Oil recovery and mitigation processes: insights from multiscale molecular simulations

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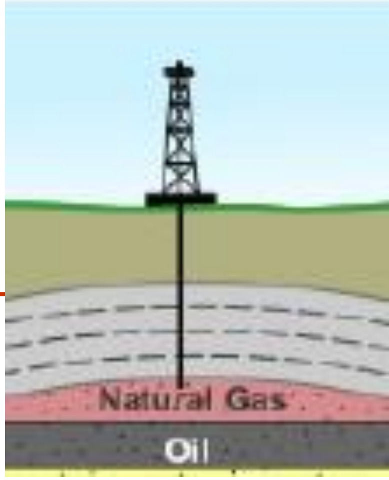
Outline



1. *Nano and O&G industry*
2. *Multiscale molecular simulations*
3. *NANO-EOR – surface driven flow*
4. *NANO-IOR – pressure driven flow*
5. *Nanoaggregation of complex molecules*
6. *Concluding Remarks*

Motivation

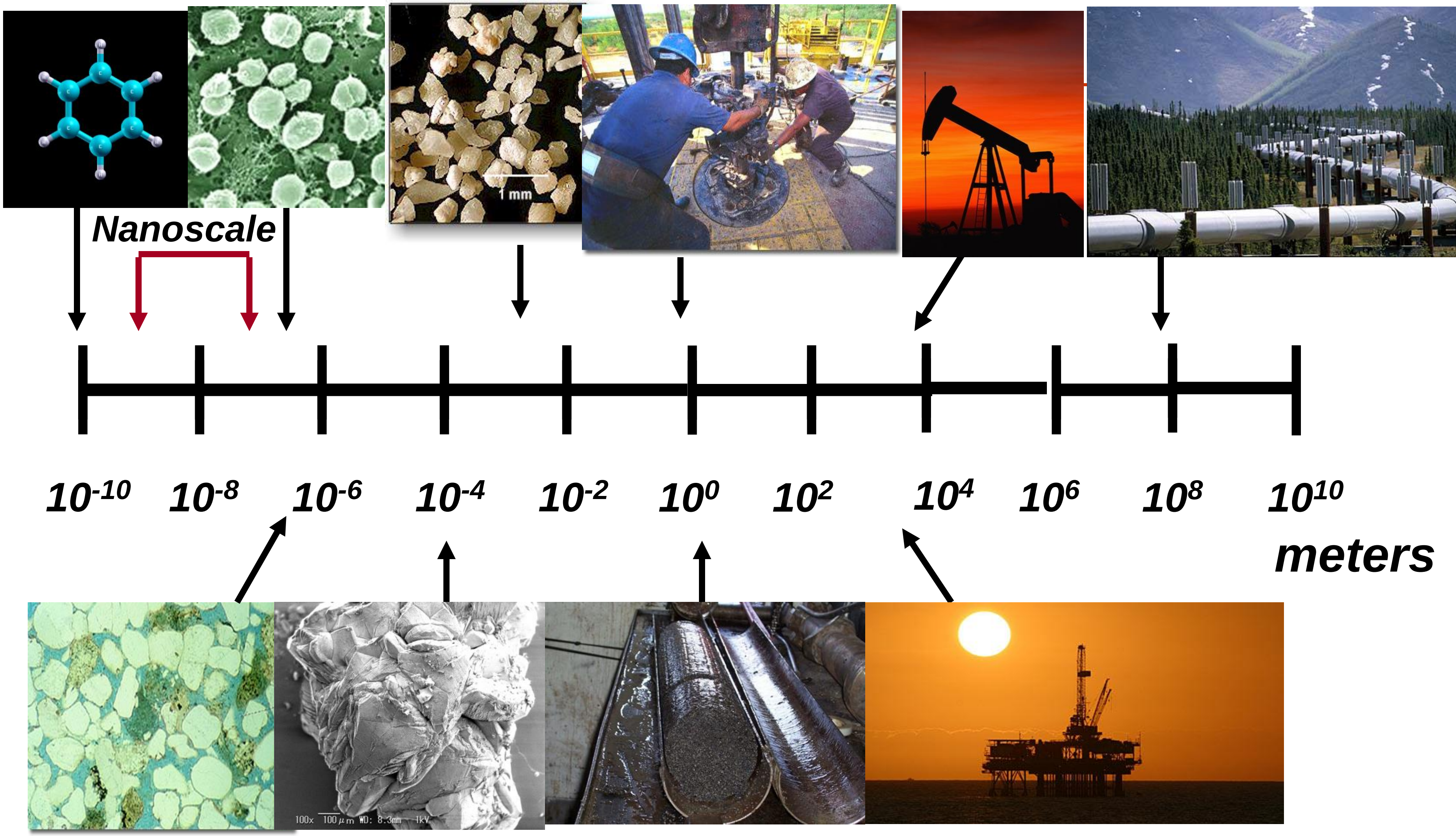
- The current average recovery factor from conventional oil reservoirs is ~35%.

- Poor sweep effect in the reservoir & capillary forces

- Would it be possible to reach 70% recovery factor in conventional oil fields?

- As oil recovery processes involve the interaction between mineral and hydrocarbons, the optimization of oil production requires deep understanding of reservoir properties at different scales.

Crossing scales in Oil & Gas



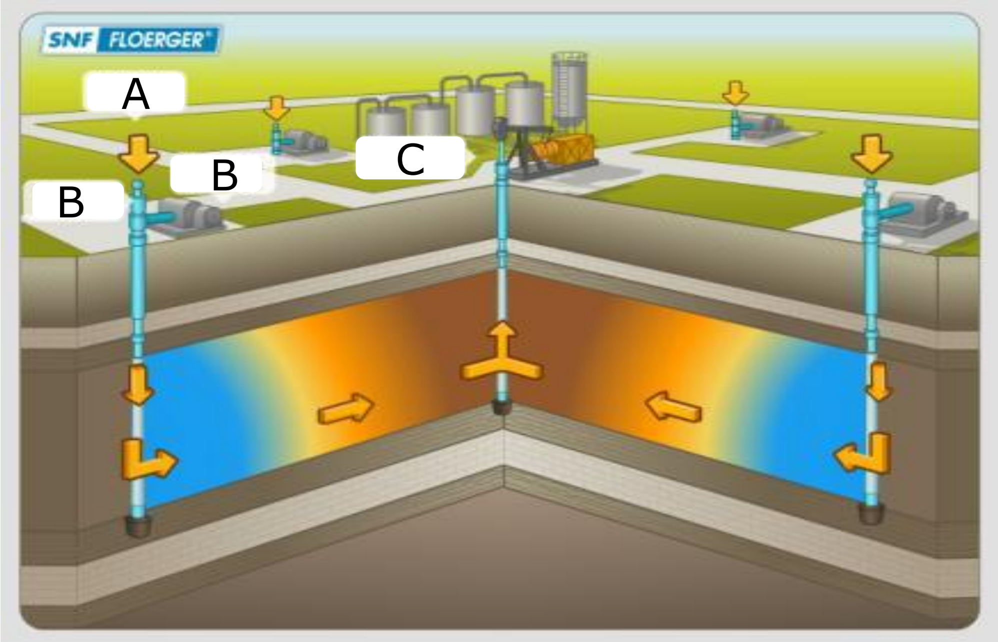
Complex physical phenomena in Materials
Oil&Gas: How the large can drive small systems ?

Temperature, Pressure, Salinity, Heterogenous and multiphase media

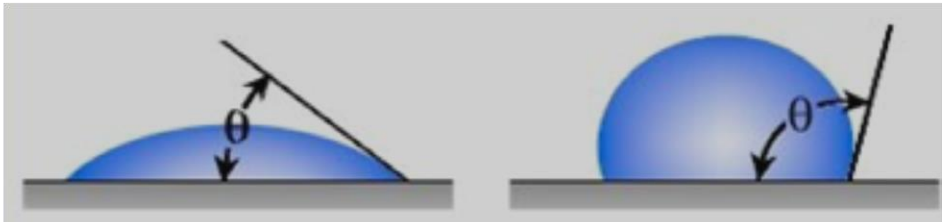
IOR & EOR

- Improved and Enhanced Oil Recovery (IOR and EOR) techniques are currently of great strategic importance to improve oil wells production.

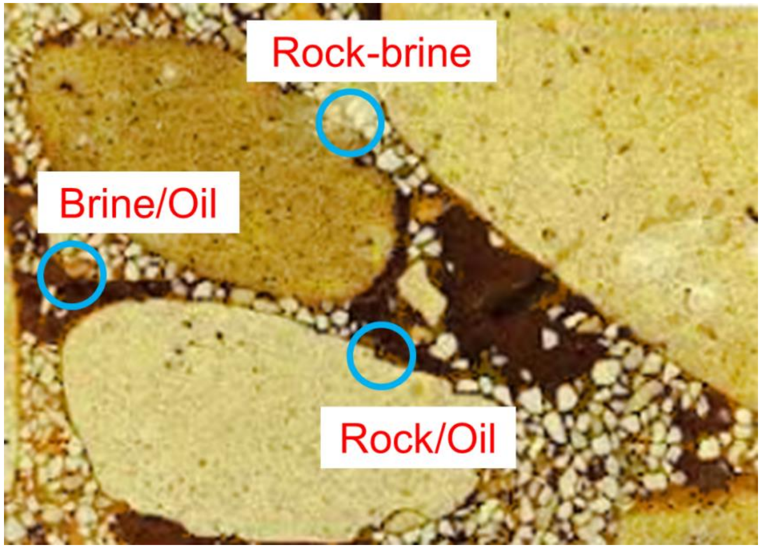
  - Water/brine
  - CO_2
  - N_2
  - Surfactants
  - Thermal
  - Bio



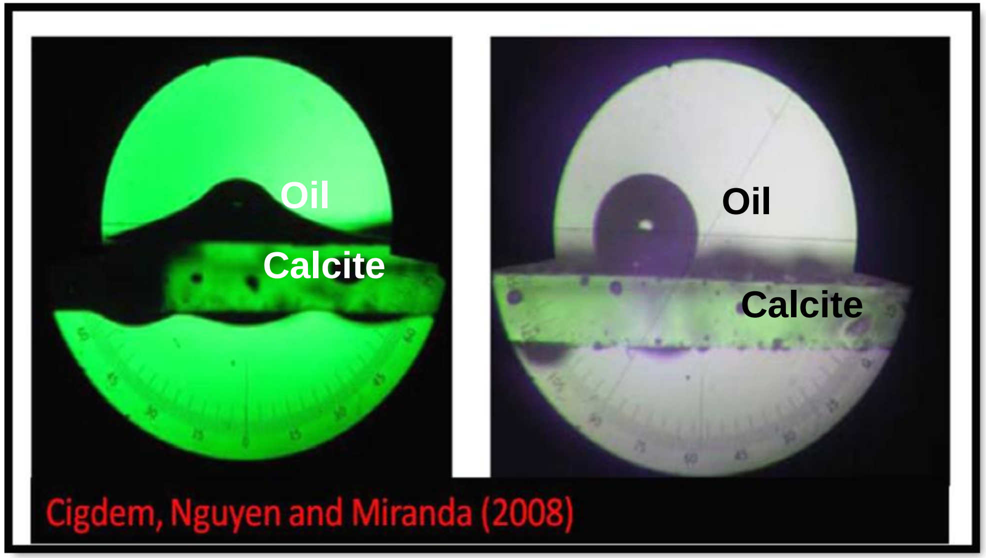
IOR & EOR



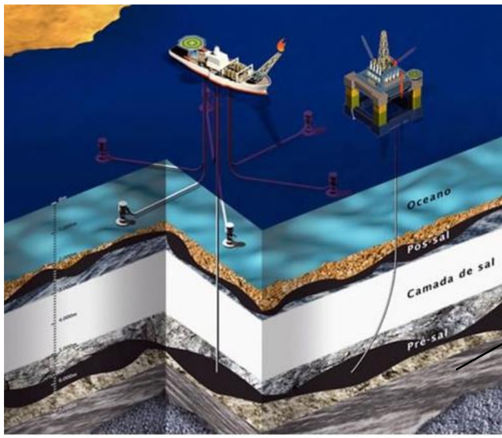
- The main strategy is to reduce the interfacial tension (IFT) or the viscosity of crude oil by molecular additives, which can be adsorbed on the oil-fluid interface, or migrate to the crude oil through the interface.

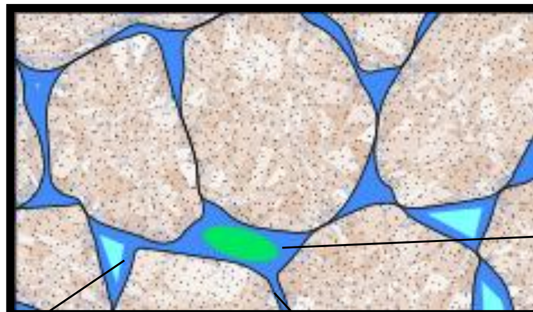


H2O + SiO2 nanoparticle

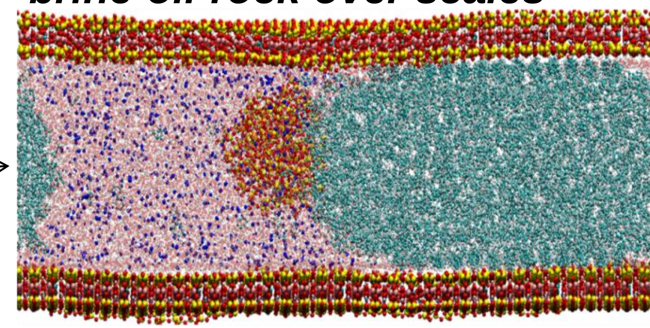


Complex physical phenomena in Materials and O&G industry from a Nanoscience perspective

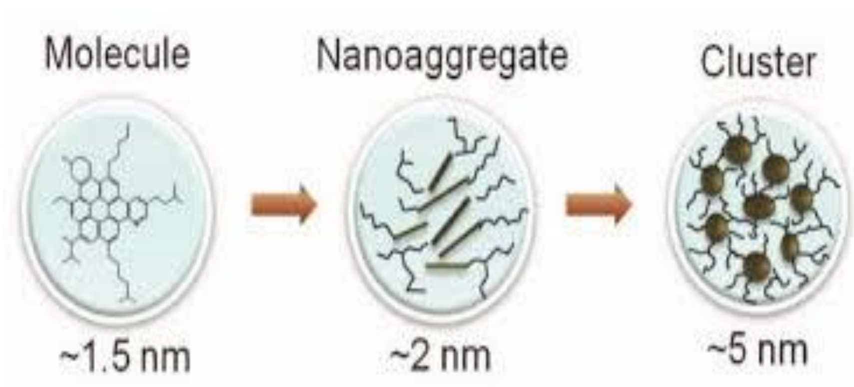




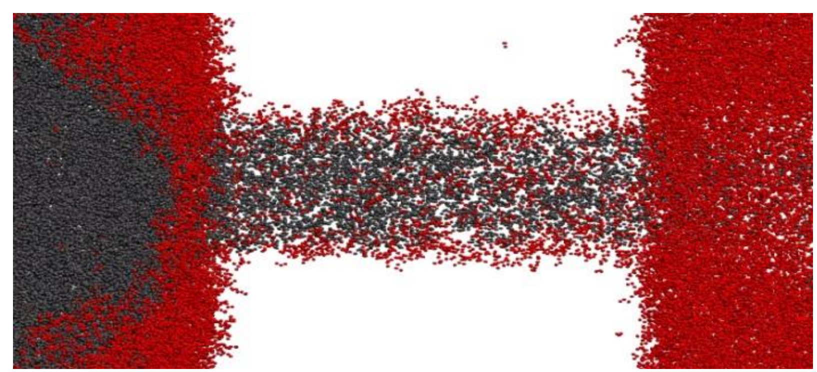
***NANO-EOR - Surface driven flow:* NPs at interfaces brine-oil-rock over scales**



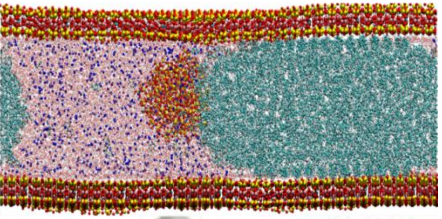
ASPHALTENES
Aggregation of complex matter

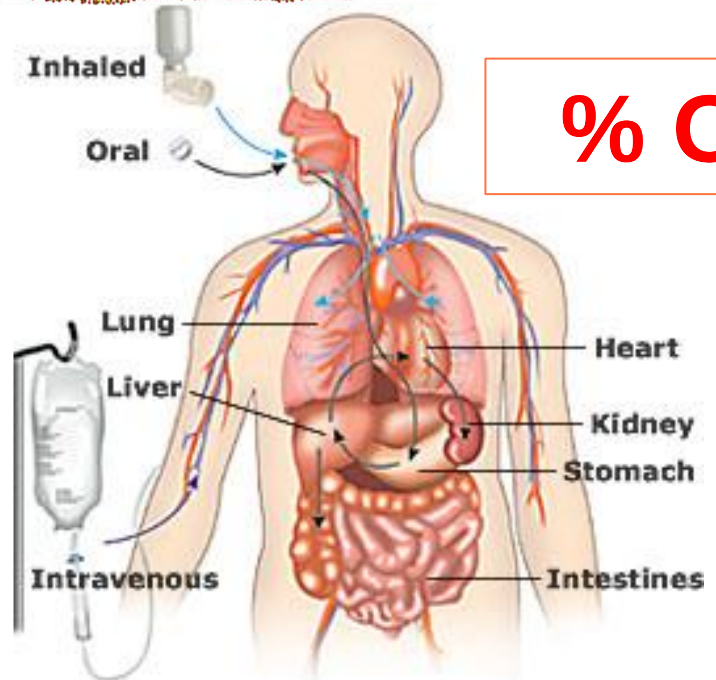


NANO-IOR – Pressure driven flow
Fluid confinament,multiphasic fluids
Flow in NANO porous media

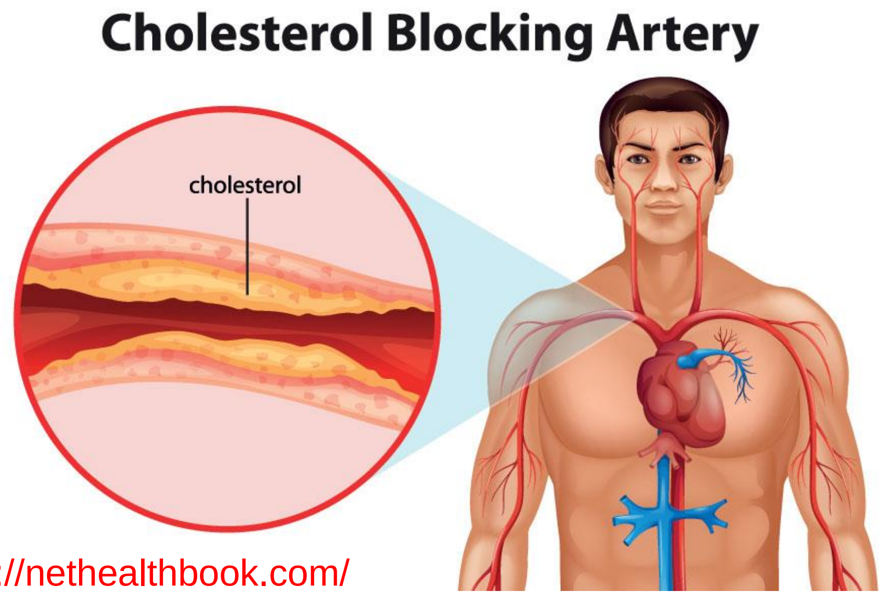


The health of oil reservoirs

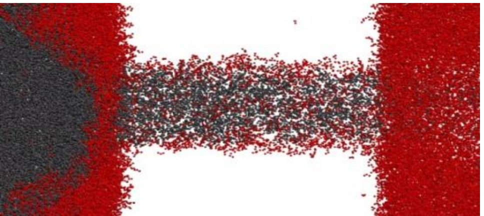


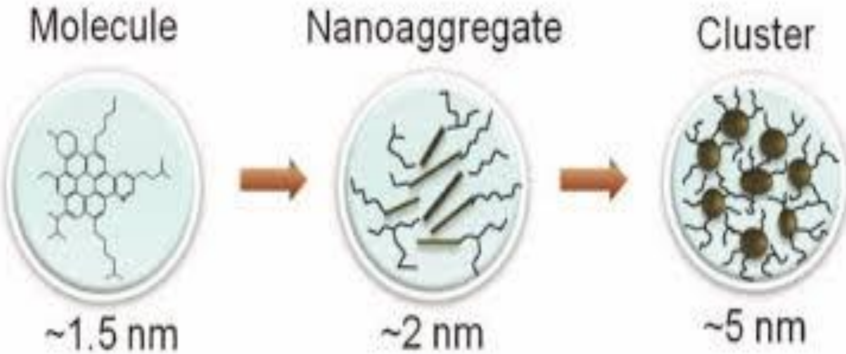


% Oil ?



http://nethealthbook.com/

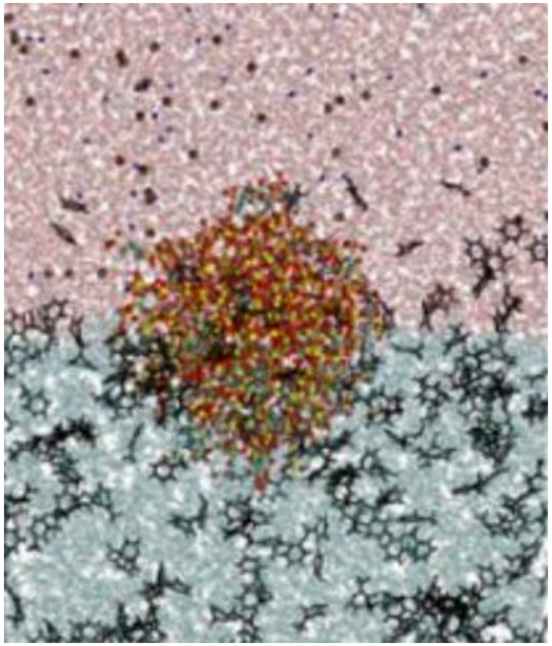




How to control interfaces and flow at nanoscale ?

To favor the mobilisation of hydrocarbons trapped at the pore scale through short range surface forces or capillarity:

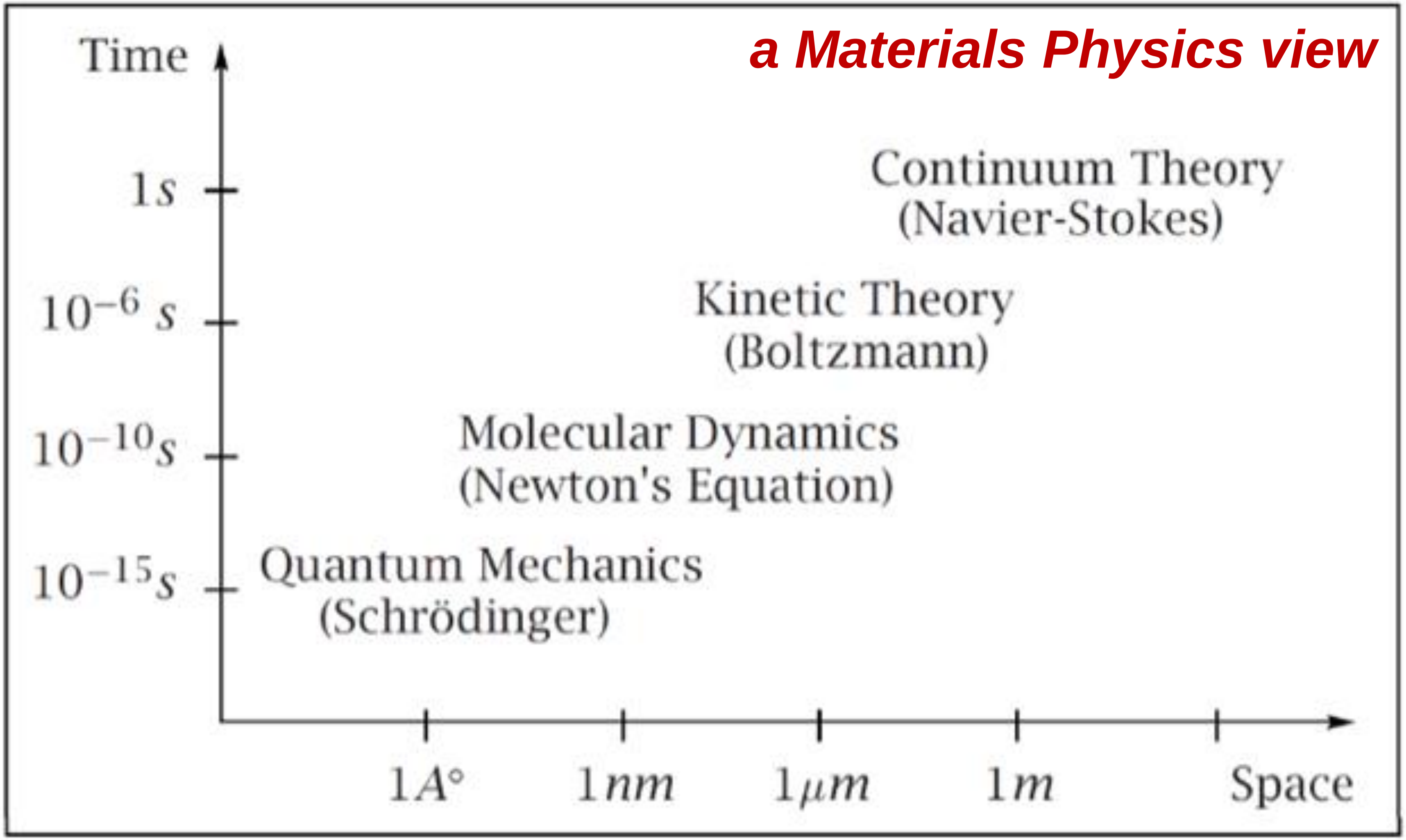
1) **Nano-EOR** – control the chemical environment: by functionalized NPs and surfactants "Wetability modifiers" - *SURFACE DRIVEN FLOW*
2) **Nano-IOR** – control confinement - Fluid flooding in nanoporous. *PRESSURE DRIVEN FLOW*
3) **Low salinity EOR** – control the electrostatic environment –"Smart water" *ELETROKINETIC DRIVEN FLOW*



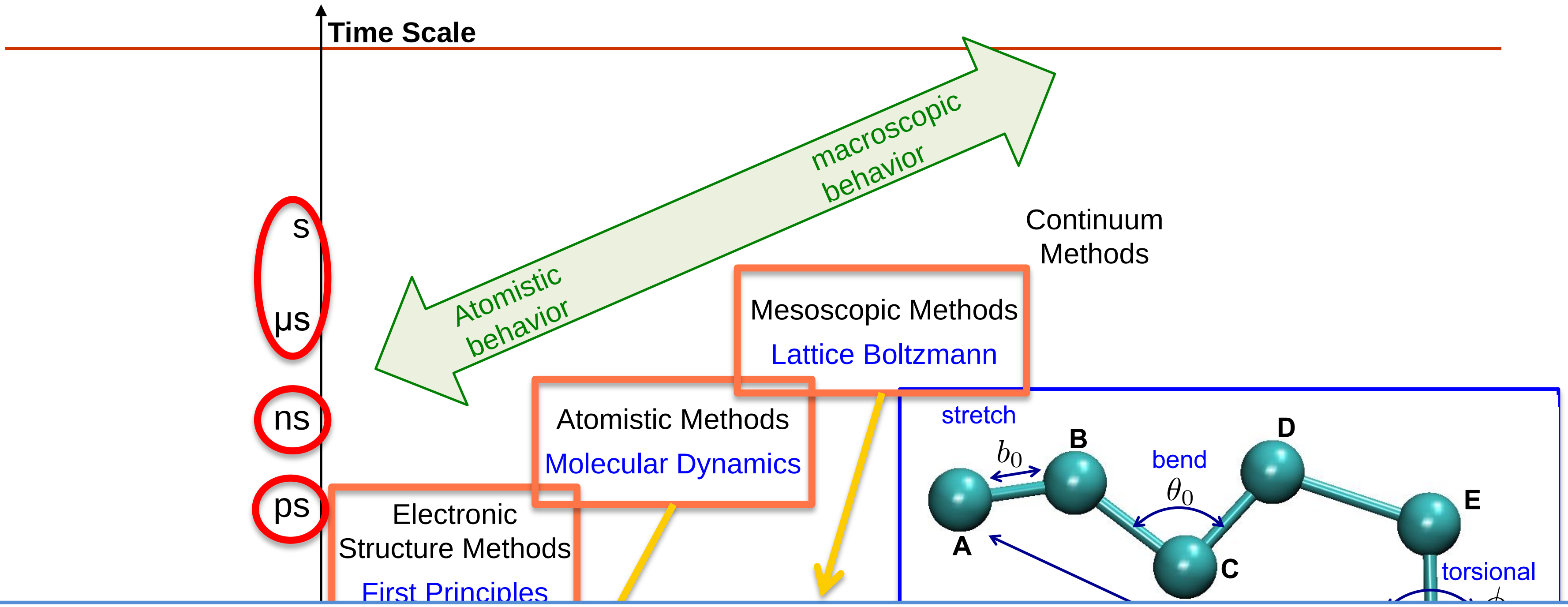
MULTISCALE MOLECULAR SIMULATIONS

(COMPLEX SYSTEMS AND CONTROLED CONDITIONS OVER SCALES)

Multiscale in the laws of Physics



Multiscale computational approach



Kinetic Theory

Lattice Boltzmann

Simplifies the Boltzmann equation by

- Understanding of fluid behavior at the microscale
- Phase separation, interface instability, bubble/droplet dynamics and wetting effects

$$\mathbf{v}\nabla_{\mathbf{x}} f + \mathbf{F}\nabla_{\mathbf{p}} f + \frac{\partial f}{\partial t} = \Omega$$

$$f_i(\mathbf{x} + \mathbf{e}_i \Delta t, t + \Delta t) = f_i(\mathbf{x}, t) + \Omega_i(\mathbf{x}, t)$$

MD ab initio and classical X LBM: a soccer perspective

- Tactical formation or random
- Collisions
- Interactions between players result in a goal

Ab initio MD

Classical MD

LBM

foosball

Simple way to describe the movement of players during a game

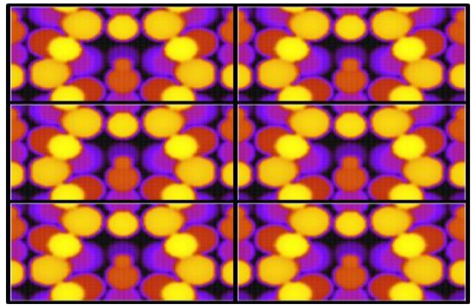
Multi-scale approach

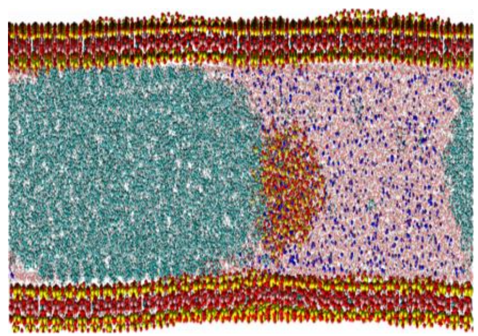
Quantum Mechanics
First principles methods

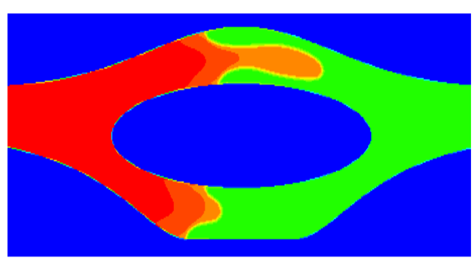
DFT + vdW
NMR, AFM,XAS

Thermodynamics & Kinetics
Molecular Dynamics

Fed for Mesoscale modeling
& experimental comparison







Lattice Boltzmann

Recent developments (~00s ~10s):

DFT:

- ***Dispersion corrections (vdW)***
- ***GIPAW (Gauge Including Projector Augmented Waves)***

MD:

- ***Development of polarazible dissociative ab initio based interatomic potentials.***
- ***Massive paralelization***
- ***New hardware (GPUs and hard-disks)***

LBM:

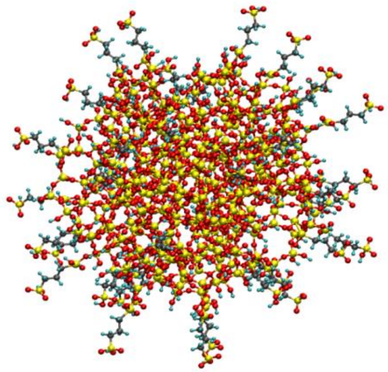
- ***Free energy approach***
- ***Viscosity differences***
- ***Multi-phase systems***
- ***Pore-scale flow in porous media***

NANO-EOR

AN INTEGRATED WAY TO APPROACH THE PROBLEM

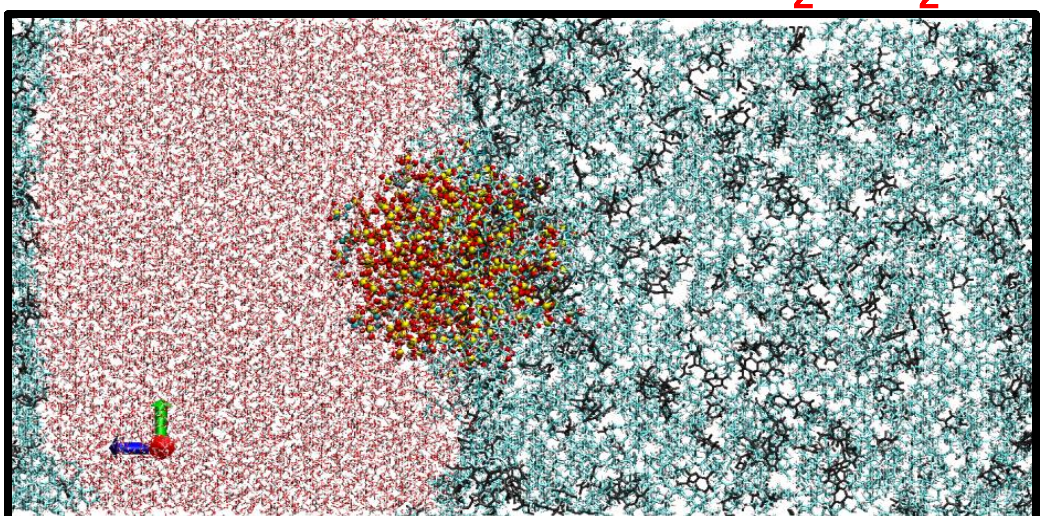
NANO-EOR

SURFACE DRIVEN FLOW



Functionalized Silica nanoparticles

- **Hydroxylated**
- **Poliethylene glycol (Hydrophylic)**
- **$-CH_2-CH_2-$Sulfonic acid (Hydrophobic)**



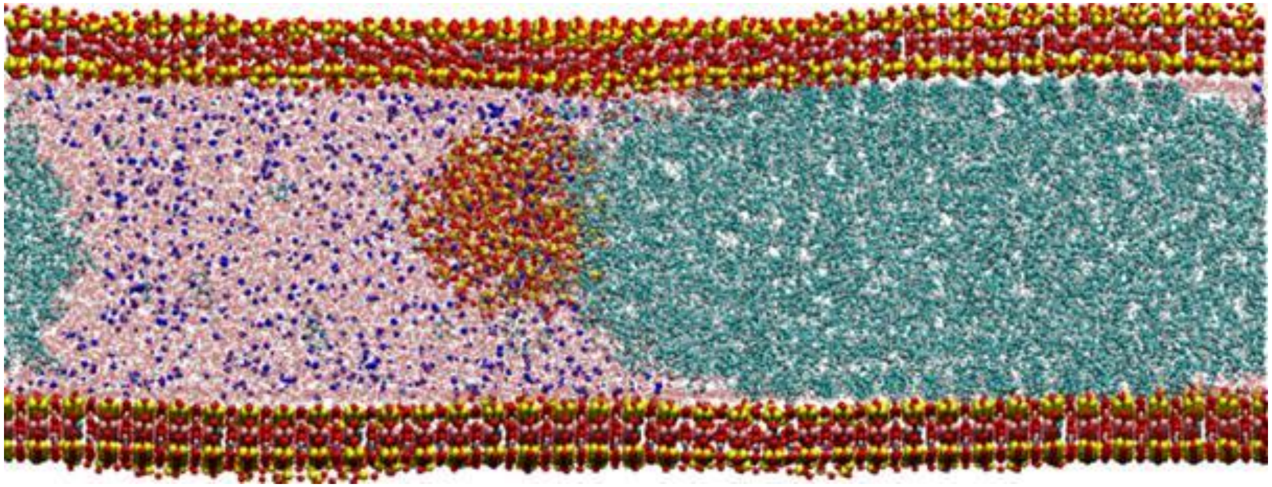
Temperature (300, 350, 375 and 400K)
Pressure (1to 400 atm) [1 – 6000 psi]

Miranda et al. SPE-157033-MS - 2012

Miranda et al., J. Phys. Chem. C, 120, 6787, (2016)
Miranda et al., J. Phys.: Condens. Matter 27 325101 (2015)
Miranda et al.,Eur. Phys. J. B 88,261 (2015)
Miranda et al.,Applied Surface Science, 292,742 (2014).

NP-clay interaction

- For *montmorillonite (MMT)* and other clay systems, the effect of clay swelling occurs, which can have an impact on the wellbore instability and formation damage.
- Montmorillonite is used in the oil drilling industry as a component of *drilling mud*.

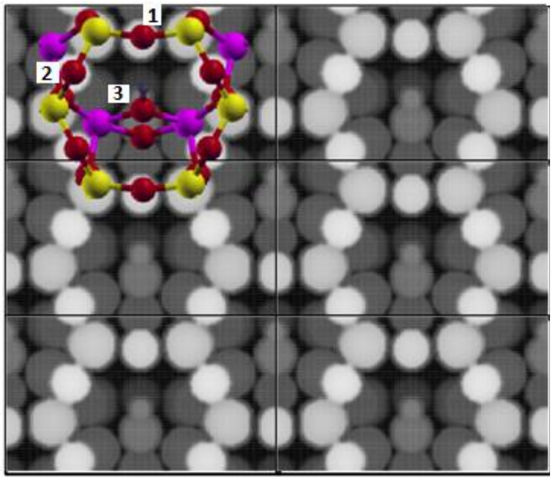


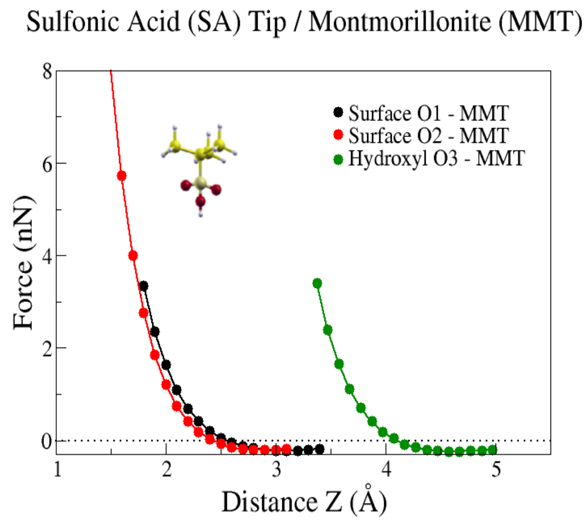
$(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$.

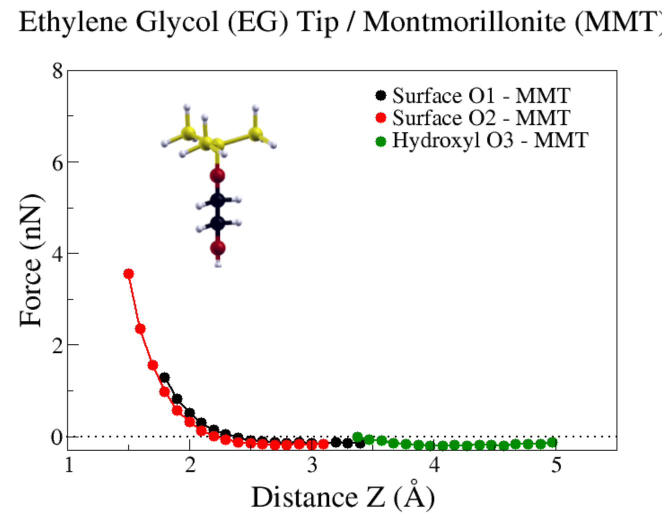
MMT is naturally hydrophilic and it has good affinity with H_2O.

AFM Simulations through the Interaction between Functionalized Silicon Tip and the Montmorillonite (001) Surface – DFT + vdW

Alvim and Miranda, J. Phys. Chem. C, 120, 13503(2016)
Alvim and Miranda, Phys. Chem. Chem. Phys.,17, 4952 (2015)





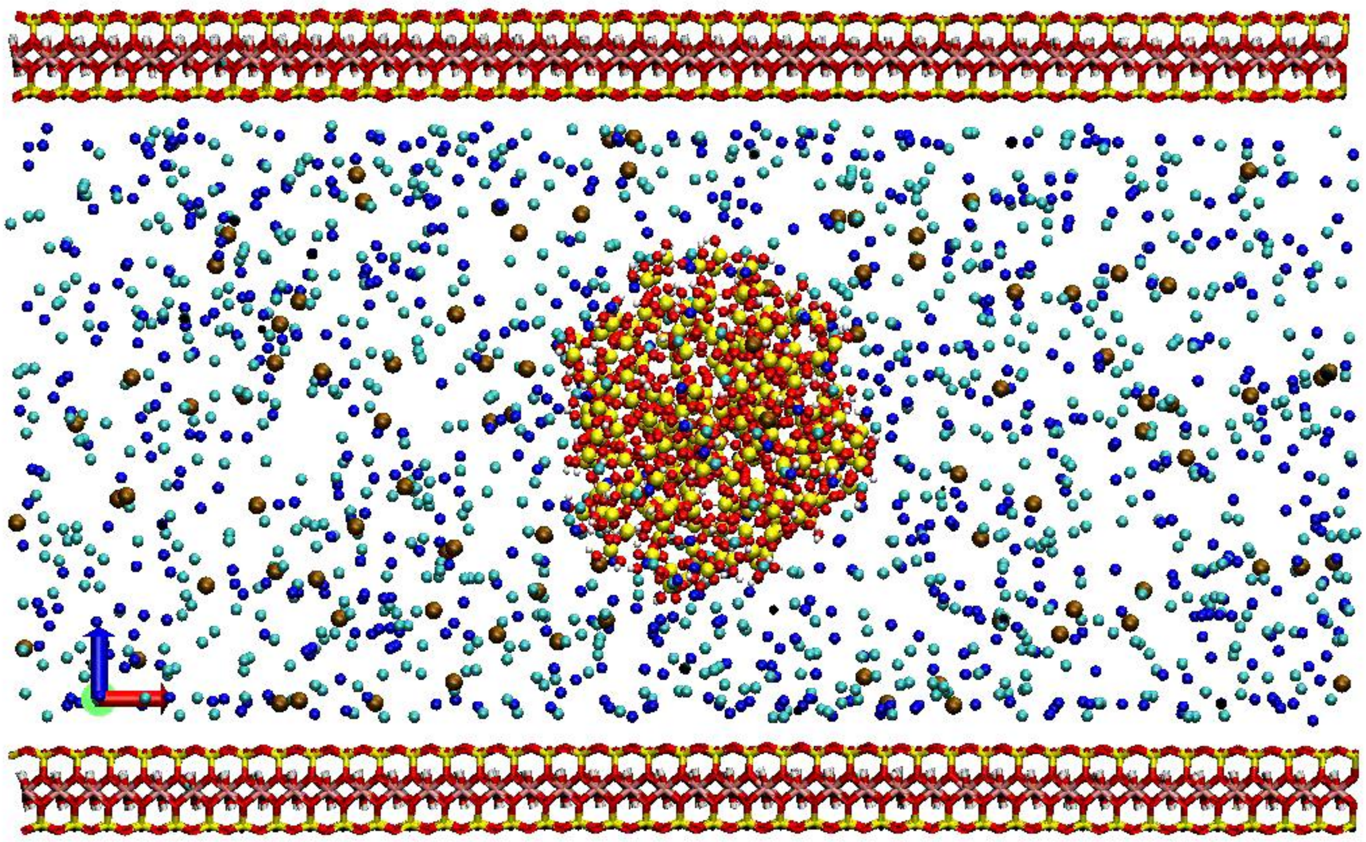


Tip Approach

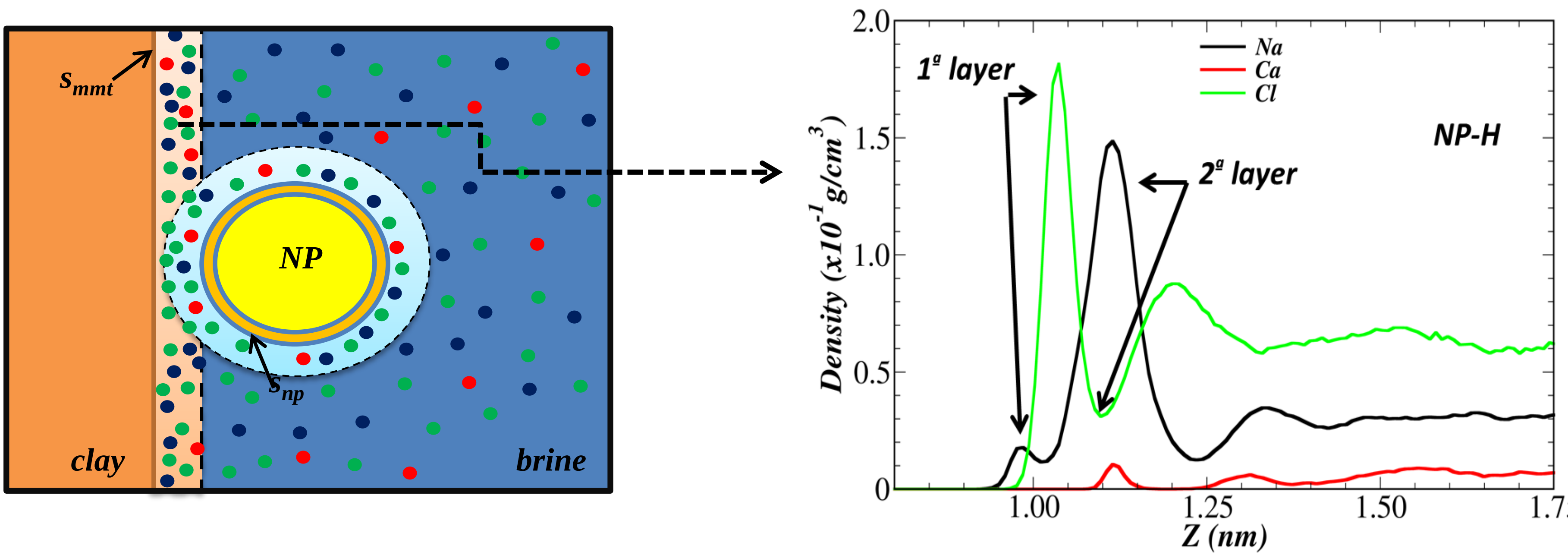
- *Strength of bonding*
- *Surface configuration*
- *Adsorption density*
- *Interatomic Forces*
- *Chemical environment*

HOW TO UPSCALE THIS VERY FUNDAMENTAL INFORMATION ?

Fully atomistic MD(Brine+NP/Oil/MMT)

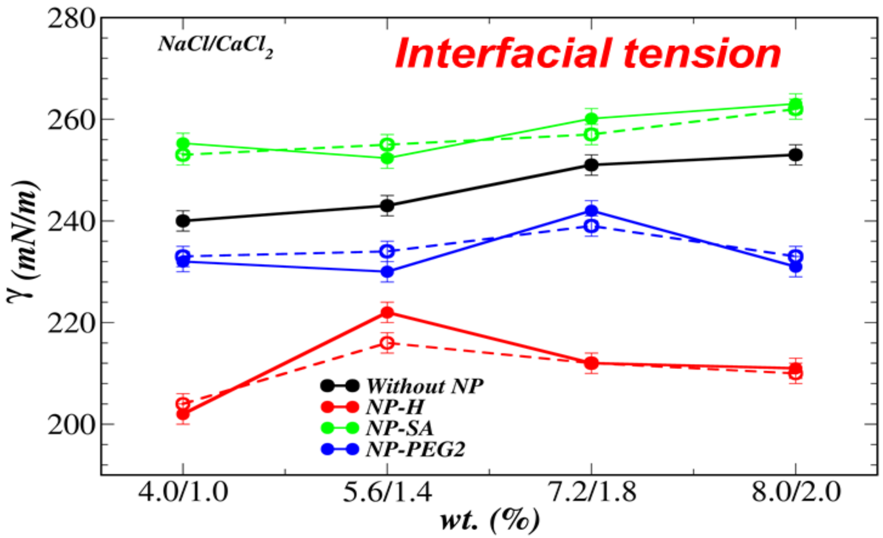


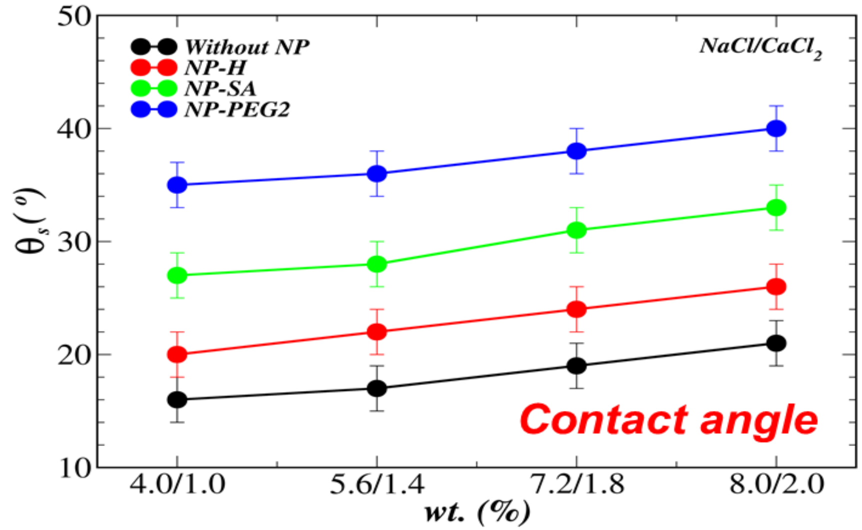
Electrical double layer

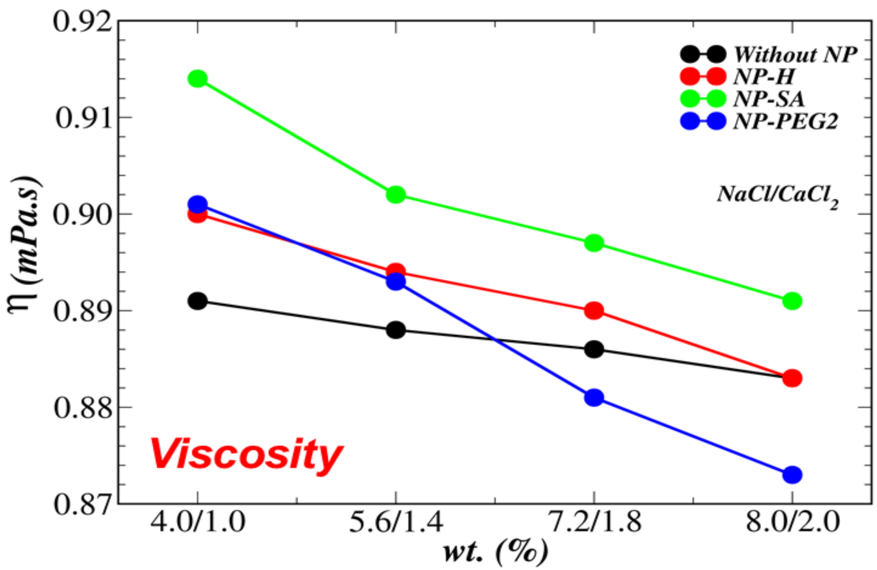


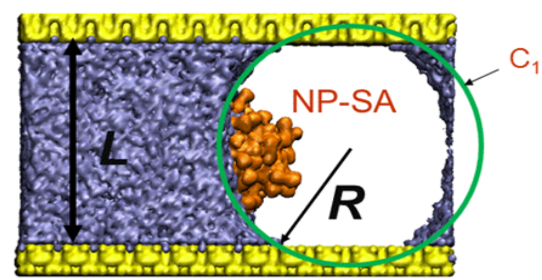
- **Electrical Double Layer (EDL) Formation**.
- **For NP adsorbed on MMT – compression of the EDL.**

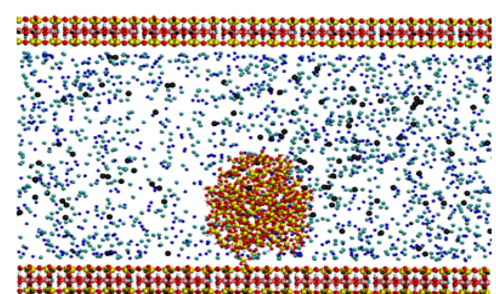
Interfacial phenomena







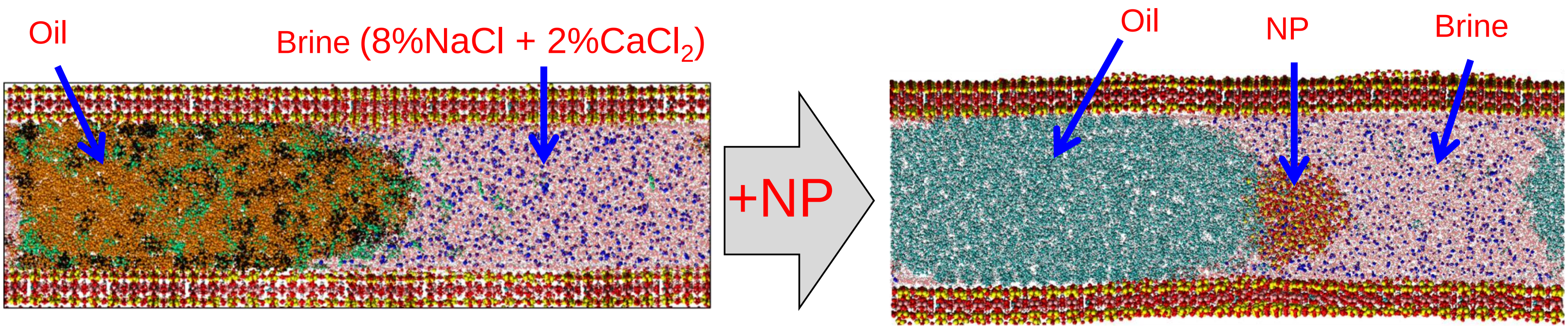




Case study: Brine+NP/Oil/MMT System

MD : nm ns
LBM : µm/mm µs/ms

T=300K – 400K
P=1 to 200atm



MD Physical properties

ρ_o=0.81 g/cm^3; ρ_b=0.96 g/cm^3;
η_o=3.62 mPa-s; η_b=0.79 mPa-s;
γ_{ob}=43 mN/m; θ_w= 28^o

ρ_o=0.81 g/cm^3; ρ_b=0.96 g/cm^3;
η_o=3.60 mPa-s; η_b=0.88 mPa-s;
γ_{ob}=38 mN/m; θ_w= 21^o

LBM parameters:
G = 0.14; G_w =-0.015;
τ_{oil} = 1.50; τ_{brine}= 0.70

G = 0.15; G_w =-0.02;
τ_{oil} = 1.50; τ_{brine} = 0.75

Hierarchical Computational Protocol: Molecular Dynamics + LBM

Versatile tool to investigate the potentialities of modified injection fluids for EOR techniques

MD Calculations (nanoscale)
Density, viscosity, interfacial tension, wetting properties

Maps MD into LBM (nano into micro)

Characteristic Scale for LBM simulations
l_0, t_0 and m_0

Computational parameters
Relaxation time, fluid-fluid and fluid-mineral interactions

Initial Condition
Density, fluid velocity and configuration, mineral geometry

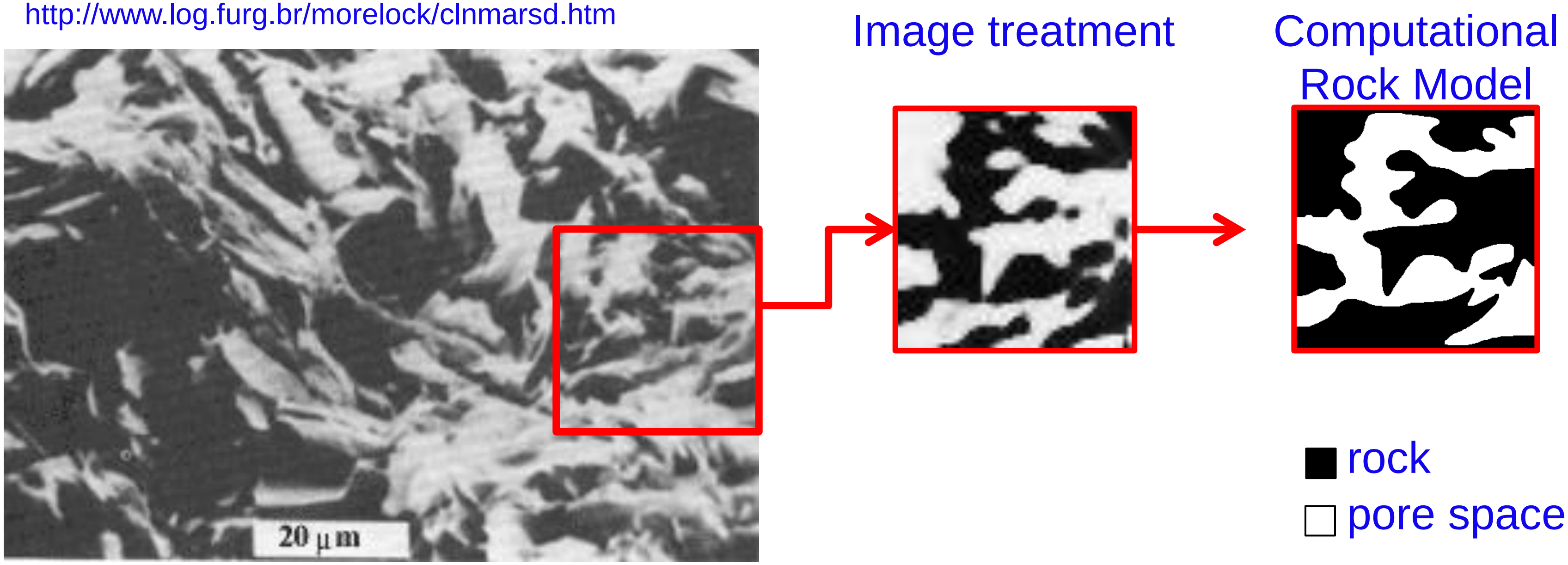
LBM Simulations
(EF-LBM)

Oil Extraction Process (pore-size scale)
Fluid dynamics, pressure, velocity, …

Pereira, Lara and Miranda, Microfluidics and Nanofluidics 2, 20 (2016)

MMT Rock Model

http://www.log.furg.br/morelock/clnmarsd.htm



LBM Parameters

	G_{12}	G_w
Without NP	0.190	0.078
NP-H	0.181	0.095
NP-SA	0.171	0.099
NP-PEG2	0.164	0.098

Characteristic Scale

$l_0 = 5.49 \times 10^{-5}$ m

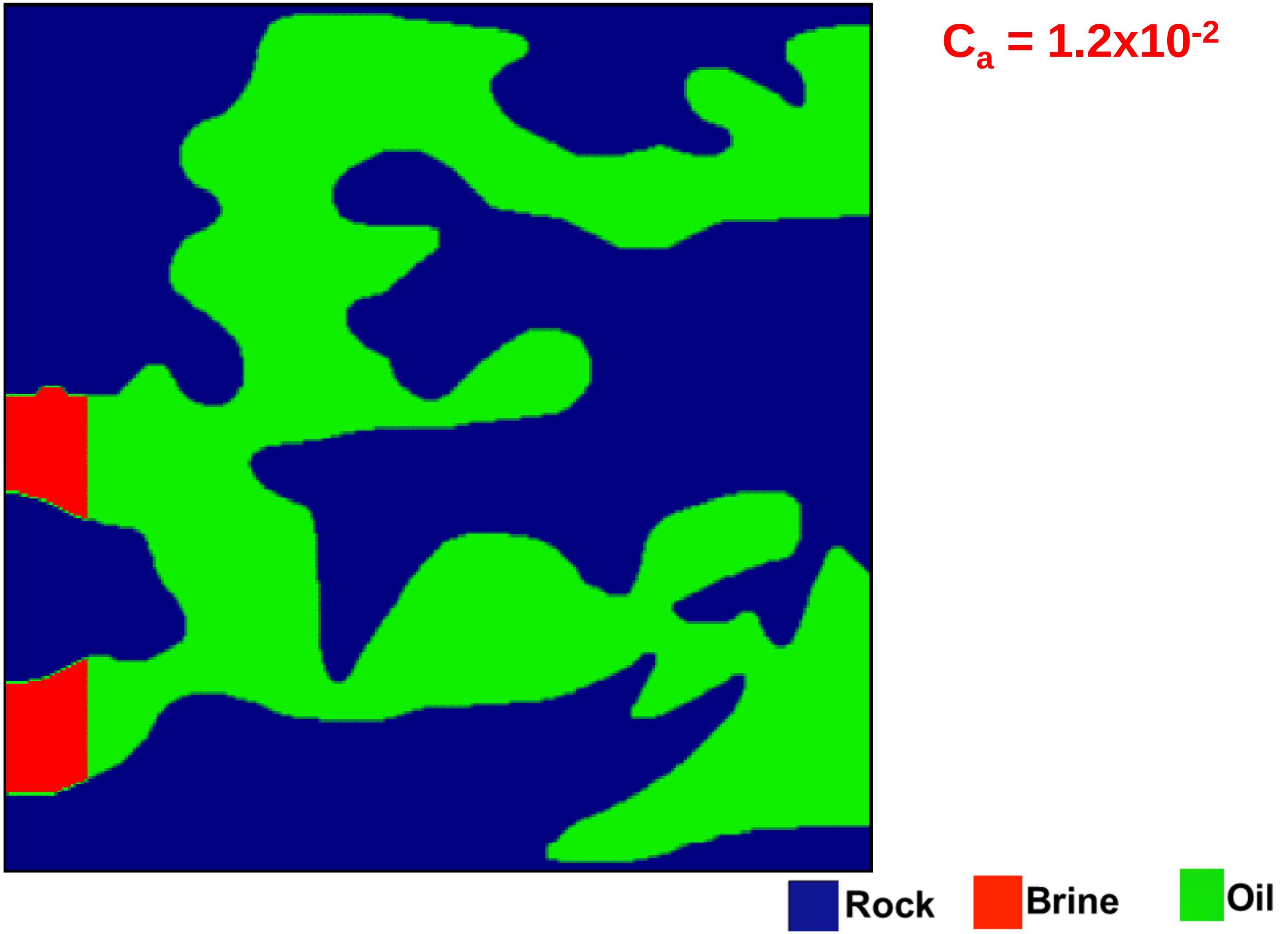
$t_0 = 1.27 \times 10^{-4}$ s

$m_0 = 1.50 \times 10^{-10}$ kg

Exploring Oil Extraction by Nanofluids in Clay Coated Pore Network Models

Oil displacement by Brine+NP-PEG2: First Injection

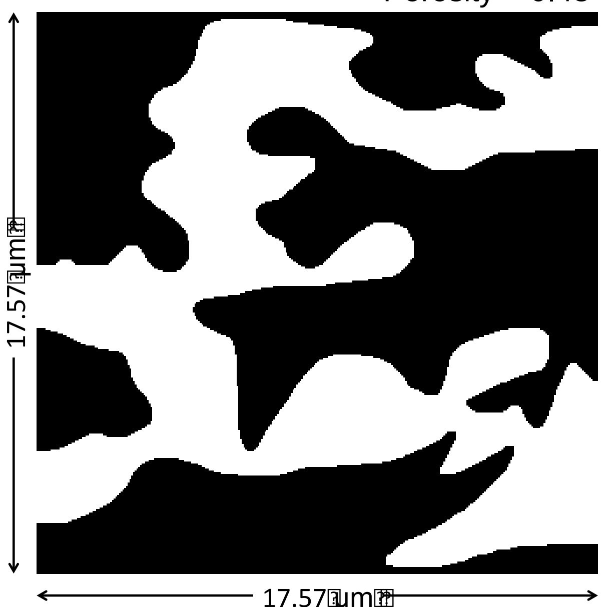
$C_a = 1.2x10^{-2}$



Exploring Oil Extraction by Nanofluids in Clay Coated Pore Network Models

LBM Simulations: Oil displacement at the pore-size scale

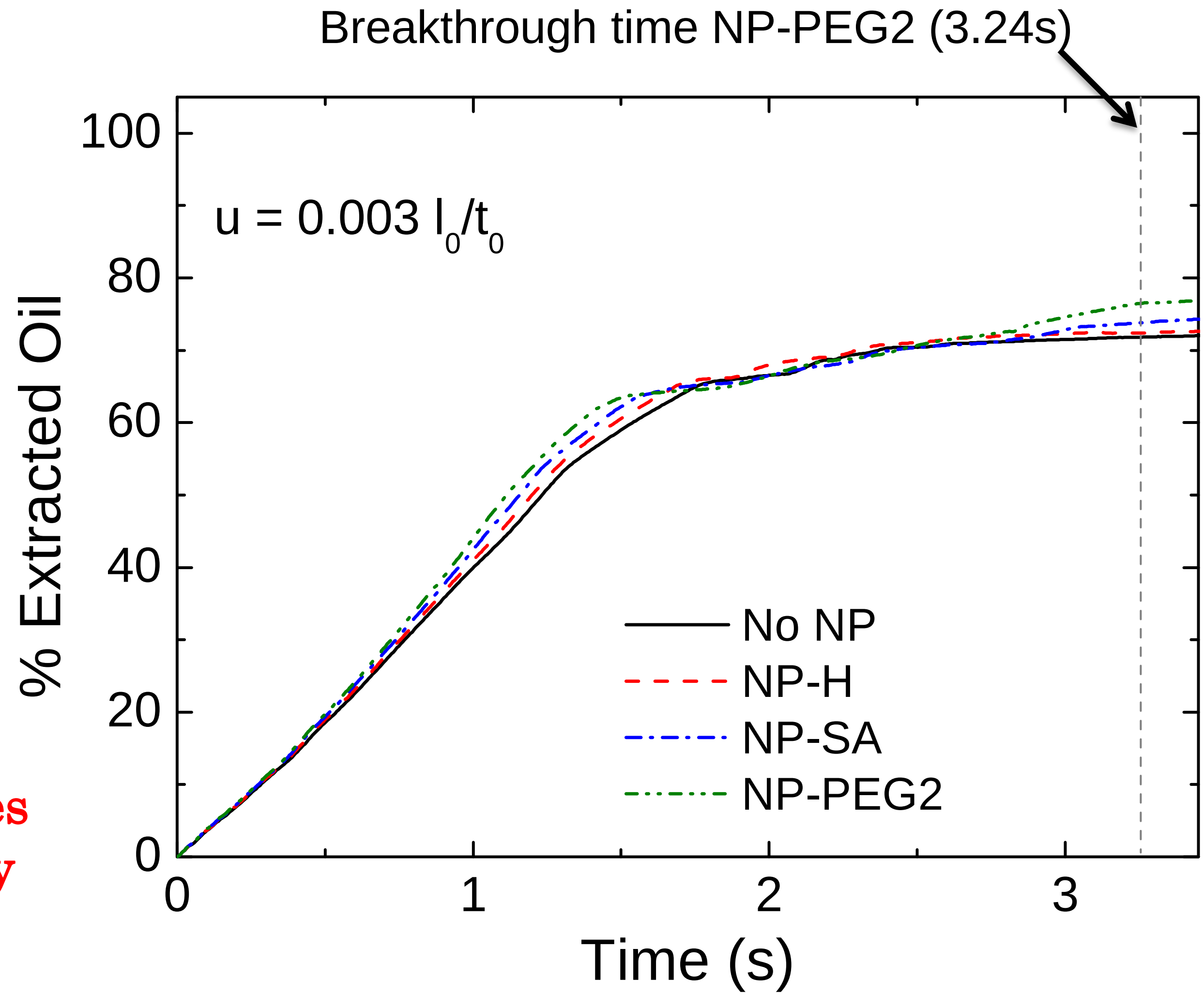
Porosity = 0.43



$l_0 = 5.49 \times 10^{-8}$ m

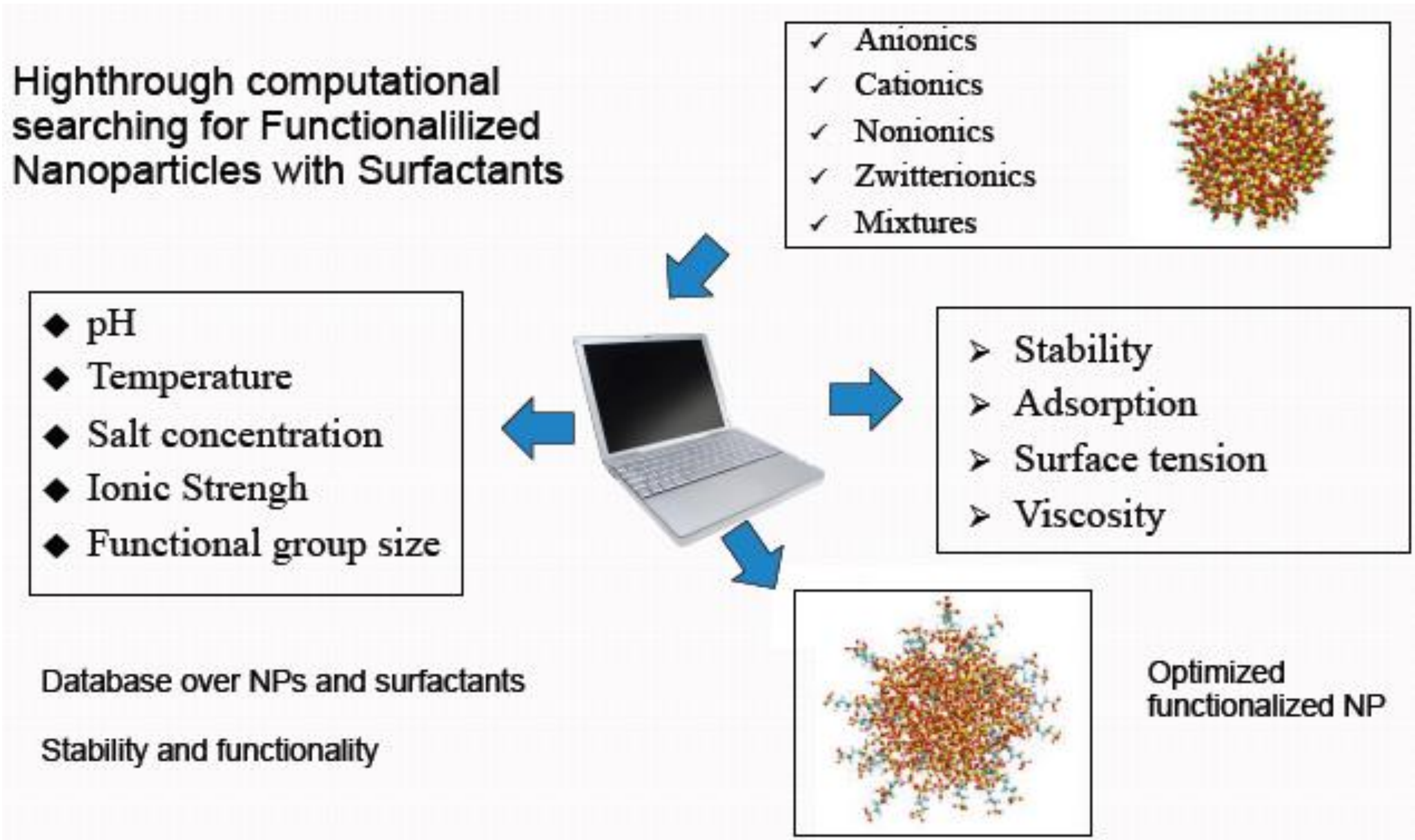
$t_0 = 5.91 \times 10^{-10}$ s

$m_0 = 1.50 \times 10^{-19}$ kg



Addition of nanoparticles improve the oil recovery process

Core-shell NP combinatorial exploration for EOR applications (on going)



Summary – NanoEOR for NPs/brine/oil/clay interfaces

- ✓ Surface characterization of Geological Materials by first principles (PDOS, AFM, XAS and NMR).
- ✓ Extensive MD for NP interacting with Clays/brine/oil.
- ✓ Adsorption and Swelling studies of NP on clay systems.
- ✓ Integrated FP, MD and LBM method.
- ✓ Cost effective way to search for NPs for EOR applications.

NANO-IOR

PRESSURE DRIVEN FLOW

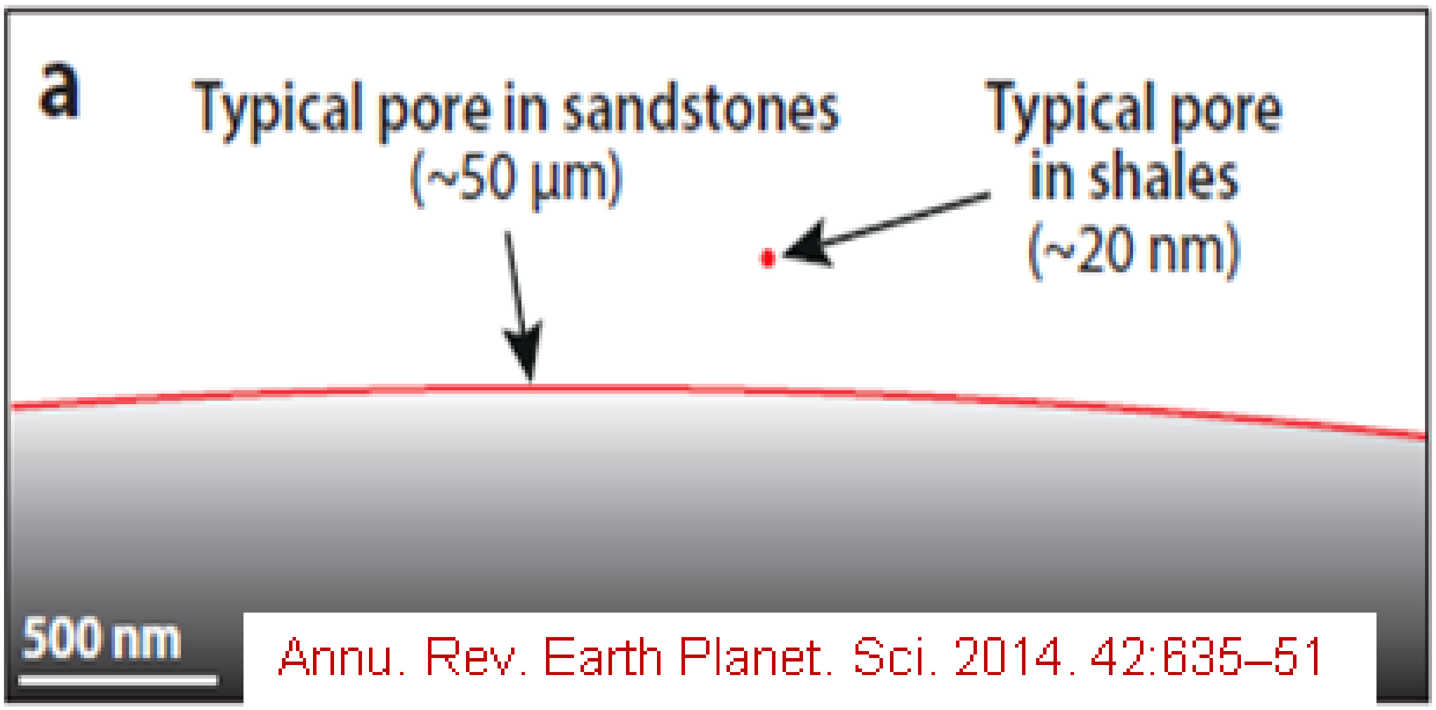
WHERE THE CONTINUUM APPROACH MAY FAIL

NANO-IOR
PRESSURE DRIVEN FLOW

- Explore the water and oil flow through silica nanopores to:

a) Model the displacement of water and oil through a nanopore to mimic the fluid infiltration on geological porous media.

b) Simulate the process of water fooding to emulate a Nano-IOR process.

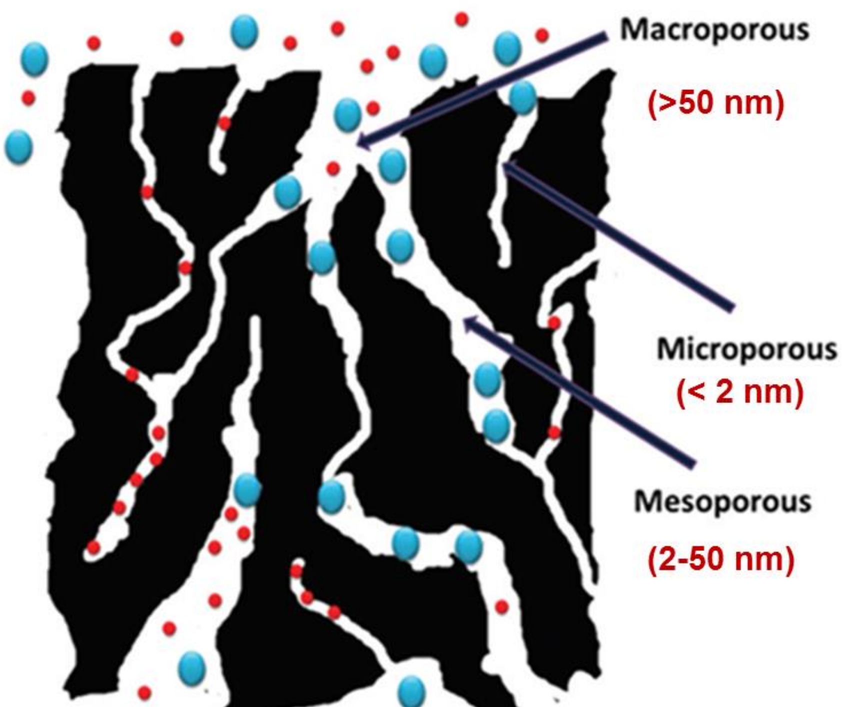


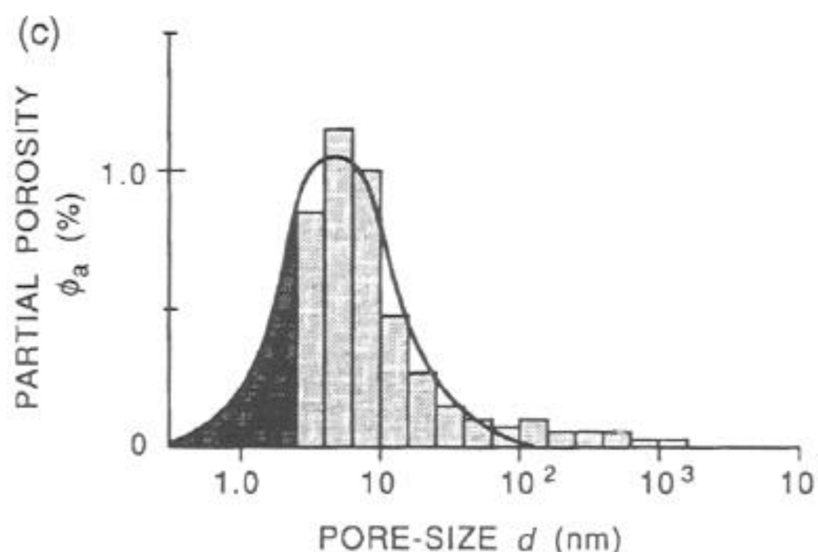
Annu. Rev. Earth Planet. Sci. 2014. 42:635–51

Fluid flow through nanoporous

Fluid flow through mineral porous occours in underground aquifers, oil and shale gas reservoirs.

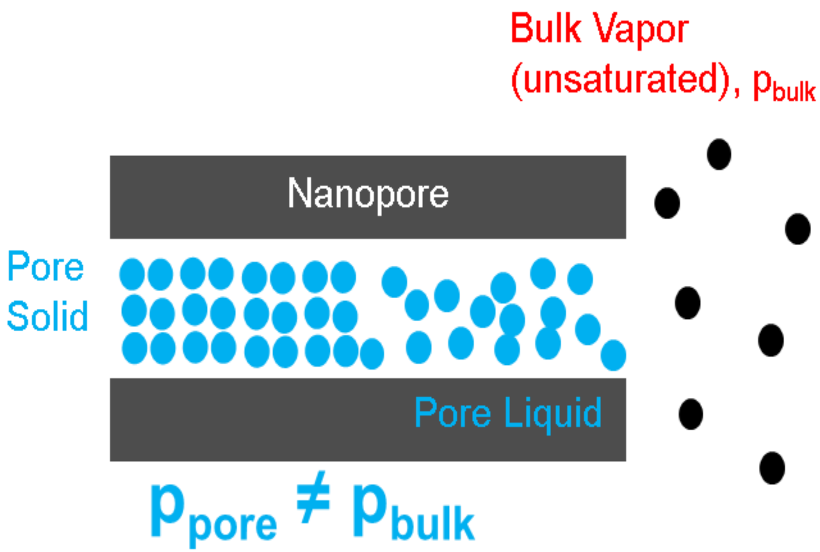
- **“Invisible pores”**
- **Large % of porosity and surface area.**
- **Interconnects larger porous**
- **Control the permeability**

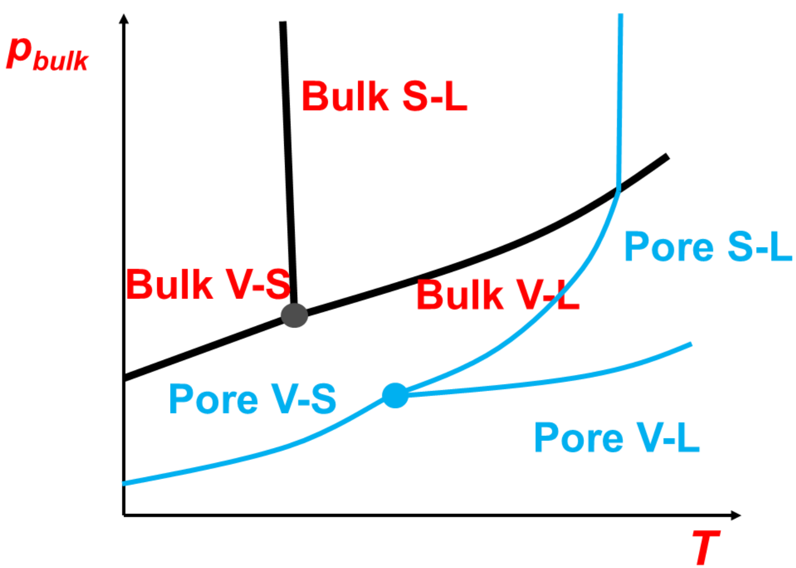




Clay Minerals (1994) **29**, 451–461

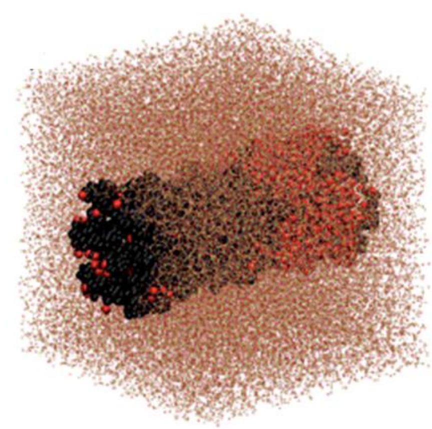
Fluids confined at nanoporous

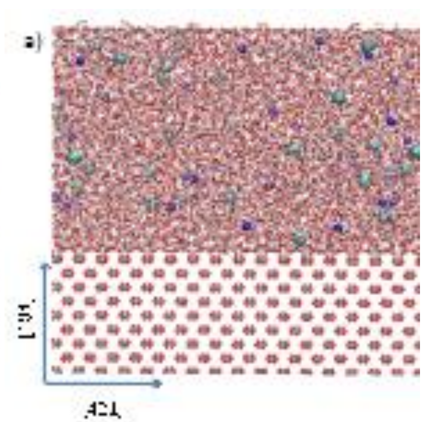




- **Under confinement, new phenomena can emerge, as *new phase transitions* and *layering near the interface.***
- **At nanoscale, the continuum models for fluids may not work.**
- **Use of an atomistic description is needed.**

SILICATES AND CARBONATES





Methodology

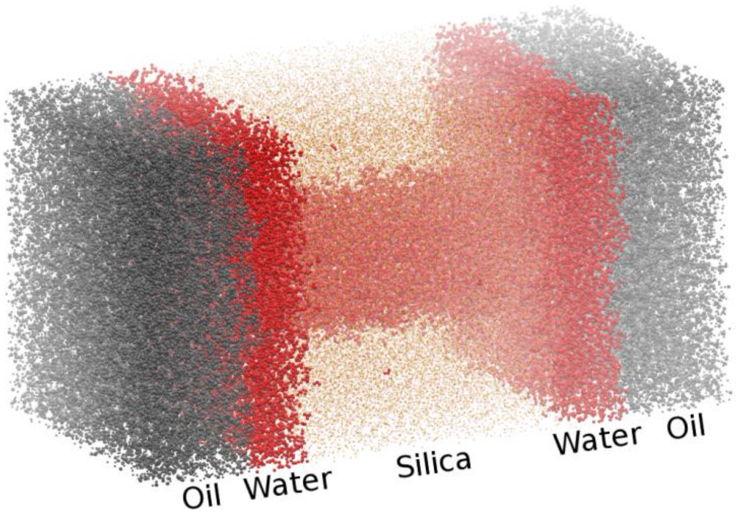
- Classical molecular dynamics (MD) simulations (LAMMPS) (over 10 ns)
- Well tested interatomic potentials : Cruz-Chu (Silica) , CHARMM (hydrocarbons) and SPCE/FH (water) with the Lorentz-Berthelot combining rules
- Realistic conditions of oil reservoirs (*300 K and 200 atm*)
- *Multicomponent oil* (light oil with alcanes and aromatic molecules)
- Induced flow process by applying an external force applied to the atoms (mimic a *pressure gradient*)

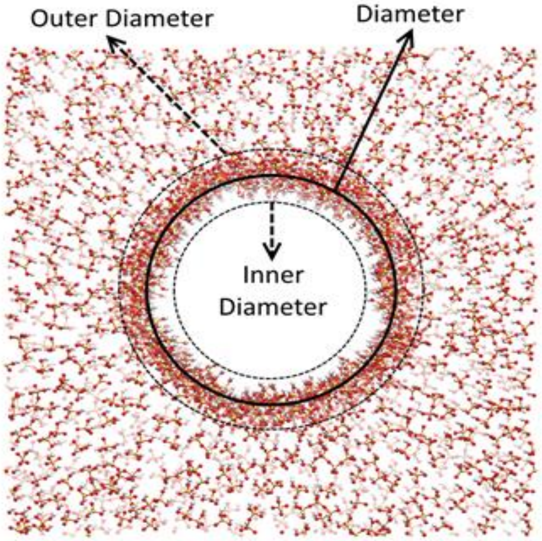
Key questions

- Would fluids infiltrate in nanoporous media (Silica) ?
- How much oil is in nanoporous ?
- At which conditions will oil infiltrate ?
- How do extract the oil ? Nano IOR

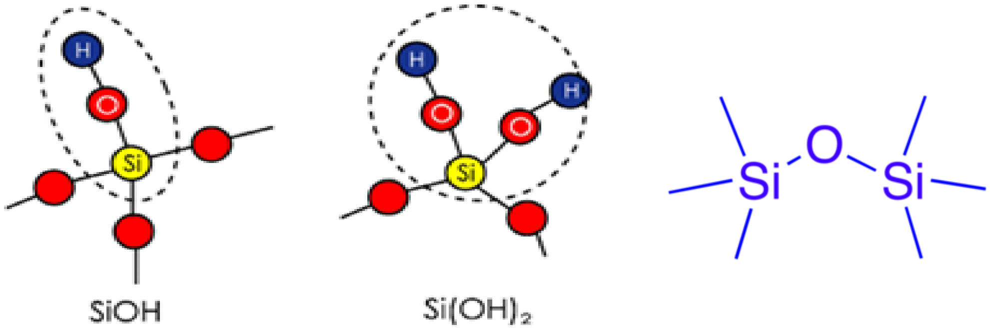
Nano IOR - Fluid infiltration in silicate nanoporous through MD

Diameters
1 nm 2 nm 3 nm 4 nm





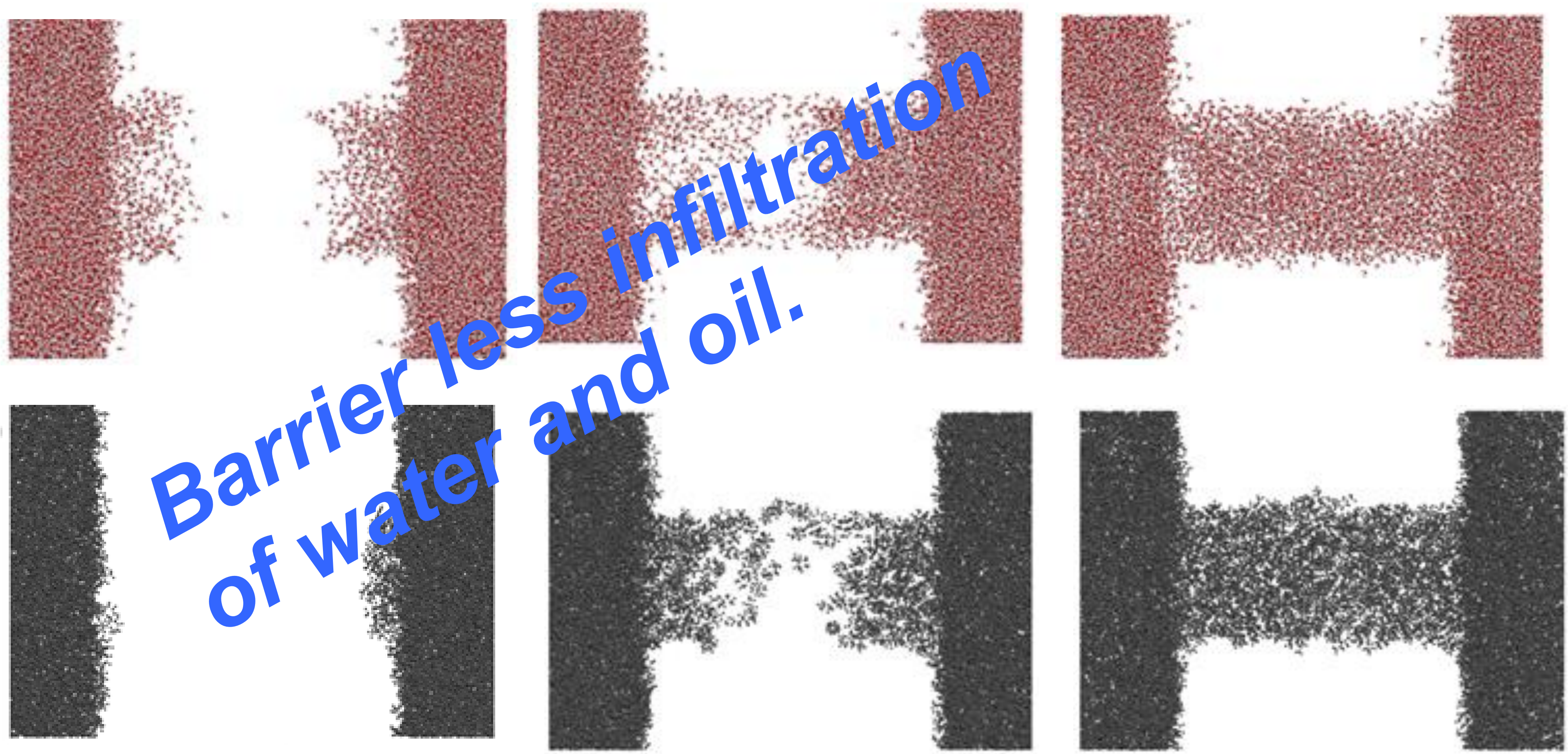
Nanoporous filled with
1) Water
2) Oil
3) Oil after water
4) Water re-injection



	Label	Diameter (Å)	SiOH terminations	$Si(OH)_2$ terminations	SiOSi terminations
Higher hydrophilicity	SiOH-Rich	39.42	6.65%	44.50%	48.86%
Lower hydrophilicity	SiOSi-Rich	36.45	30.76%	4.60%	65.71%

Do water and oil infiltrate on silica nanoporous ?

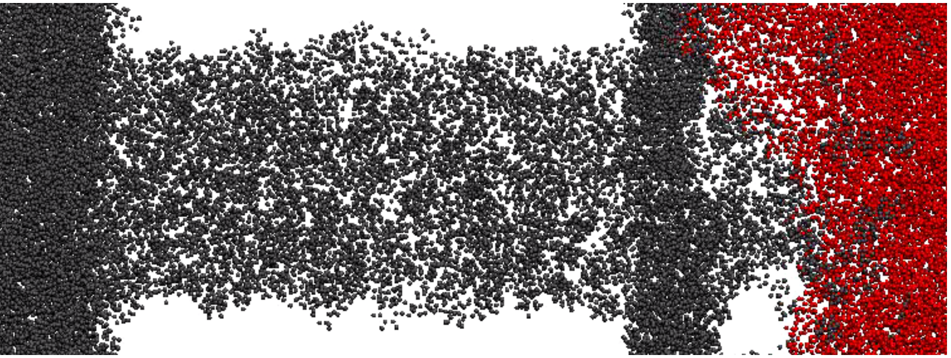
Empty nanopores (4nm) with water or oil adjacent reservoirs were simulated.

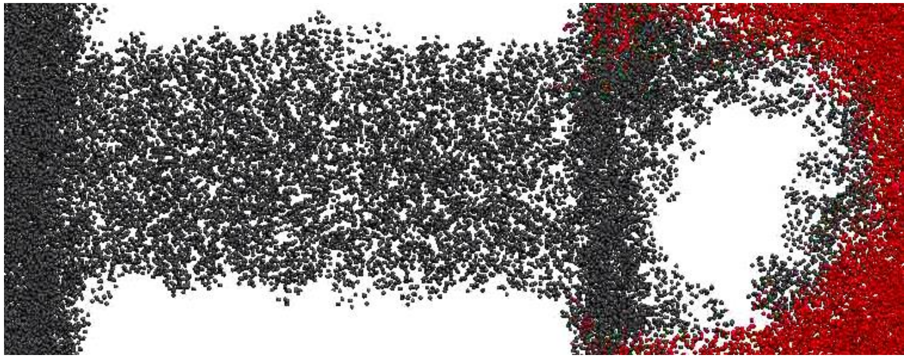


Both water and oil inltrated quickly (less than 1 ns) on the nanopores.

Model I - Water and oil filling in nanoporous silicates – (without previous contact with water)

- Water flooding - 4nm (hydrophilic)
  - Oil filled pore, with no water monolayer.

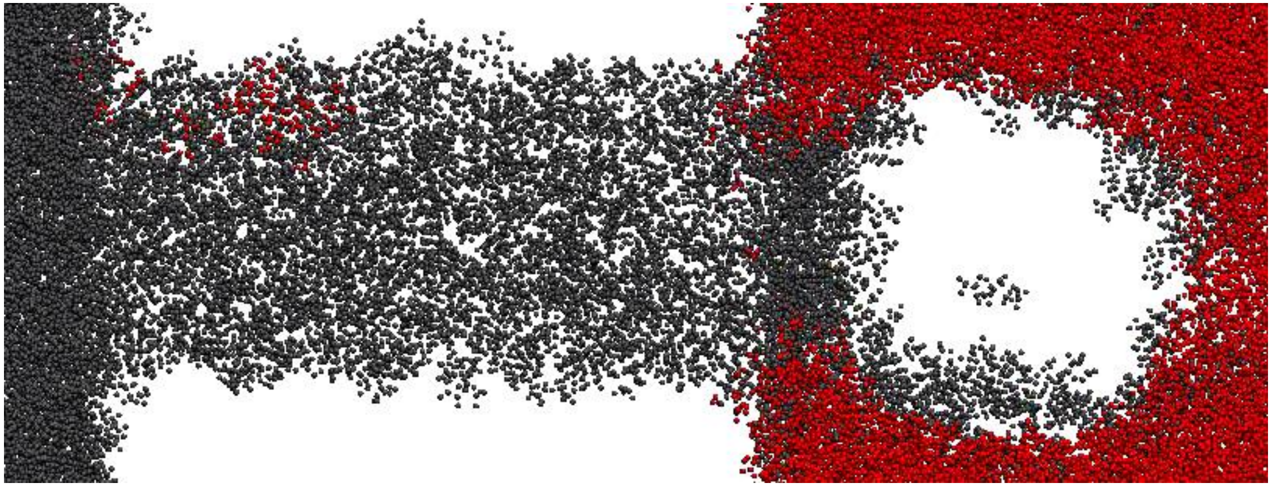




Up to 2500 atm :

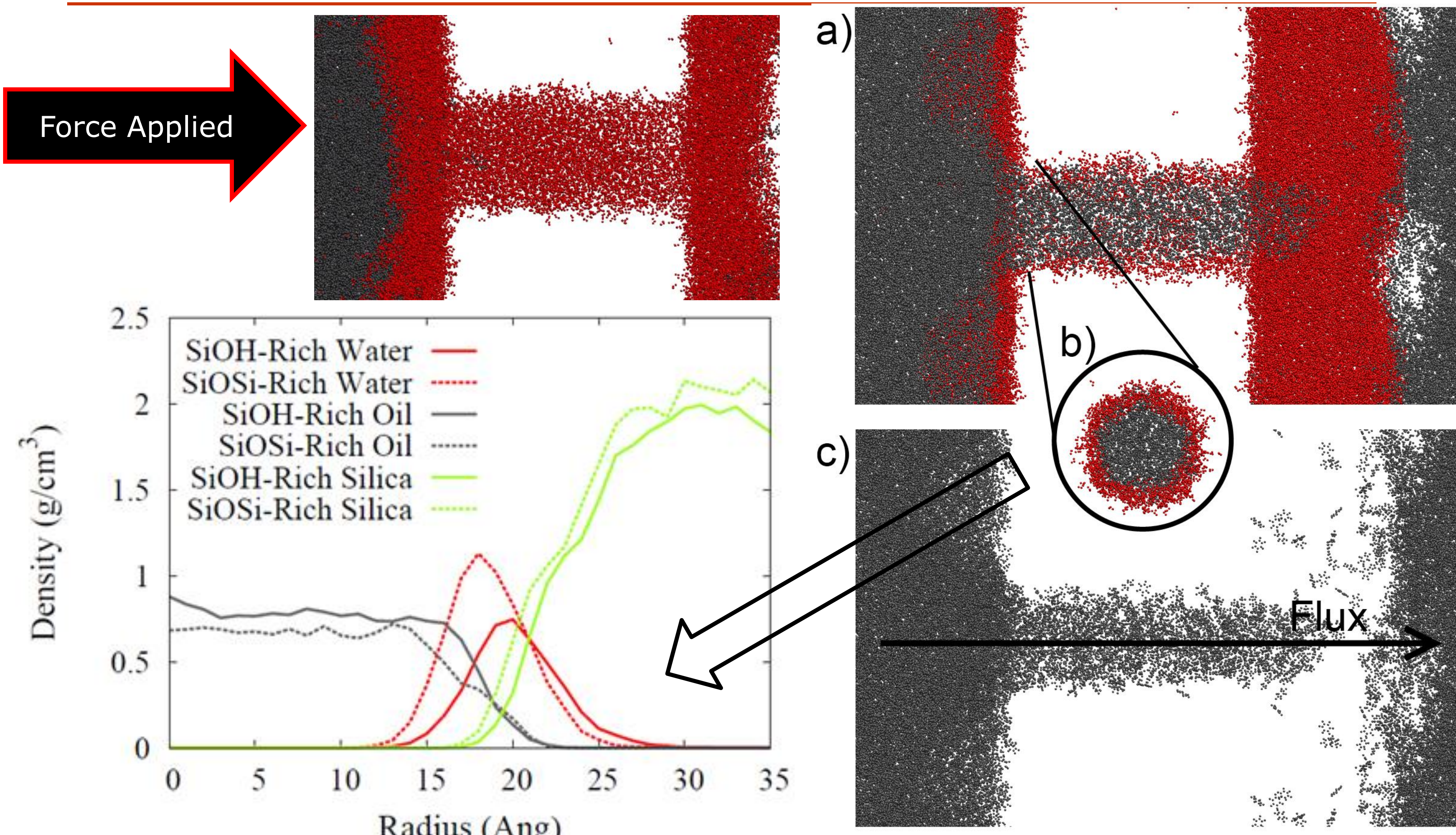
No water infiltration.

Just a few molecules enter the nanopore.



Almeida & Miranda, Scientific Reports 6:28128 (2016)

Model II (with previous contact with water)
Oil displaces water. (geological formation)



Oil infiltration observed only for pressures above 600 atm.

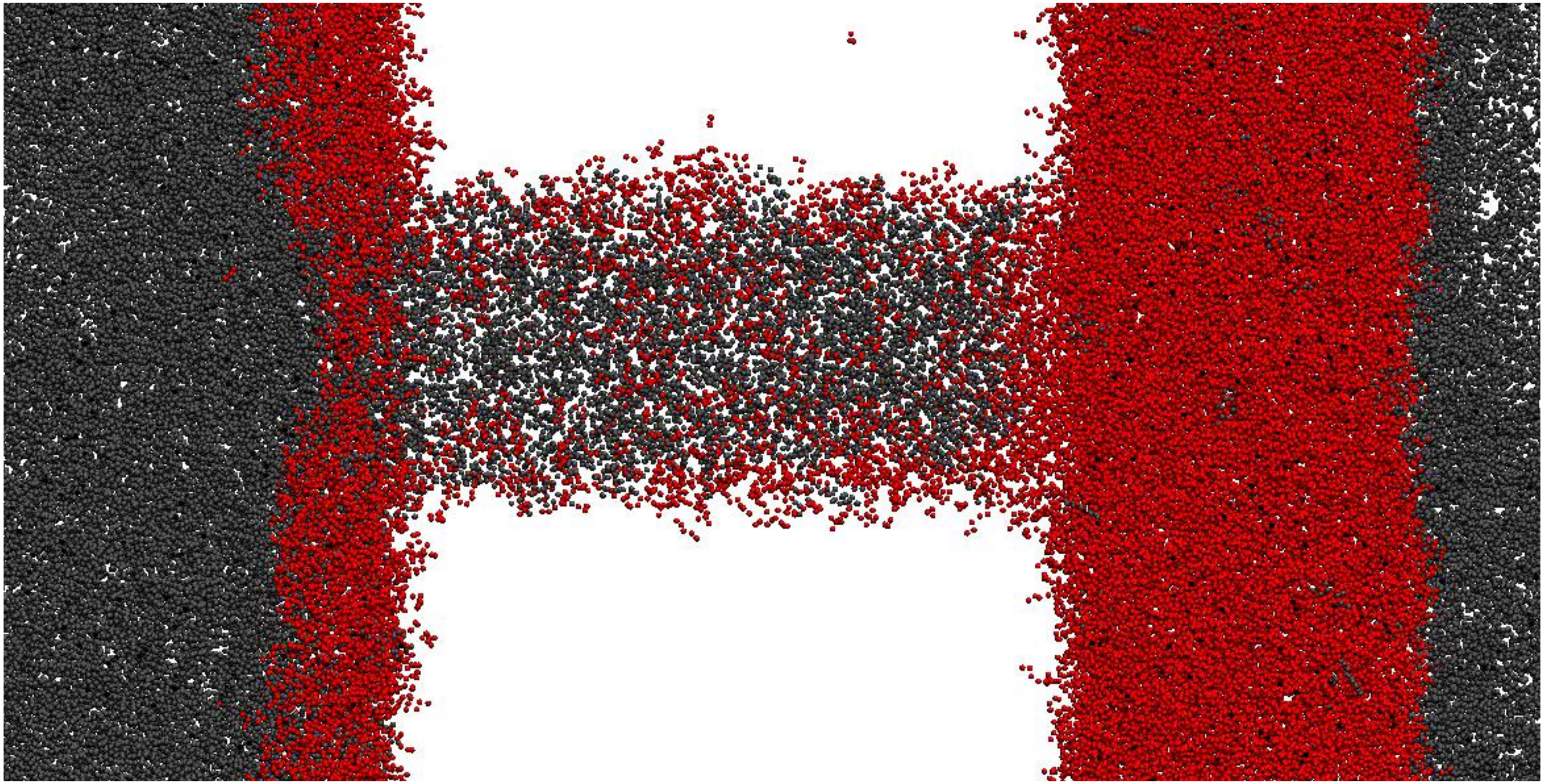
NanoIOR

- For 4nm porous, oil infiltrates above 600 atm.
- For 1000 and 1500 atm, a dripping effect at the exit end of the nanochannel is observed.
- For 2500 atm, a steady flux with no dripping occours.

Can we take it out ?

Nano IOR – Oil filling in nanoporous silicates Model II (with previous contact with water)

- Water flowing back 4nm hydrophilic, 2500 atm.



Water infiltration observed for pressures as low as 10 atm.

Key questions

- Would fluids infiltrate in nanoporous media (Silica) ?

YES – no barrier

- How much oil is in nanoporous ?

Considerable, with water thin film adsorbed

- At which conditions will oil infiltrate ?

Above 600 atm

- How do extract the oil ? Nano IOR

YES, only if water is adsorbed.

Almeida & Miranda, Scientific Reports 6:28128 (2016)

Summary - Nano-IOR in nanoporous silicates

- Modeling of nanoporous silicates (hydrophobic to hydrophilic) from 1 to 4 nm.
- MD simulations used to determine the wettability and contact angle between injected fluids (brine and CO2) with light oil (not shown).
- Plethora of dynamics in nanoporous media observed (Cavitation, bubble formation, fluid flow)

NANOAGGREGATION OF COMPLEX MOLECULES ASPHALTENES

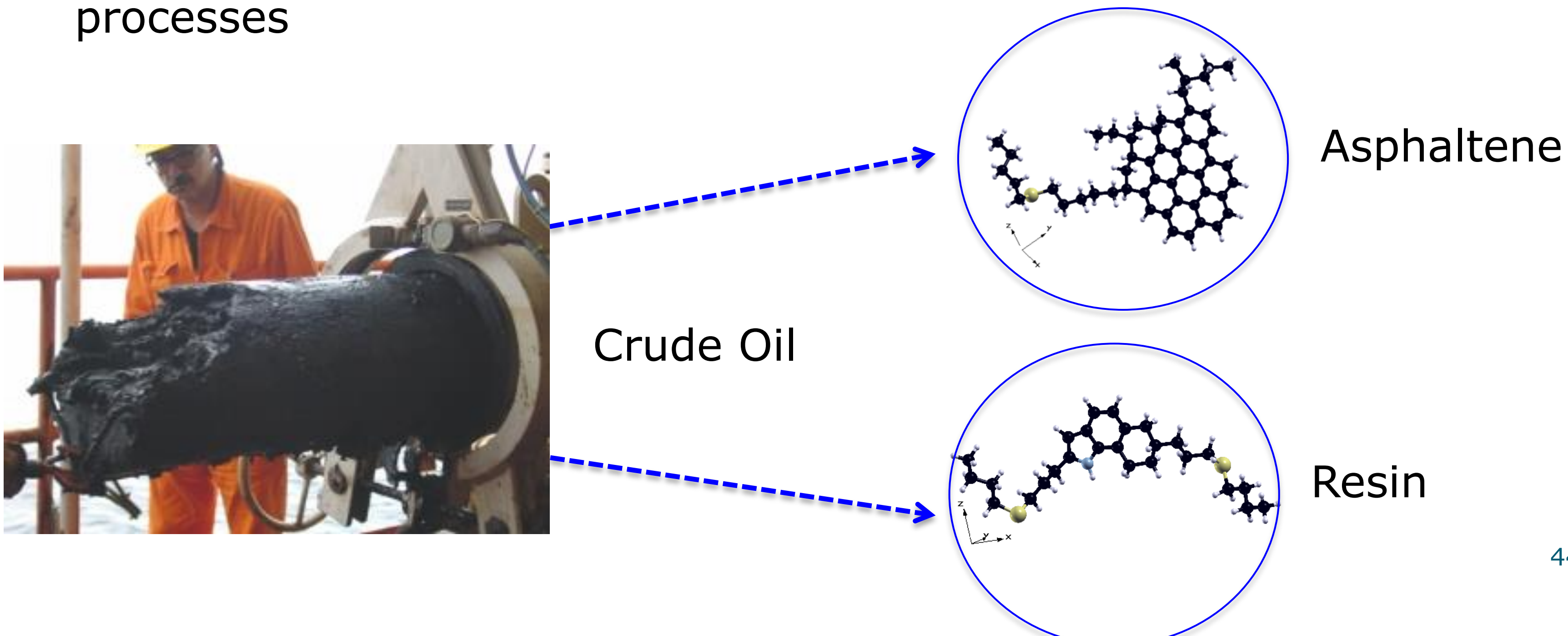
WHERE MD IS NOT ENOUGH

“Asphaltenes: the petroleum cholesterol”

- Asphaltenes are the most polar and surface-active fraction of the oil that is insoluble in n-alkanes, but soluble in aromatic solvents.

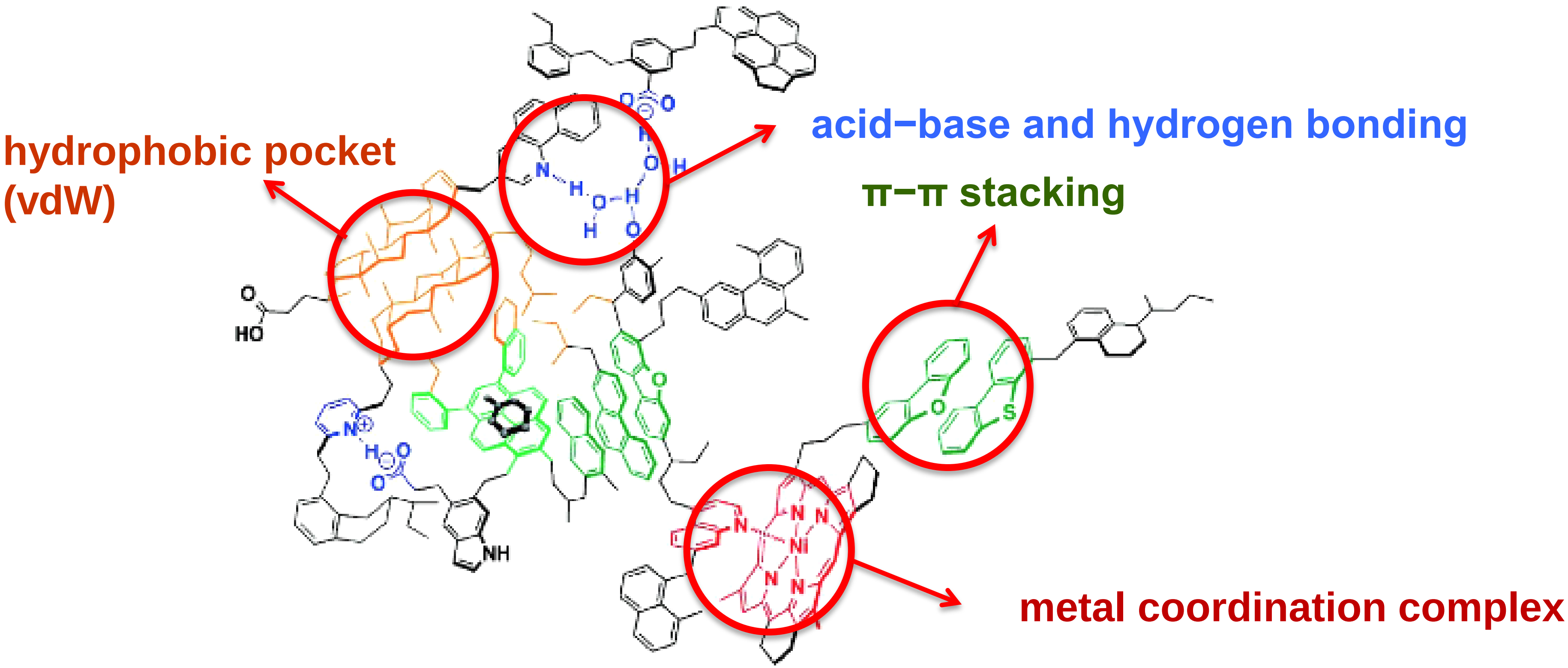
- They can precipitate, aggregate and deposit on wells, formations, pipelines and surface facilities

- They play a key role in the Oil industry chain from oil E&P to refining processes



Asphaltene and resin interactions

- Tendency to nanoaggragate, clustering and adsorb at solid surfaces
- Very rich and complex chemistry



Adams, J. J., *Energy & Fuels*, 2014, 28, 2831-2856.

Summary - nanoaggregation

- The proposed *nanoaggregation mechanism* is based on the competition of the π- orbitals, leading to degeneracy broken of the electronic states with an increasing of the displacement of the HOMO orbital towards the center of the nanoaggregate.

- The growth of the nanoaggregate is further limited given their charge rearrangement, which leads to a dipole moment decreasing.

- These findings can guide new methods for asphaltene stability control.

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