - Resolution of Stokes equation (velocity field)
  - Resolution of the transport equation including the adsorption term
- Initial conditions
  - Dirac (pulse) injection (Δt=1)
  - Continuous (slug) injection (Δt>1)





- Langmuir model shows high adsorption for low surface saturation as it does not account for separated monomer and aggregate adsorption [1]



[1] Zaafouri et al. Adv. In Water Resour. 2022, 162, 104143

CONCLUSIONS & PERSPECTIVES

- Molecular simulation techniques are well adapted to model the phase behavior of fluids under confinement & at interfaces if the contribution of fluid-solid interactions are of the same order of magnitude of “normal” fluid-fluid
  - This situation is observed in the case of microporosity (<2 nm) and in the lower limit of mesoporosoty (2-10 nm)
  - Complex fluids capable of aggregation (surfactants)
- Experimental validation of the intermolecular force fields is crucial to keep the simulations as realistic as possible. Unfortunately, there is a lack of data in the literature of VLE of confined fluids.
- Advanced molecular/mesoscopic simulation techniques (confined Gibbs ensemble MC, NPT-BPMC, DPD) can:
  - Enhance the comprehension of the behavior of fluids under strong confinement
  - provide valuable synthetic data to parametrize and validate modified EoS and thermodynamic adsorption models.
- The strategy of combining different multi-scale approaches is the most efficient way to inject the highest degree of physical & chemical coherence required to modeling of the complex phenomena involved in the phase behavior of confined fluids → LBM, grid matrix/fracture simulation.
- Challenges for the future:
  - Inclusion of more realistic models of mineral & heterogenous (cement) surfaces for the extension of the MS synthetic data for more realistic applications.
  - The inclusion of aqueous phases with high ionic concentrations in equilibrium with polar surfaces (Storage of H_2 in natural reservoirs)

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