Métodos numéricos para escoamentos em nano e microescalas

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Cronograma

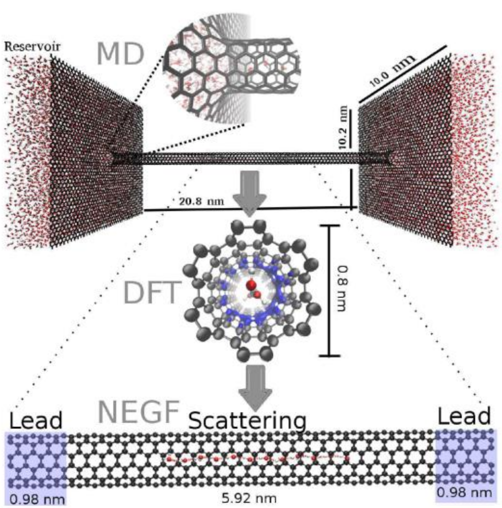
	Ter	atividade	Instrutor
set	8		
	15	Apresentação do Curso / Métodos Multiescala	Caetano
	22	Ambientação - Máquina Virtual / Projeto / Linux	Caetano / Kirch
	29	Dinâmica Molecular 1	Caetano / Kirch
out	6	Lab 1 - Dinâmica Molecular -Fluidos bulk (Estrutura e Transporte)	Caetano / Kirch
	13	Dinâmica Molecular 2	Caetano / Kirch
	20	LAB 2 - Dinamica Molecular -Interfaces (Tensão Interfacial) & Viscosidade	Caetano / Kirch
	27	LBM	Julio / Adriano
nov	3	LBM	Julio / Adriano
	10	CFD	Julio / Rafael
	17	CFD	Julio / Rafael
	24	CFD	Julio / Rafael
	1	CFD	Julio / Rafael
dez	8	Projeto - Apresentação	Julio / Rafael / Caetano
	15		

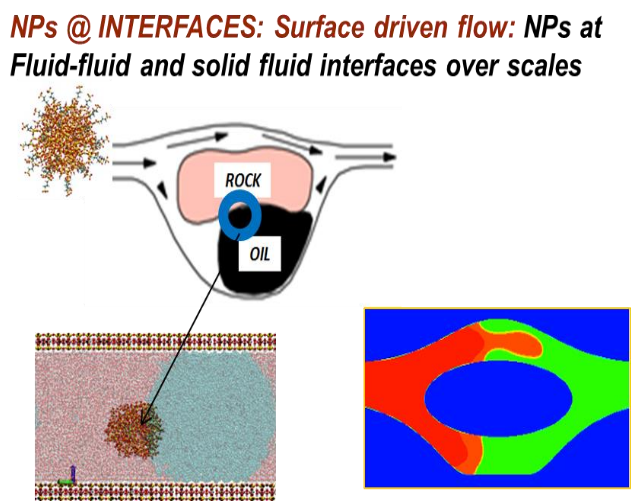
FLUID DYNAMICS AT NANOPOROUS: ARE THE MACROSCOPIC LAWS STILL VALID?

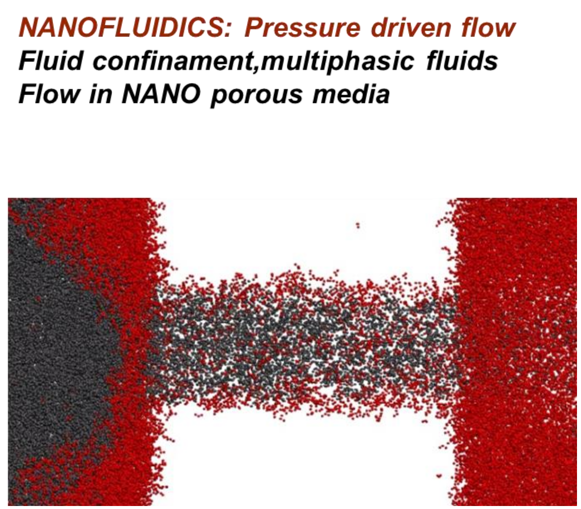
Outline

Dynamics of fluids in (nano) porous media

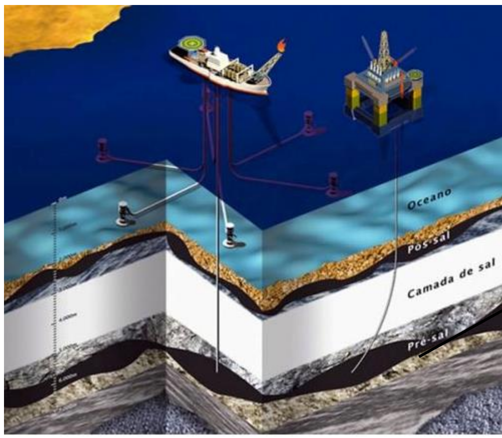
a) Nanofluidics
b) Multiscale molecular simulations
c) Phenomena at nano scale at CNTs and rock’s nanopores



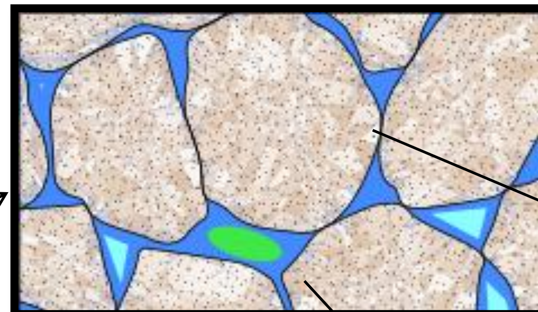




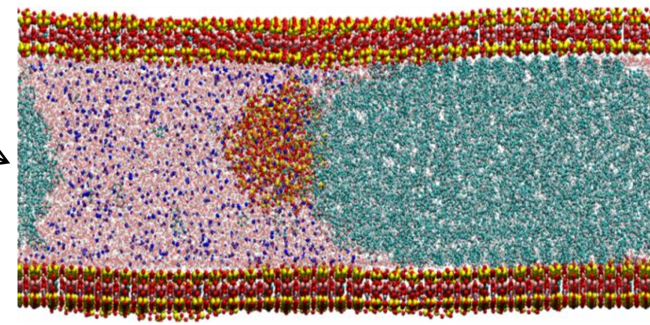
Dynamics of fluids, NPs and surfactants in porous media from nano to pore



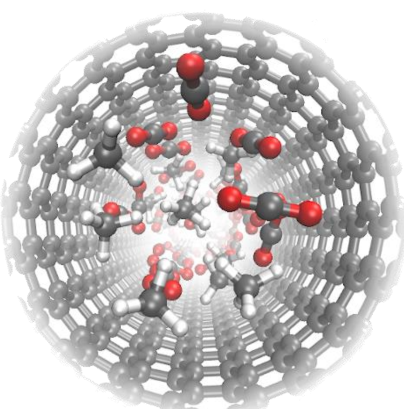
MINERAL – OIL – BRINE interfaces
Carbonates, Silicates, Clays and Cement



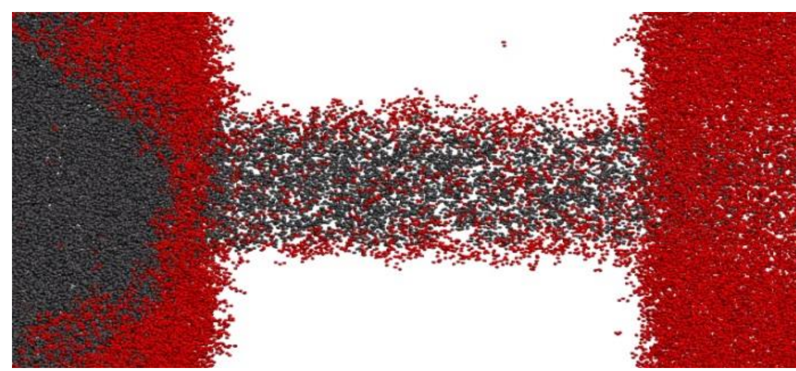
NANO-EOR - Surface driven flow:
NPs and surfactants at interfaces brine-oil-rock over scales



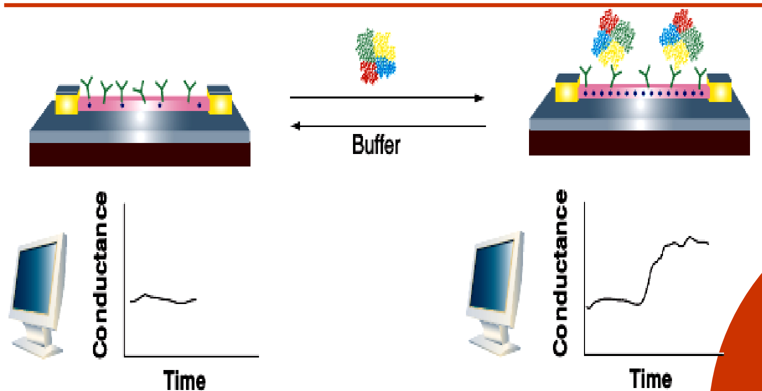
Membranes
Separation of natural gas



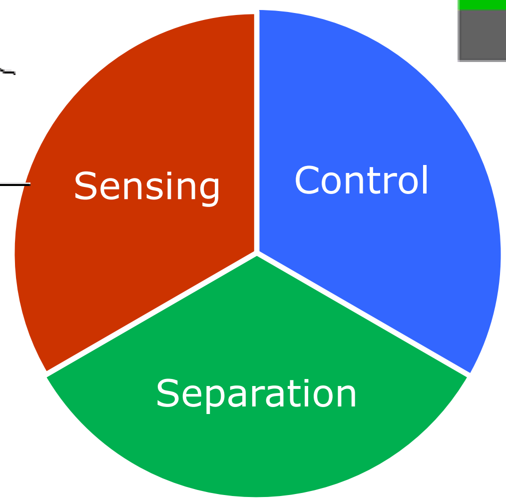
NANO-IOR – Pressure driven flow
Fluid confinament,multiphasic fluids
Flow in NANO porous media

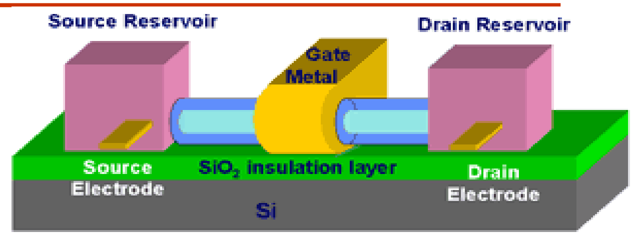


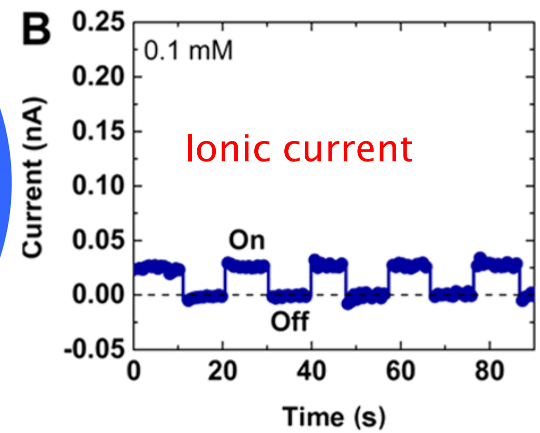
Nanofluidics: flow in nanoporous media



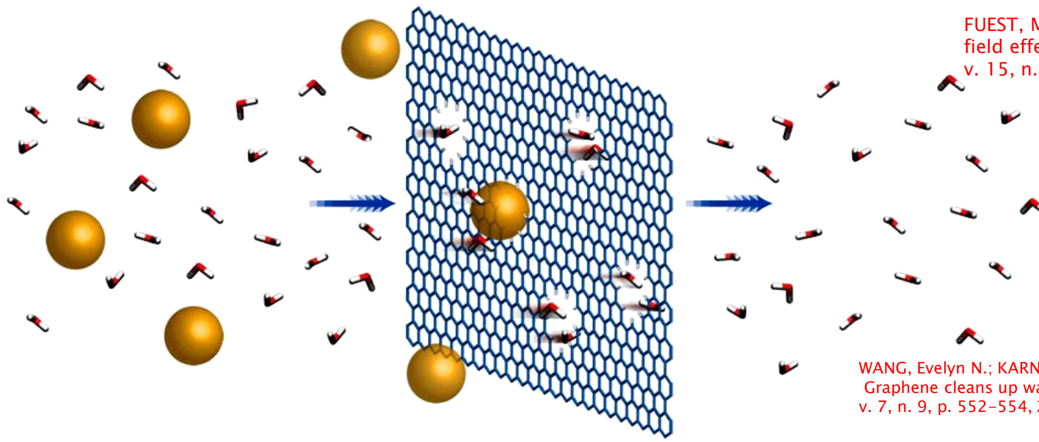
PATOLSKY, Fernando; ZHENG, Gengfeng; LIEBER, Charles M. Nanowire sensors for medicine and the life sciences. 2006.





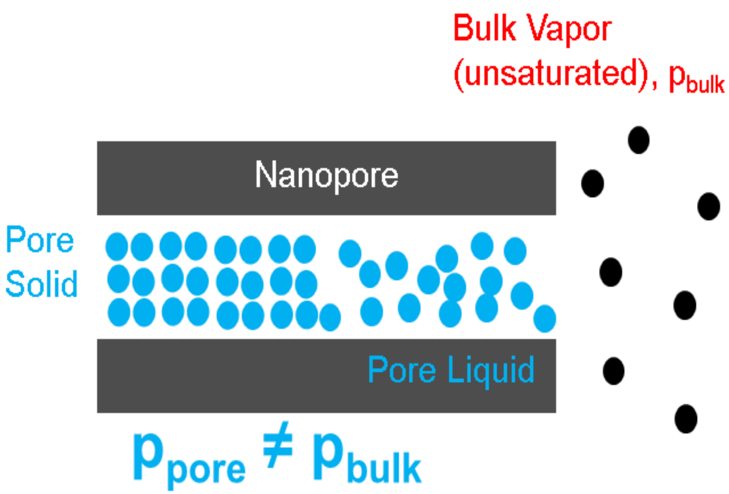


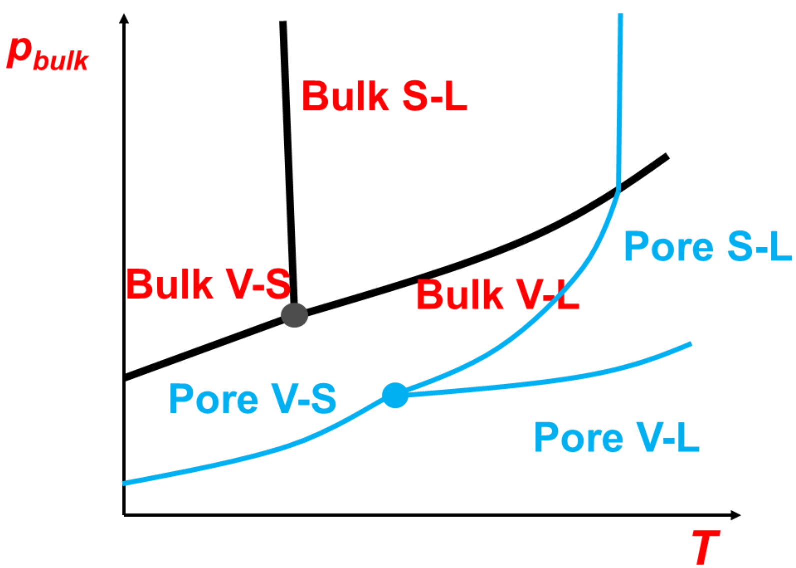
FUEST, Marie et al. A three-state nanofluidic field effect switch. **Nano letters**, v. 15, n. 4, p. 2365-2371, 2015.



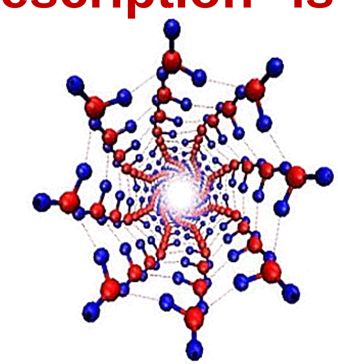
WANG, Evelyn N.; KARNIK, Rohit. Water desalination: Graphene cleans up water. **Nature nanotechnology**, v. 7, n. 9, p. 552-554, 2012.

Fluids confined at nanoporous





- **Under confinement, the structuring is frustrated by surface effects, that disrupts the hydrogen bond networks.**
- **New phenomena can emerge, as *new phase transitions*, *layering near the interface*, eg. *first layer of immobile water*.**
- **At nanoscale, the continuum models for fluids may not work.**
- **Use of an atomistic description is needed.**



Li, Shujuan & Schmidt, Burkhard (2015). Molecular dynamics simulations of proton-ordered water confined in low-diameter carbon nanotubes. *Physical Chemistry Chemical Physics, 17*, 7303-7316.

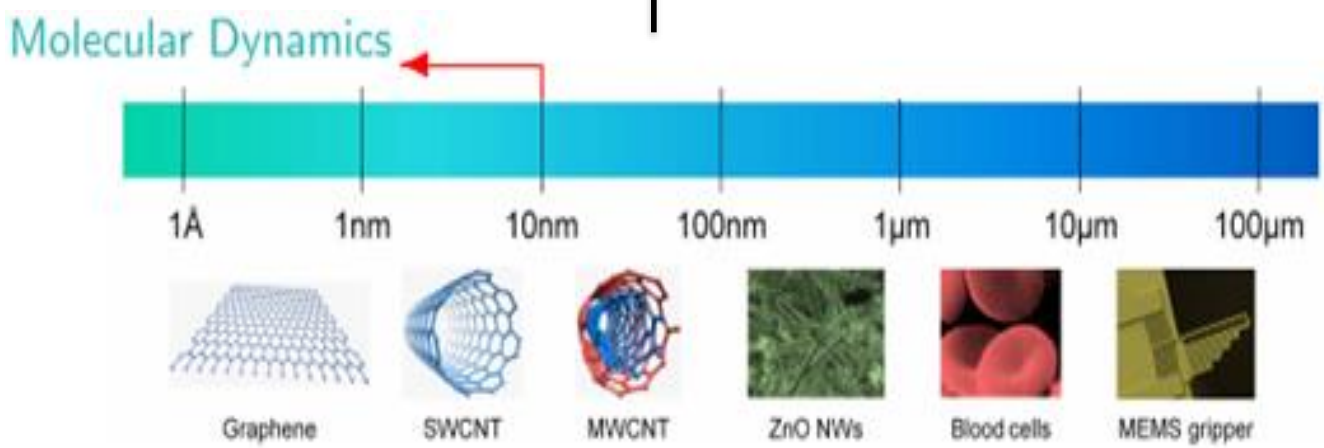
Phenomena at nanoscale

Molecular Dynamics

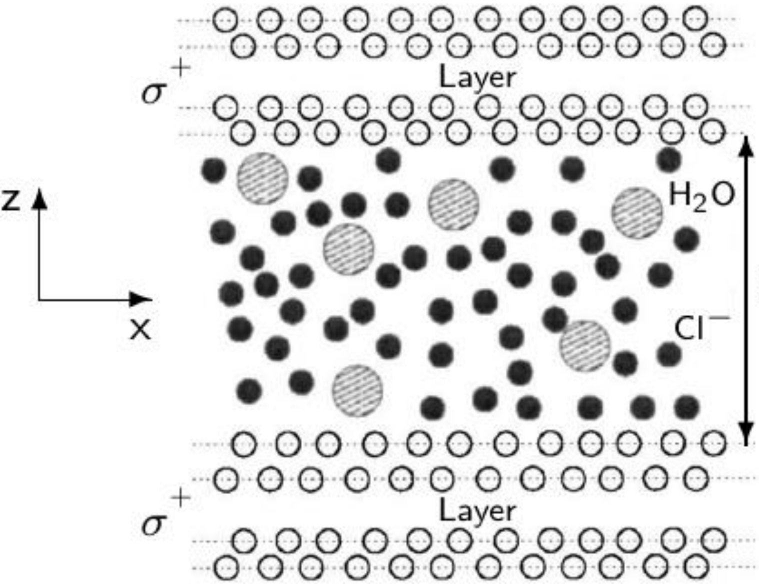
- **Newton´s eq. of motion**
- **Interatomic potential**

Continuum Theory

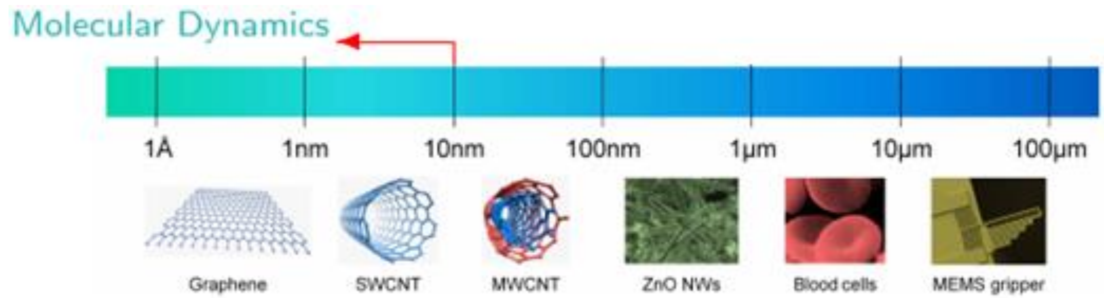
- **Electrostatic (Poisson – Boltzmann)**
- **Hydrodynamic (Navier – Stokes)**

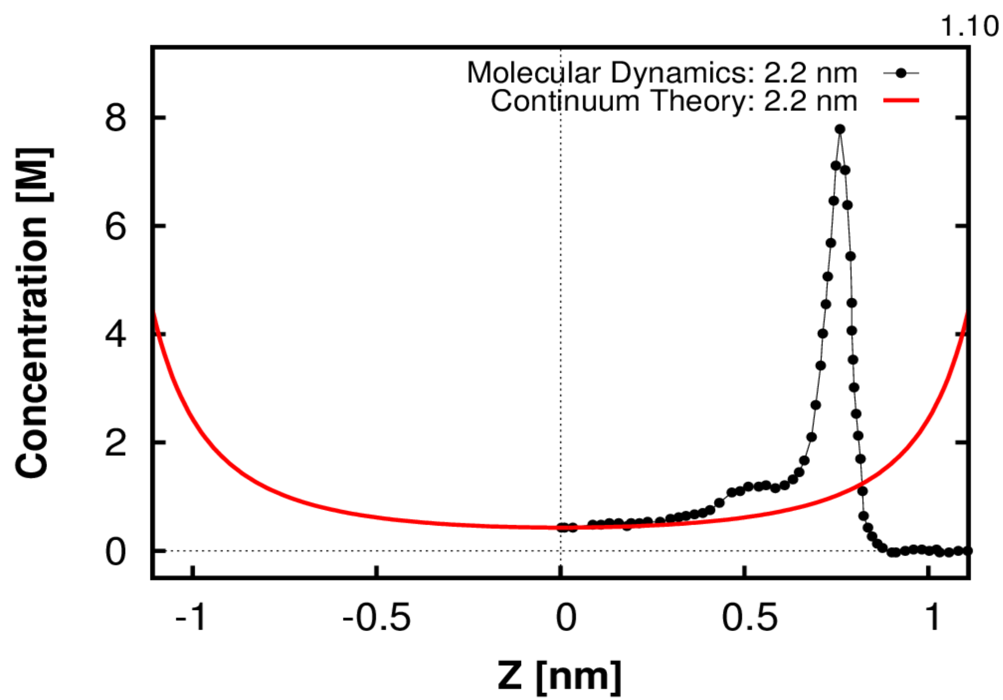


Limitations of Molecular Dynamics at nanoscale



Schematic of the channel system under investigation



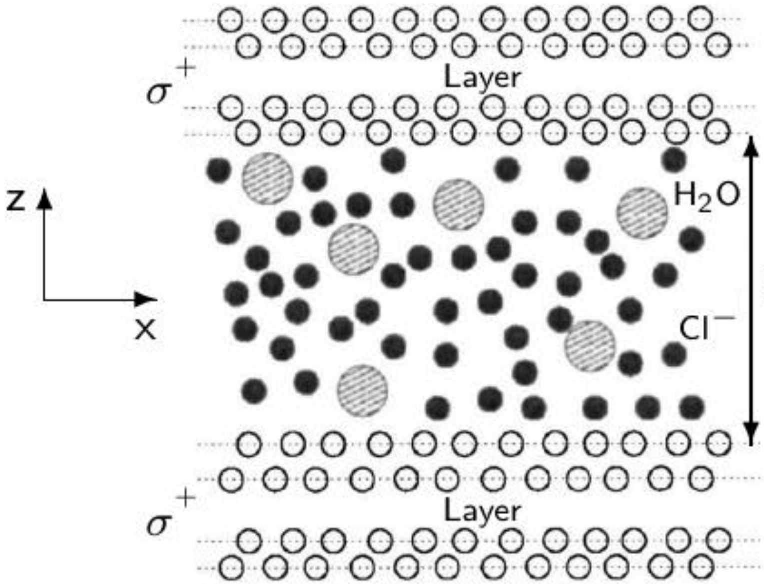


Ion concentration (Cl)

Limitation:

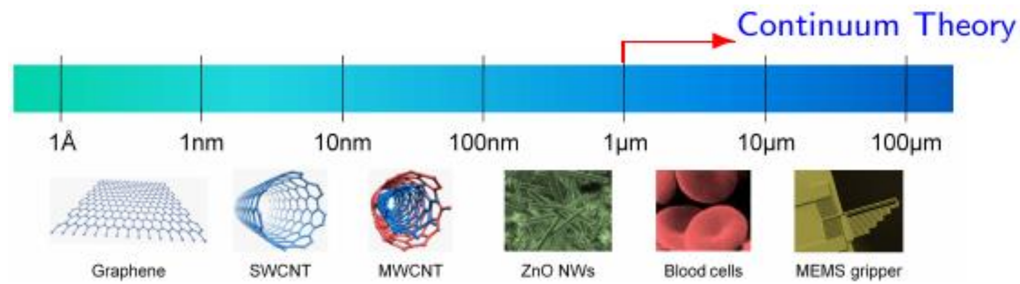
- Computational cost
- Time and length scale

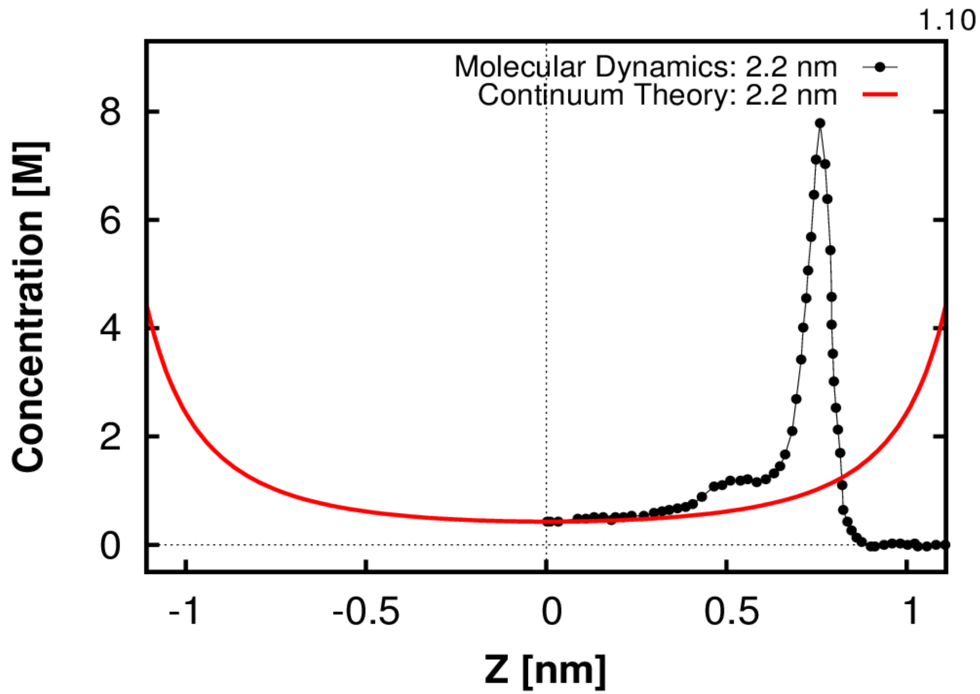
Limitations of Continuum theory at nanoscale



Schematic of the channel system under investigation

Limitations:
- Interactions ion-wall
- Interactions ion-ion
- Interactions ion-solvent





Ion concentration (Cl)

Multiscale Modeling strategies

- Different ways to combine each levels of resolution (energy, time and/or length):

(i) ***Sequential***: the simulation models on different scales are treated separately by simply transfer information between levels of resolution. (mature)

(ii) ***Hybrid:*** different levels of resolution are running simultaneously with a direct link between them, (developed)

(iii) ***Adaptive:*** switch between resolution levels on the fly (work in progress – problem specific)

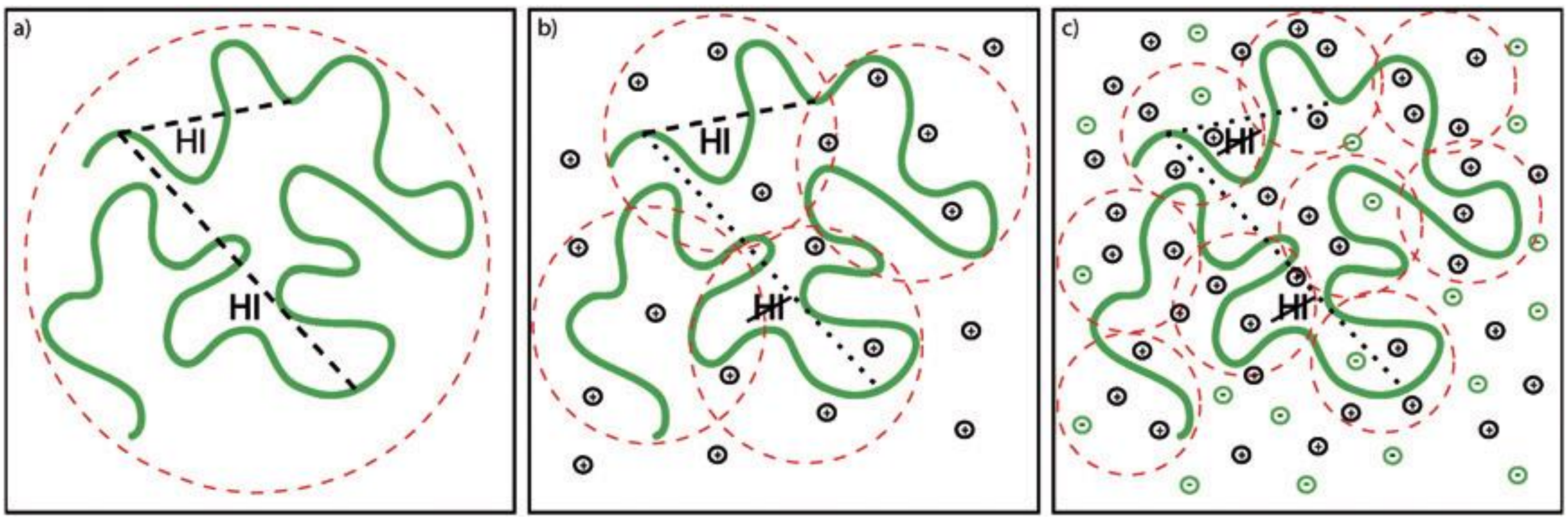
Multiscale Modeling strategies

- The exchange of information, interaction or particles requires a high level of consistency between the individual models:

i. Energy and forces
ii. Structural
iii. Mechanical properties
iv. Electrostatic environment
v. Hydrodynamics

Particles immersed in a fluid excite long-ranged flows as they move, and similarly move in response to fluid motion.

a) uncharged polymer, the hydrodynamic interactions are unscreened
b) Salt limits the hydrodynamic interaction
c) More salt, the chain can be hydrodynamically decoupled.



Mesoscale modelling of polyelectrolyte electrophoresis - Kai Grass and Christian Holm - DOI: 10.1039/b902011j

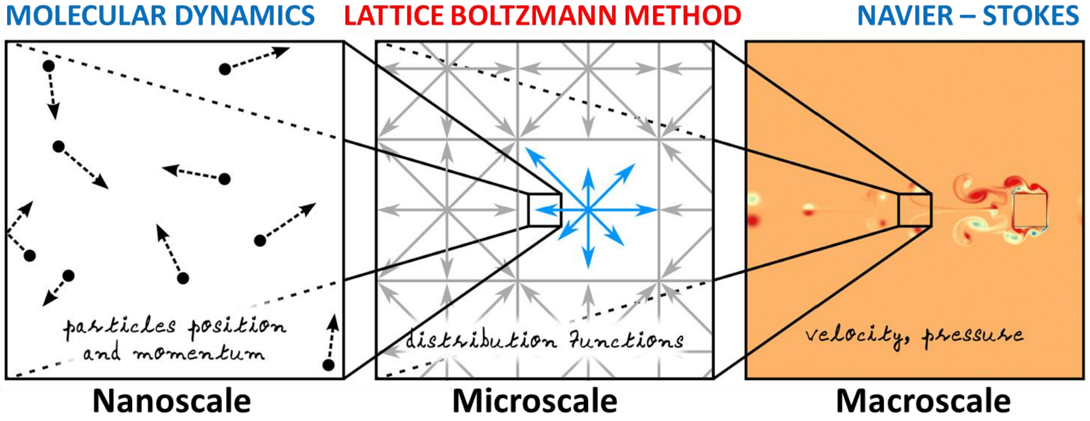
Linking levels of resolution: energies, forces and structures

- Scale bridging requires systematic development of the individual models which are thermodynamically, mechanically and/or structurally consistent.

- Here, we use the following approaches:

1) Part 1 - from the quantum mechanical to atomistic
2) Part 2 - from atomistic to lattice levels

LINKED VARIABLES:
ENERGY and FORCES
HYDRODYNAMICS
ELASTIC MEDIA
ELECTROSTATIC MEDIA



www.-m2.ma.tum.de/bin/view/Allgemeines/MA5344SS15

Multiscale Modeling Strategies

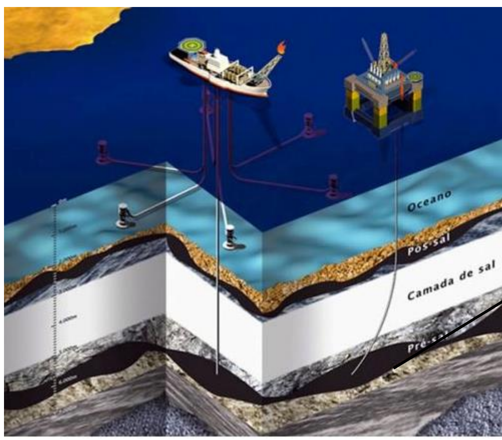
- Assuming Quasi-Equilibrium:
  - Microscopic Scale, fast process
  - Macroscopic Scale, slow process
  - Assume quasi-equilibrium of micro
  - Use molecular info in constitutive laws at macro scale

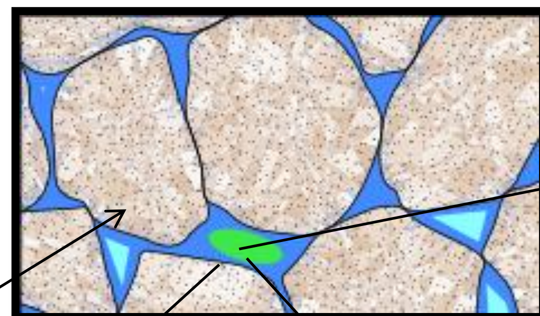
- Example: Dynamics of particles in porous media
- *Aplication: Enhanced Oil Recovery (EOR)*
  - Constitutive Law: Momentum Flux Equation (LBM)
  - Microscopic Level: Molecular Dynamics used on fluid particles to estimate wetability and viscosity properties for macro

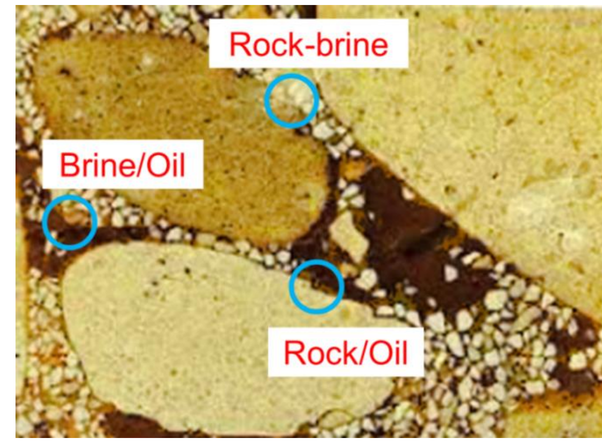
NANO-EOR

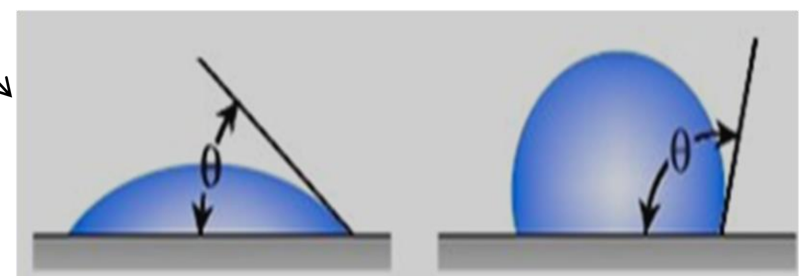
Complex physical phenomena in materials: a O&G perspective

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









As oil recovery processes involve the interaction between rock-brine-oil.

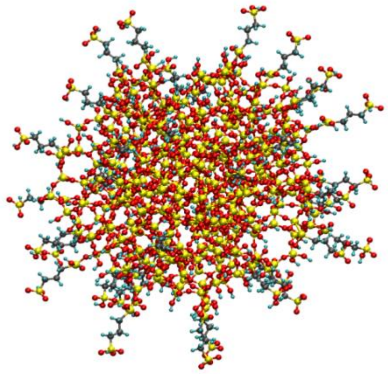
The optimization of oil production requires deep understanding of reservoir properties at different scales.

Main strategies:

Reduce the interfacial tension (IFT) and the viscosity of crude oil by molecular additives

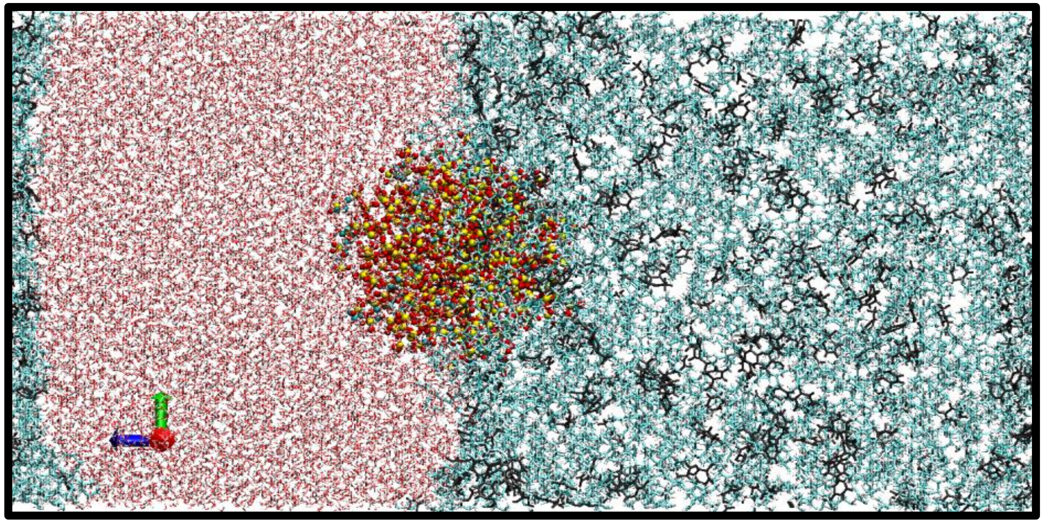
NANO-EOR

SURFACE DRIVEN FLOW



Functionalized Silica nanoparticles

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

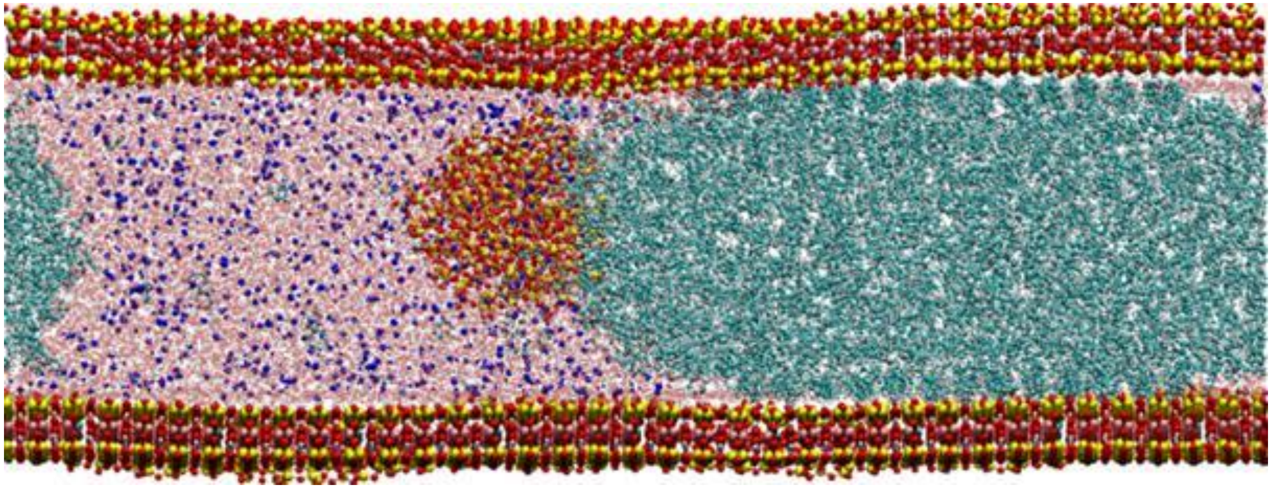


Temperature (300, 350, 375 and 400K)
Pressure (1to 400 atm) [1 – 6000 psi]

Miranda et al. SPE-157033-MS - 2012

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*.

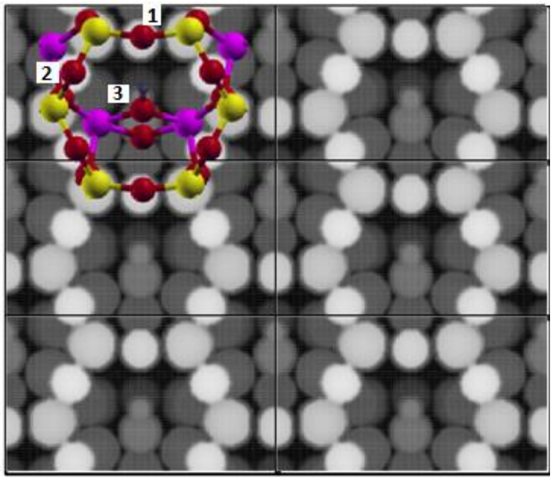


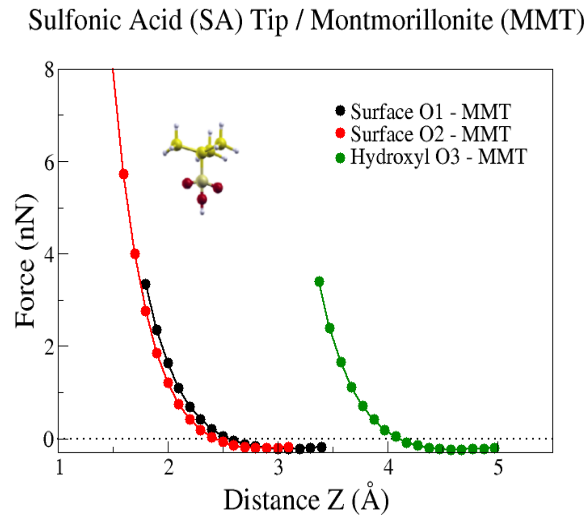
$(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$.

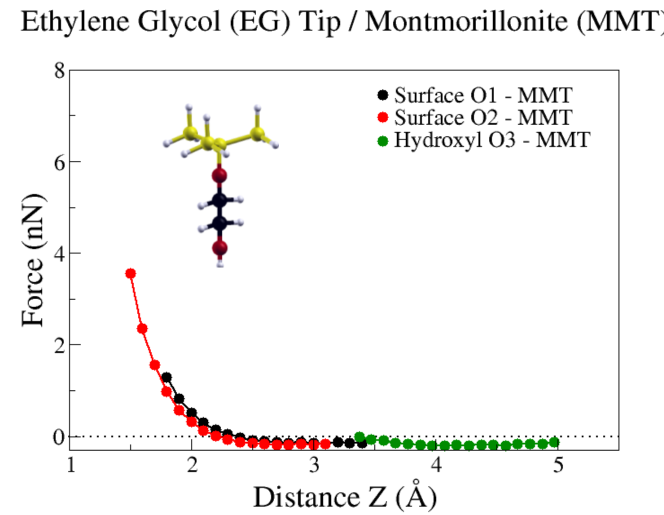
MMT is naturally hydrophilic and it has good affinity with H_2O.

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

Alvim, R. S.; Miranda, C. R ***JPC_C (2016)***





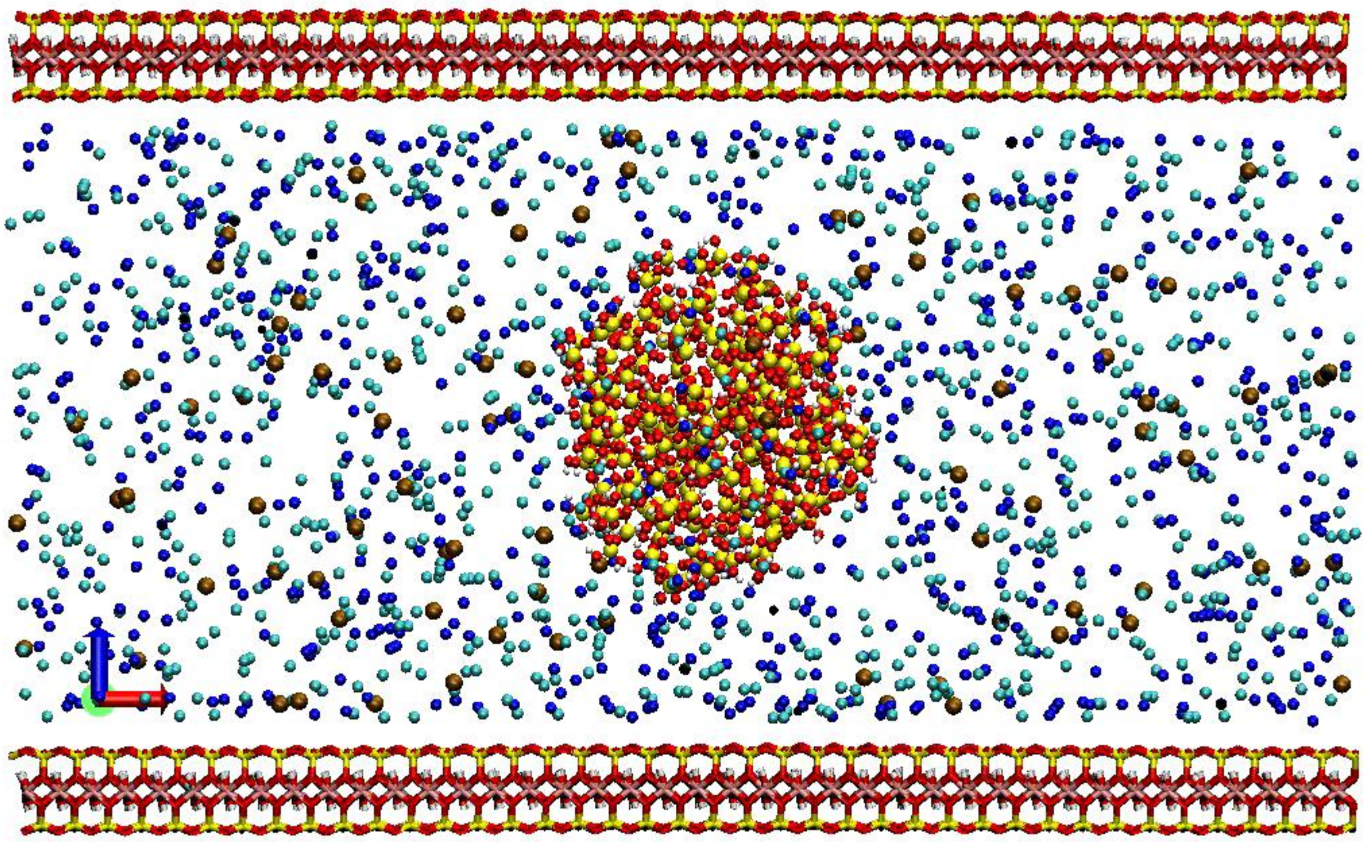


Tip Approach

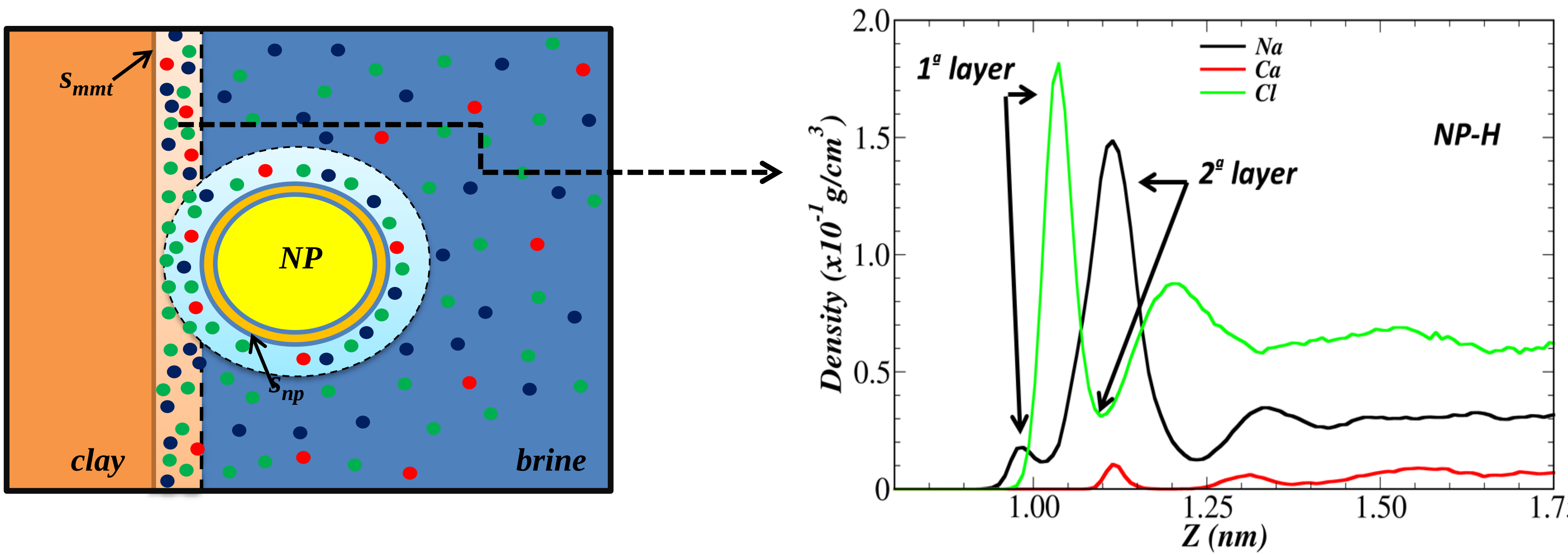
- *Strength of bonding*
- *Surface configuration*
- *Adsorption density*
- *Interatomic Forces*
- *Chemical environment*

HOW TO UPSCALE THIS VERY FUNDAMENTAL INFORMATION ?

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

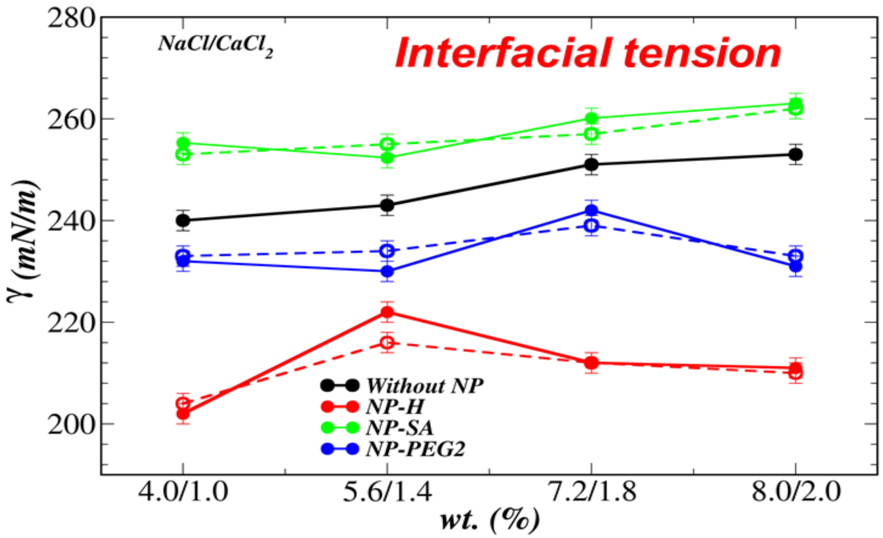


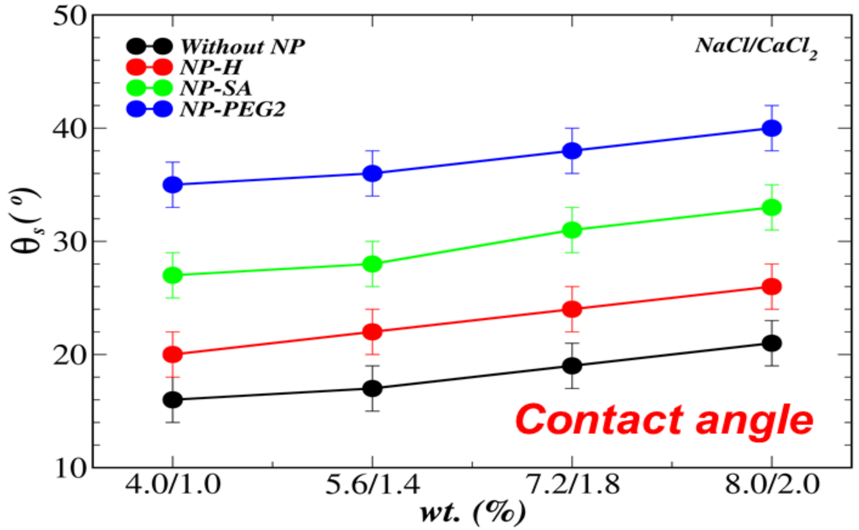
Electrical double layer

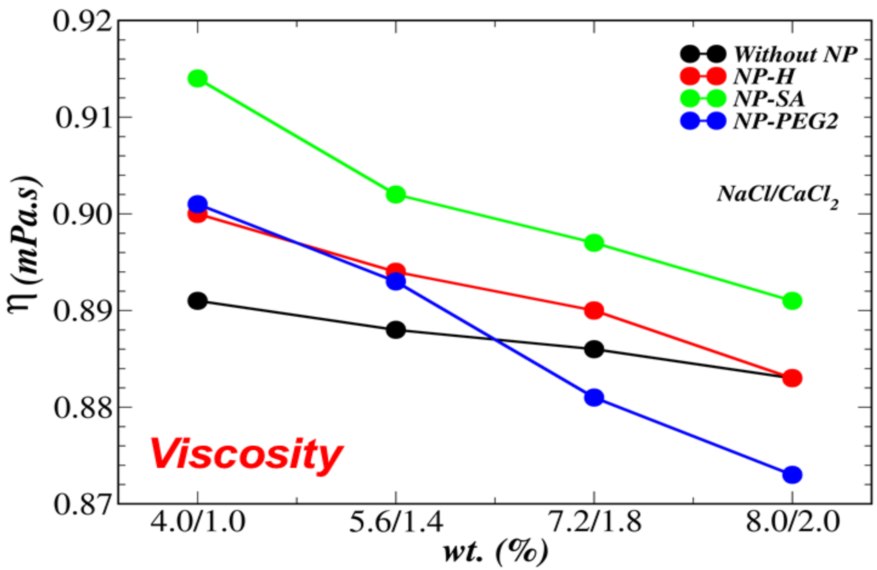


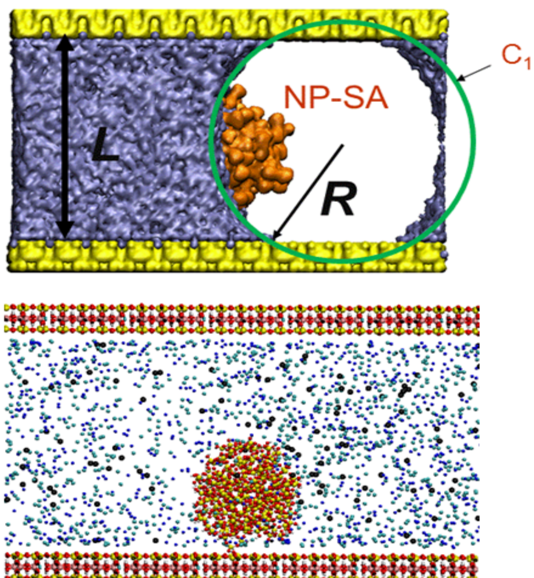
- **Electrical Double Layer (EDL) Formation**.
- **For NP adsorbed on MMT – compression of the EDL.**

Interfacial phenomena







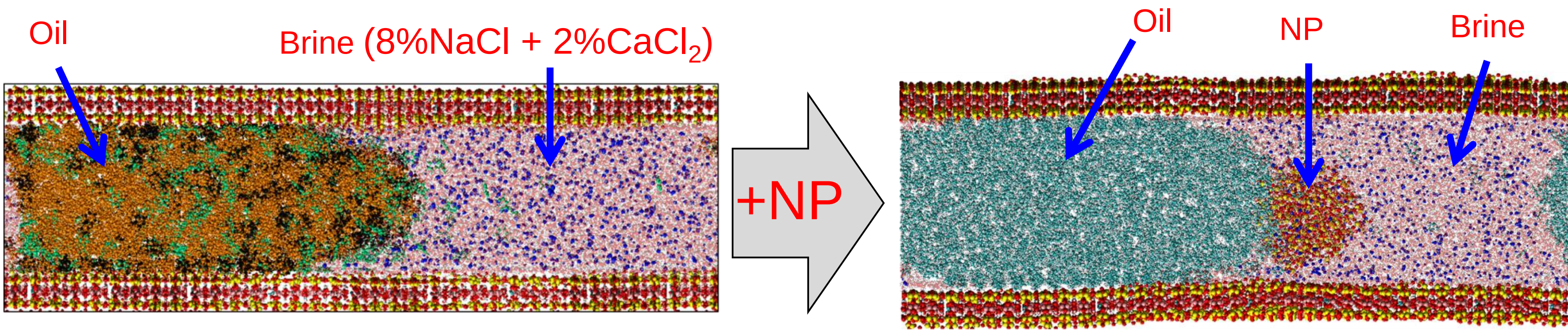


Case study:

Brine+NP/Oil/MMT System

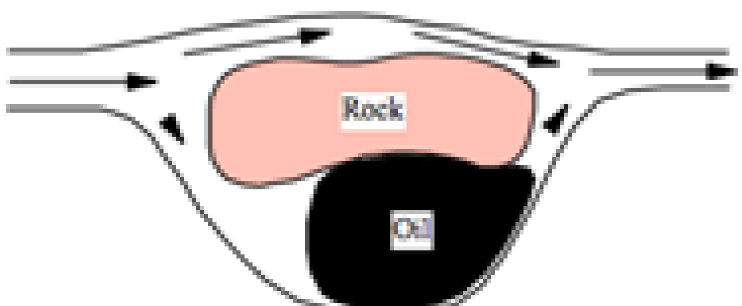
MD : nm ns
LBM : μm/mm μs/ms

T=300K – 400K
P=1 to 200atm



MD Physical properties

Without NP	With NP
ρ_o=0.81 g/cm^3; ρ_b=0.96 g/cm^3;	**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;	**η_o=3.60 mPa-s; η_b=0.88 mPa-s;**
γ_{ob}=43 mN/m; θ_w= 28^o	**γ_{ob}=38 mN/m; θ_w= 21^o**



LBM parameters:

Without NP	With NP
G = 0.14; G_w =-0.015;	***G = 0.15; G_w =-0.02;***
τ_{oil} = 1.50; τ_{brine}= 0.70	***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

Characteristic Scale for LBM simulations
l_0, t_0 and m_0

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

Maps MD into LBM (nano into micro)

Initial Condition
Density, fluid velocity and configuration, mineral geometry

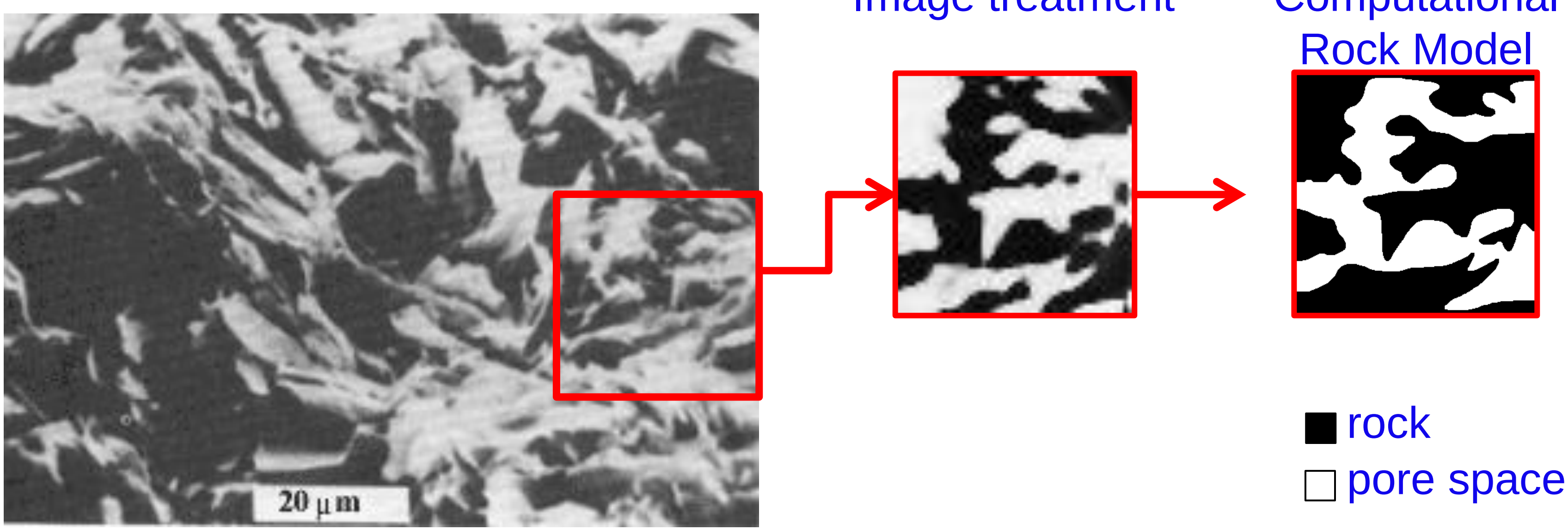
LBM Simulations
(EF-LBM)

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

Pereira, Lara and Miranda, Microfluidics and Nanofluidics (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

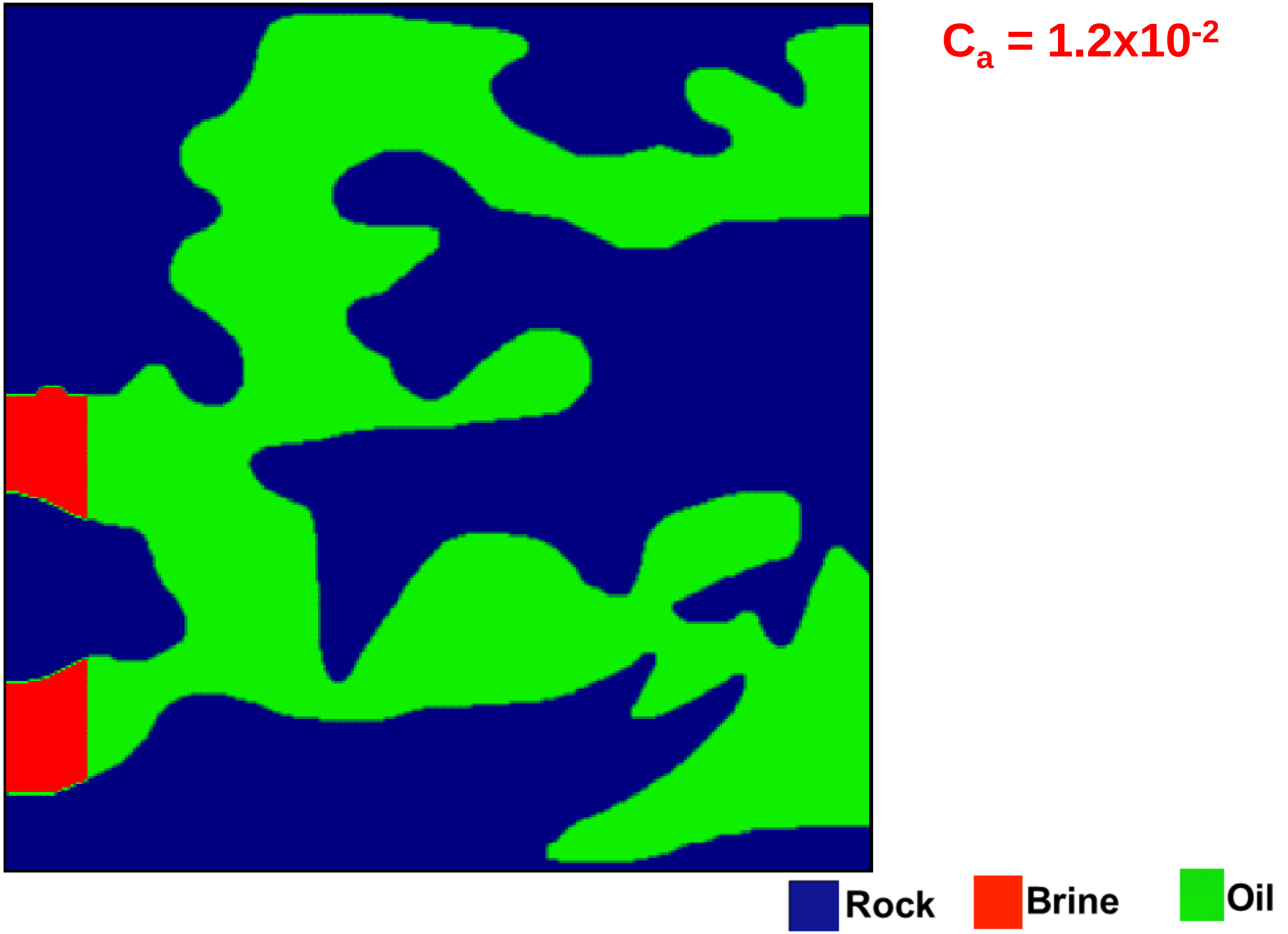
$t_0 = 1.27 \times 10^{-4}$ s

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

Exploring Oil Extraction by Nanofluids in Clay Coated Pore Network Models

Oil displacement by Brine+NP-PEG2: First Injection

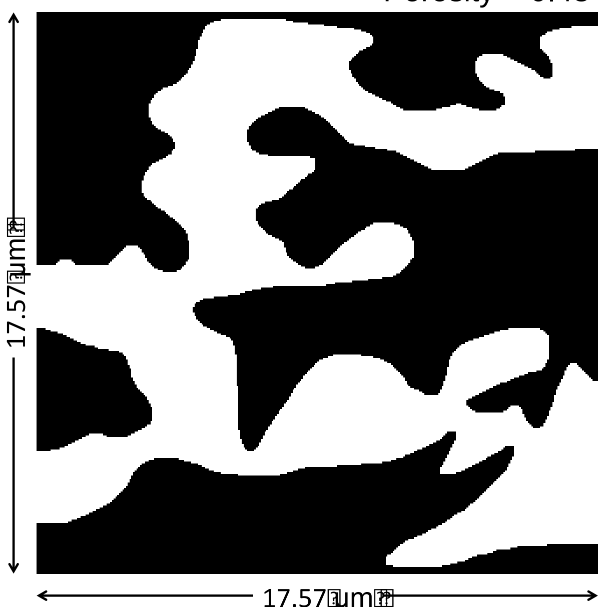
$C_a = 1.2x10^{-2}$



Exploring Oil Extraction by Nanofluids in Clay Coated Pore Network Models

LBM Simulations: Oil displacement at the pore-size scale

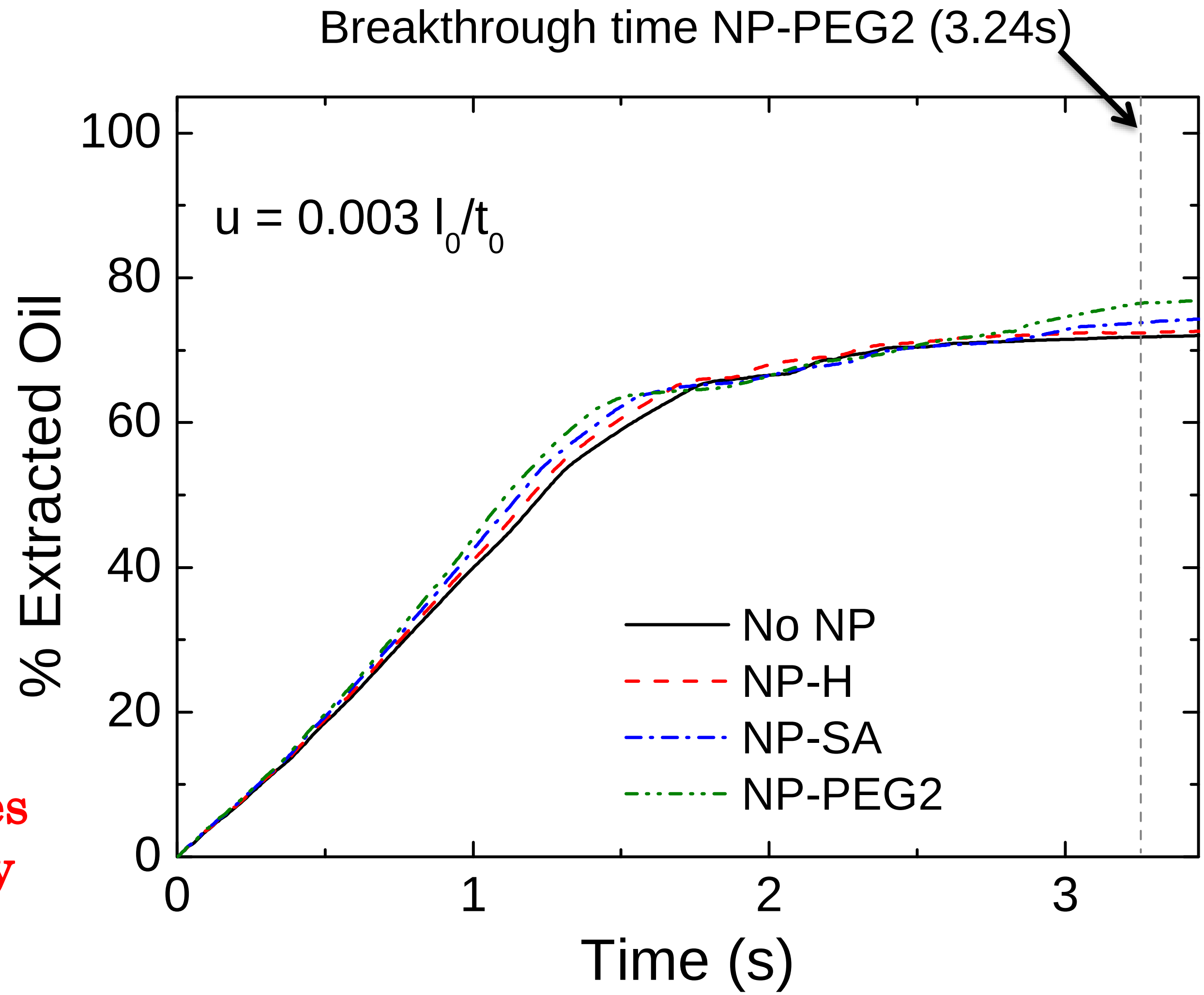
Porosity = 0.43



l_0=5.49x10^{-8} m

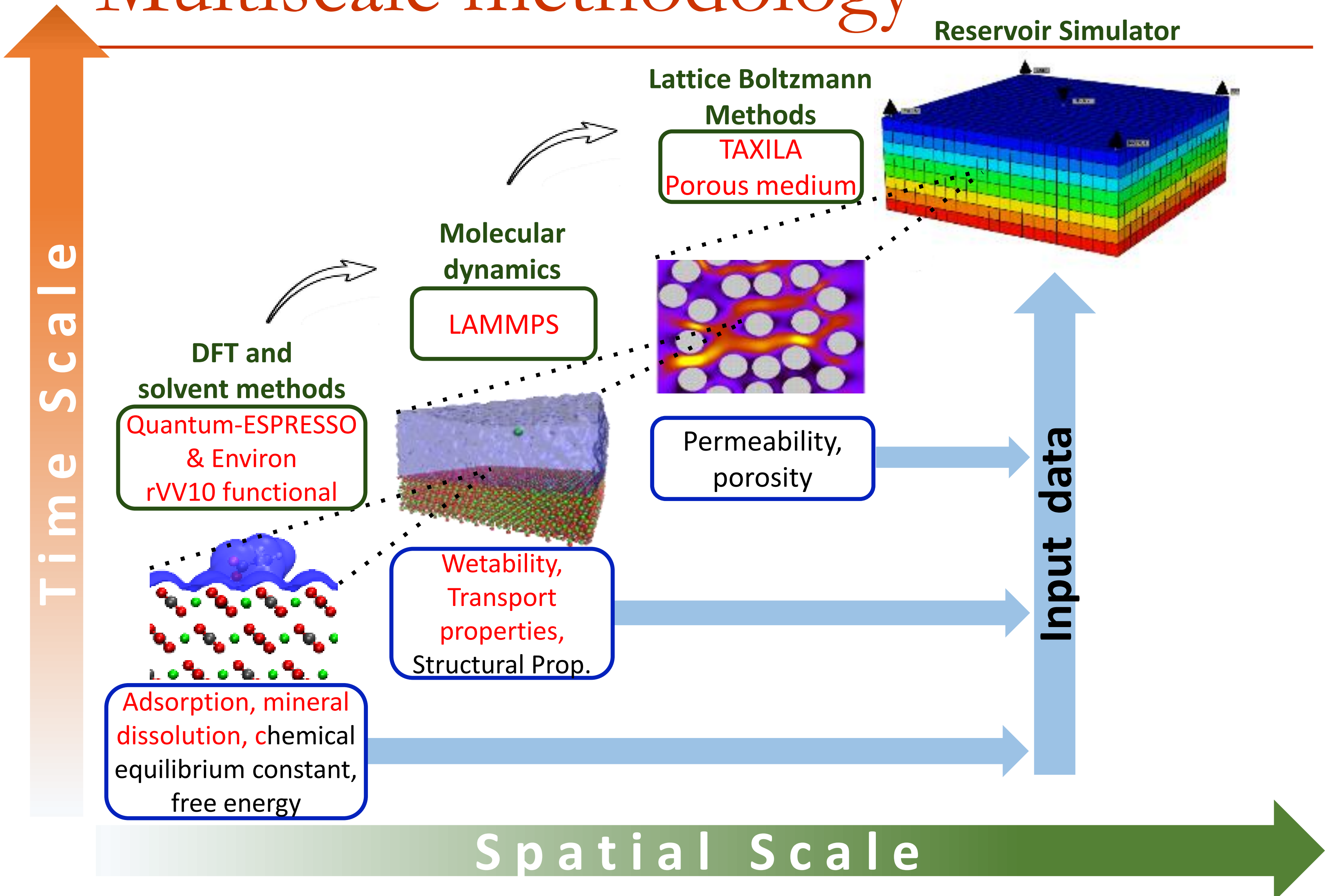
t_0 =5.91x10^{-10} s

m_0=1.50x10^{-19} kg



Addition of nanoparticles improve the oil recovery process

Multiscale methodology



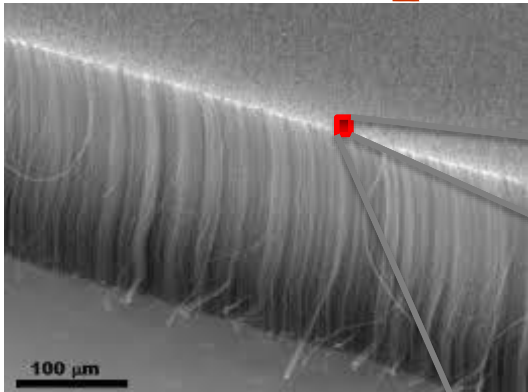
Summary – NanoEOR for NPs/brine/oil/clay interfaces

- ✓ 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.

FLUIDS CONFINED AT NANOSCALE

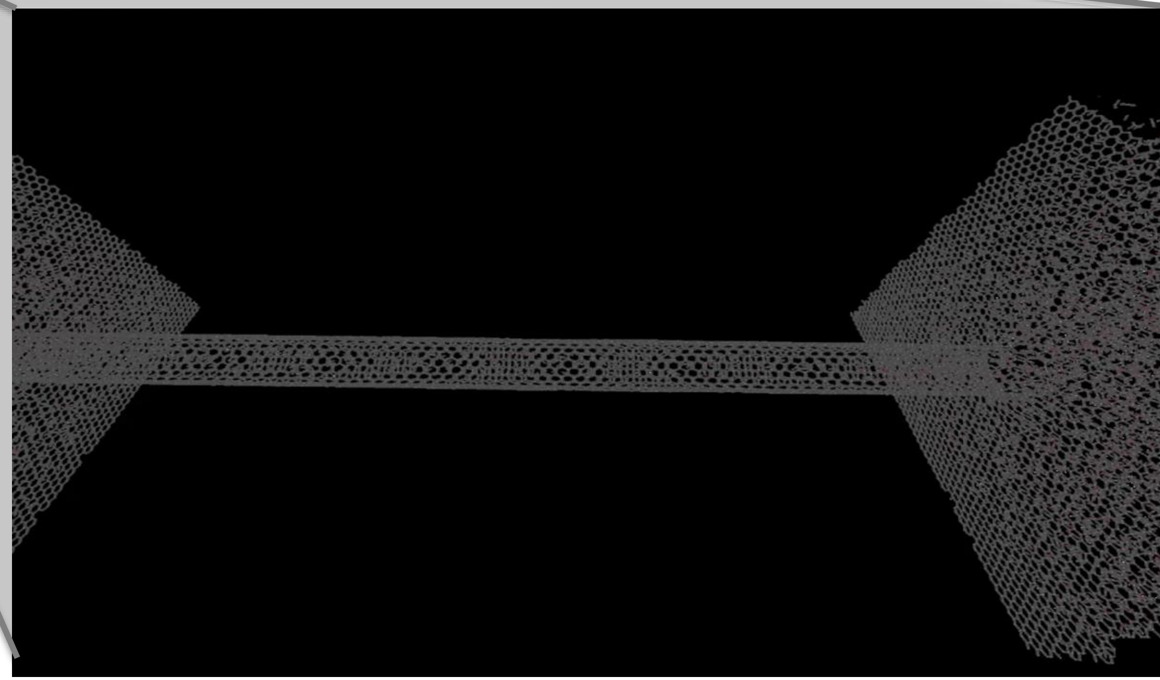
ALEXSANDRO KIRCH, TERESA D. LANNA, HENRIQUE M. CEZAR, NAIYER RAZMARA, JULIO MENEGHINI

Gas separation technologies



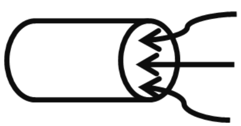
Selectivity over $N_2/H_2/CH_4$

Molecular Model



- Size effects

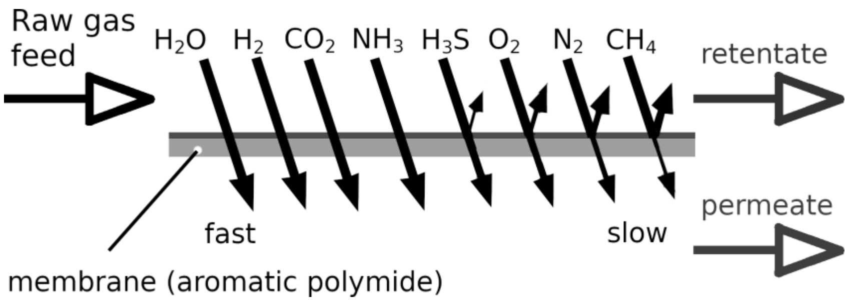
- Fluid flow

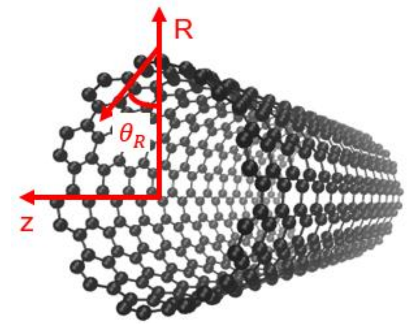


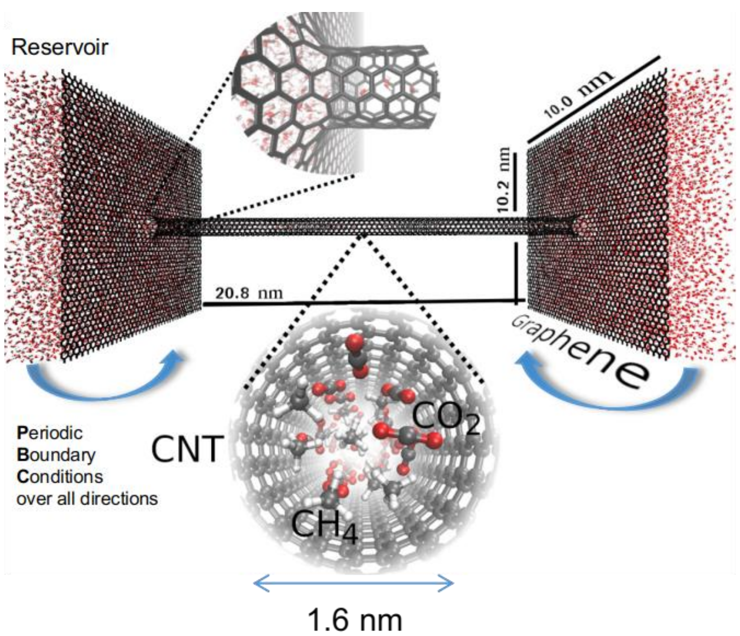
- Gas compostion

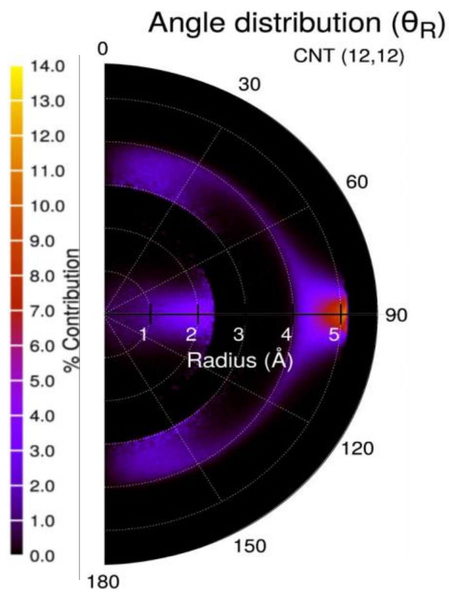
Access information at the molecular level

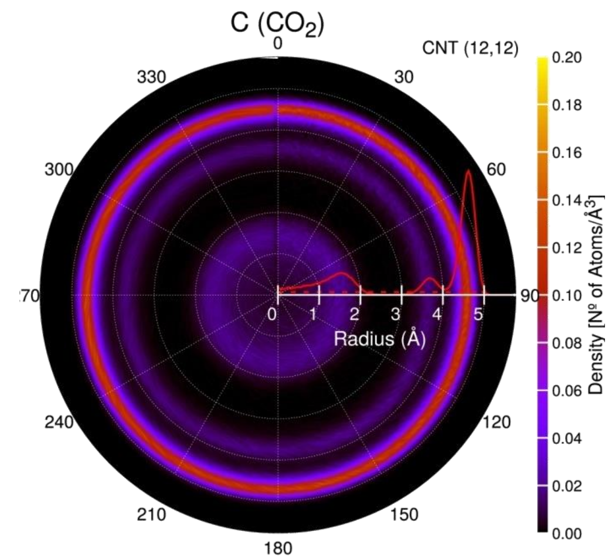
Fluid flow @ CNTs











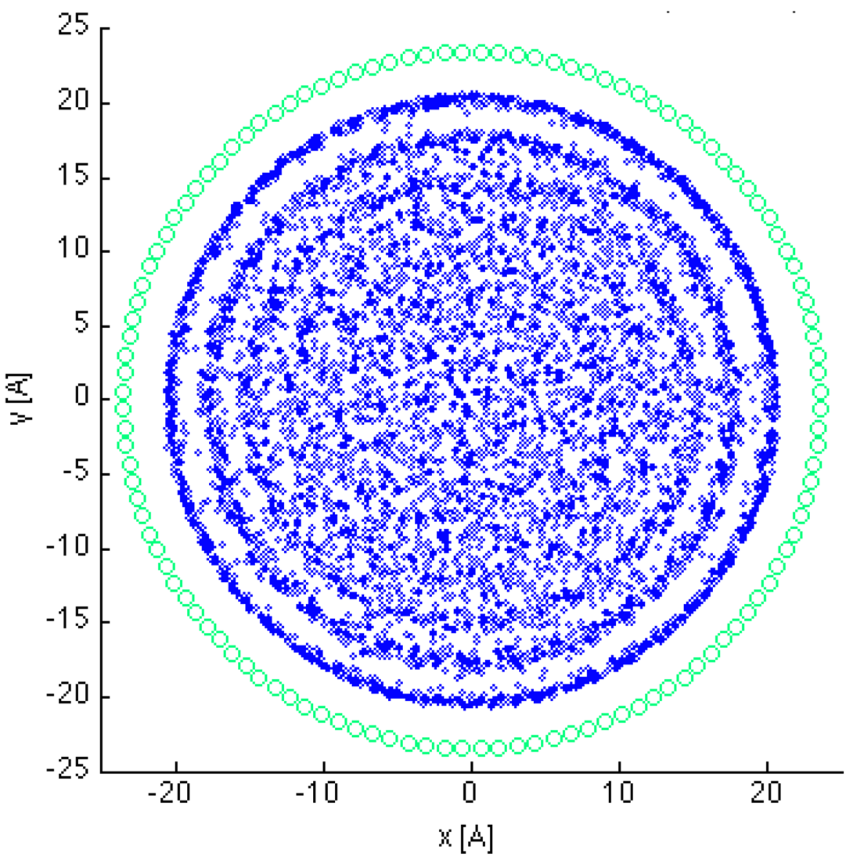
A Kirch, JM de Almeida, CR Miranda - Journal of chemical theory and computation, 2018

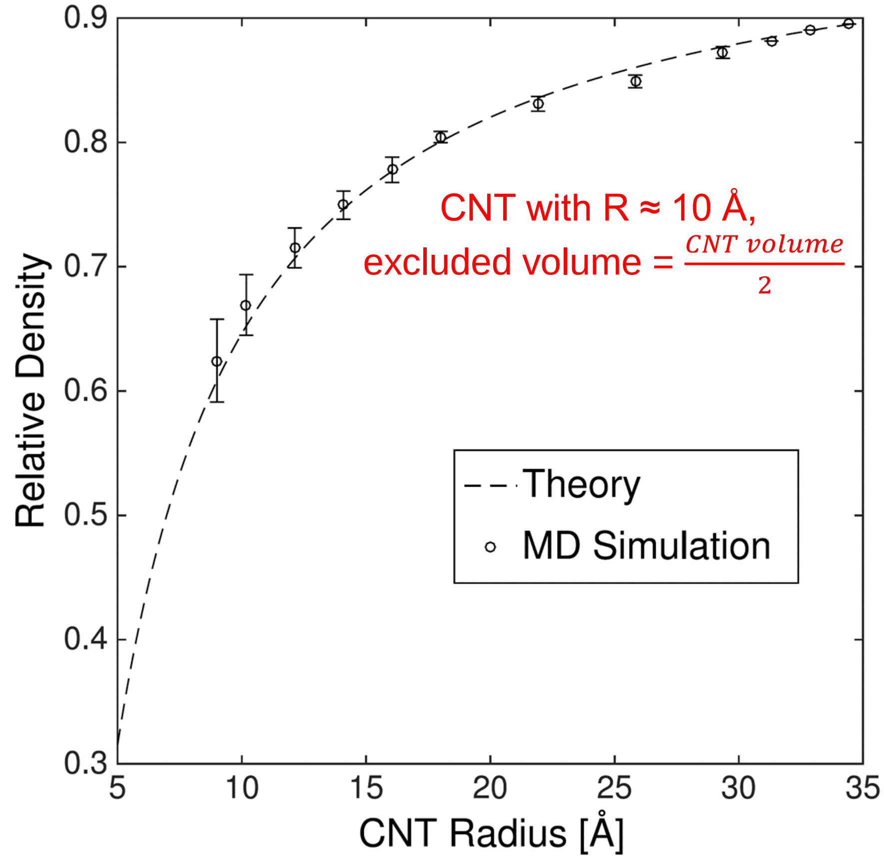
A.Kirch, T. Lanna, N. Razmara, J. Meneghini, C. Miranda
Bulletin of the American Physical Society, 2019

Why are fluid densities so low in carbon nanotubes?

Finite range of molecular interactions

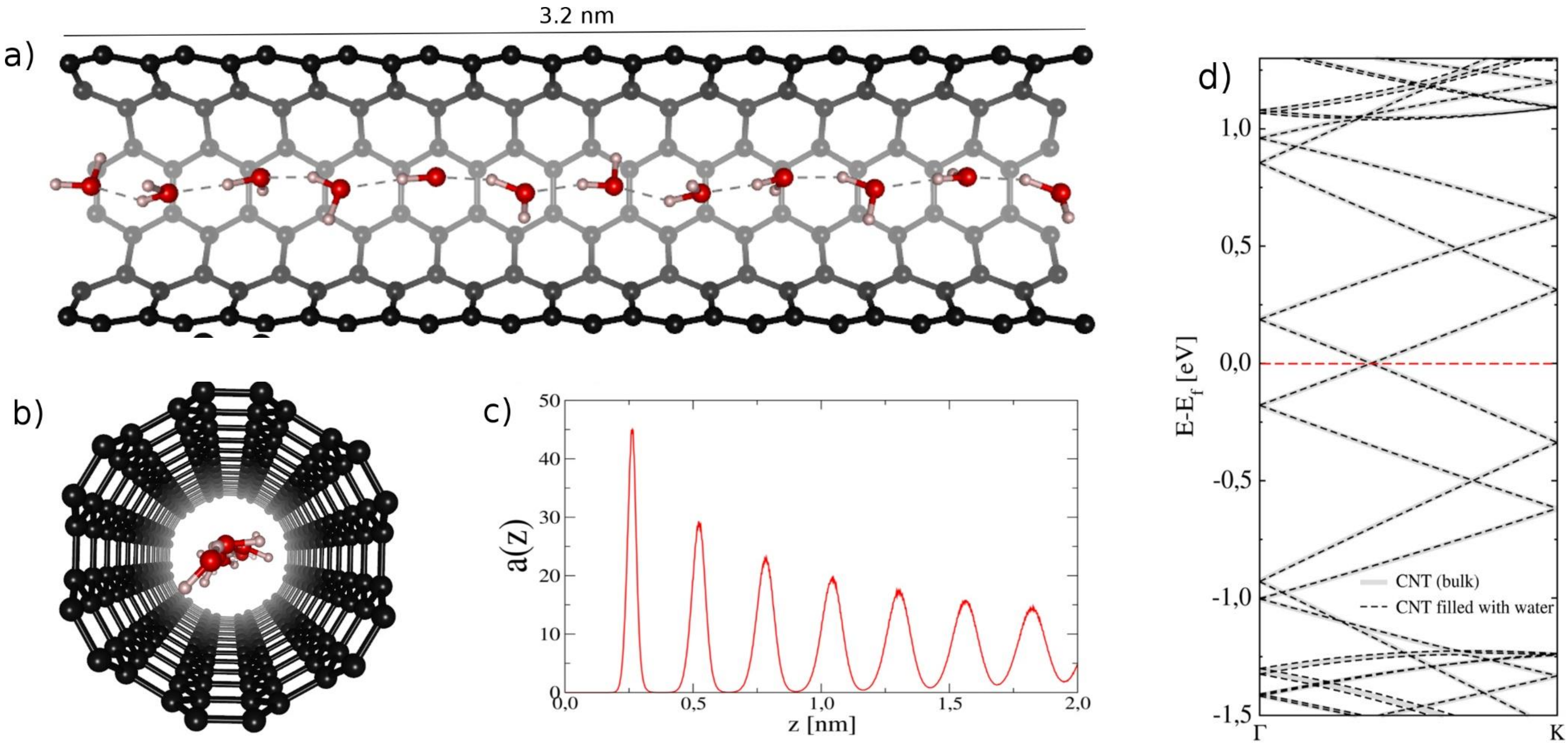
Excluded volume between the CNT wall and the fluid ∝ one molecular diameter





Gerald J. Wang and Nicolas G. Hadjiconstantinou, Physics of Fluids 27, 052006 (2015)

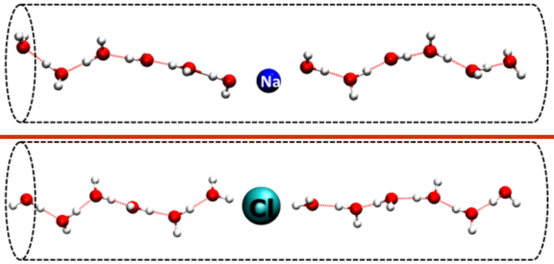
Coupling MD and First Principles



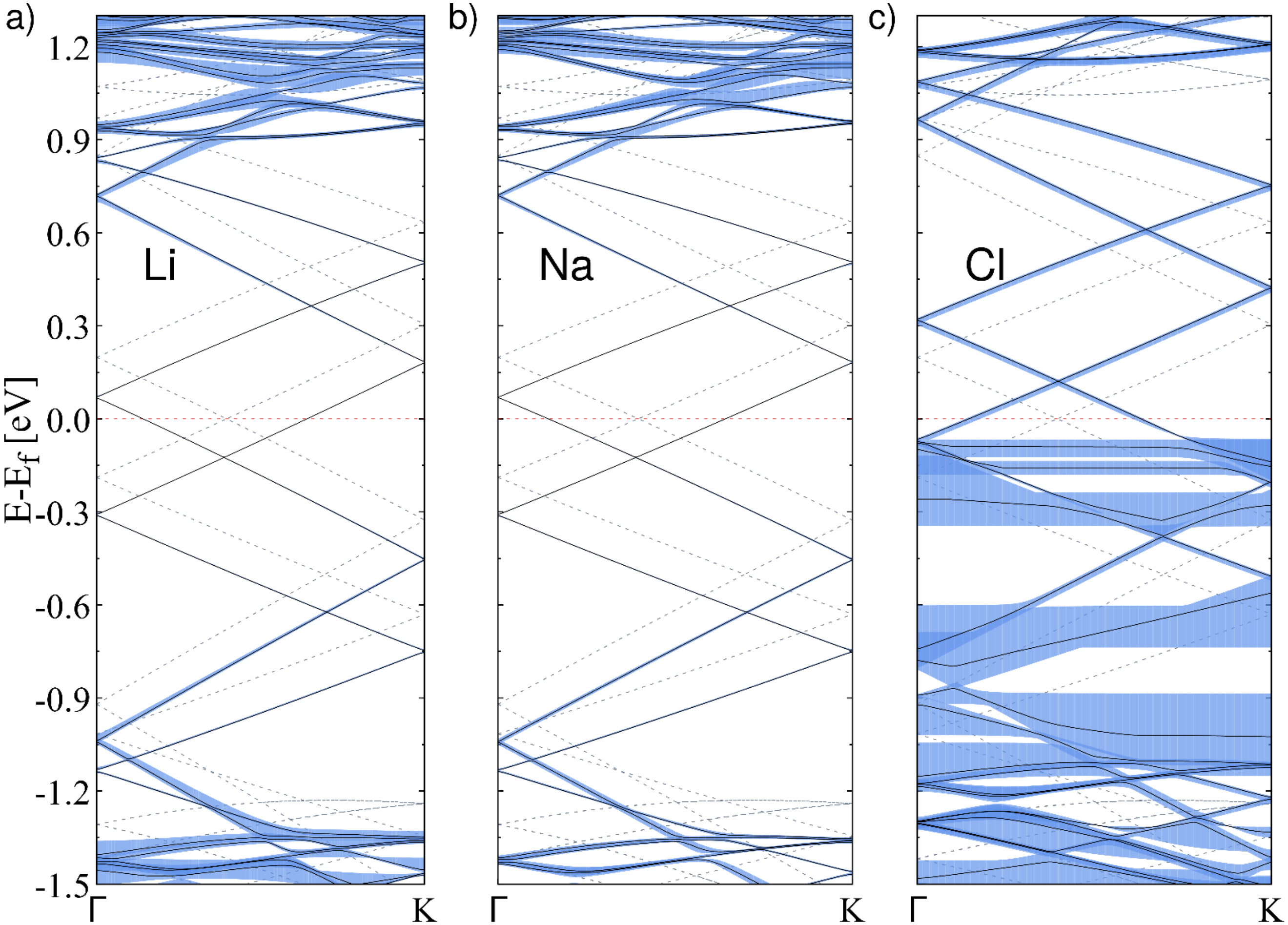
A Kirch, JM de Almeida, CR Miranda - Journal of Chemical Theory and Computation, 2018

A Kirch, JM de Almeida, CR Miranda - Journal of Chemical Theory and Computation, 2018

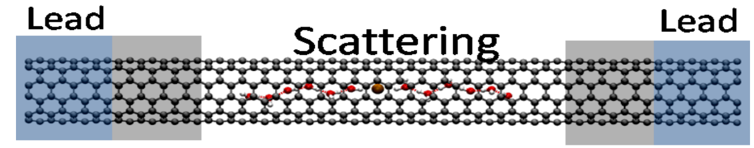
Electronic Structure



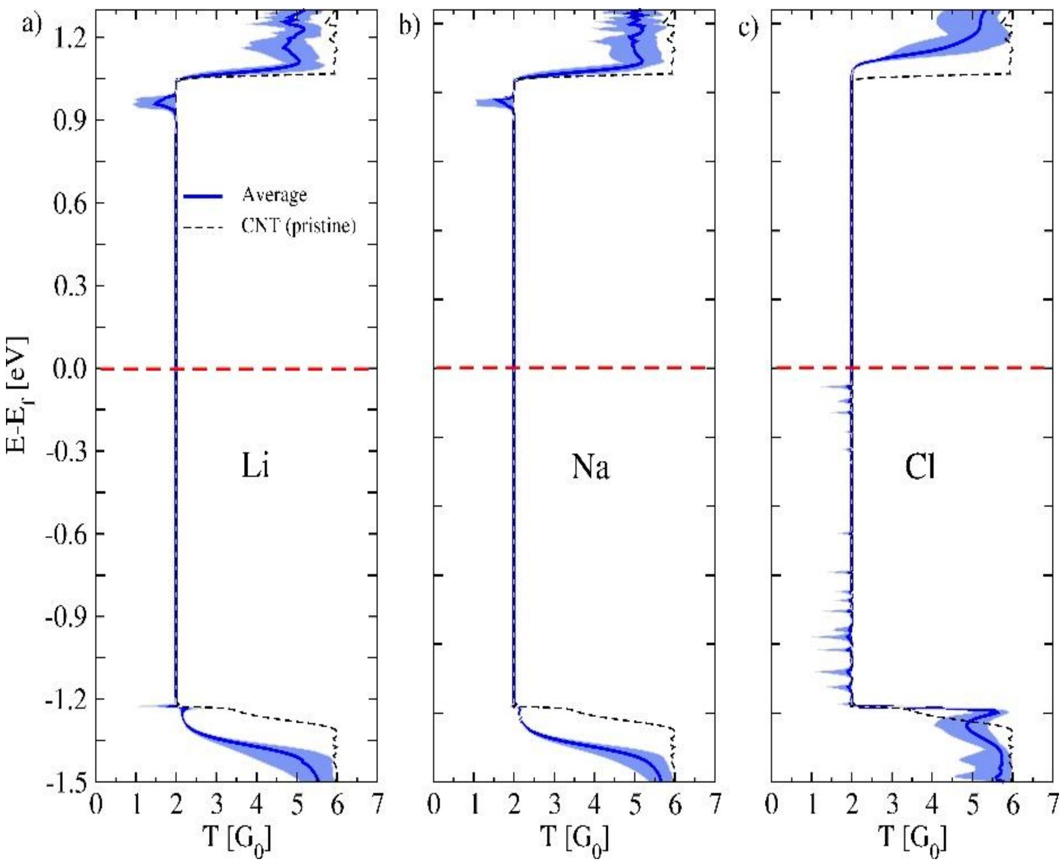
Energy band structure



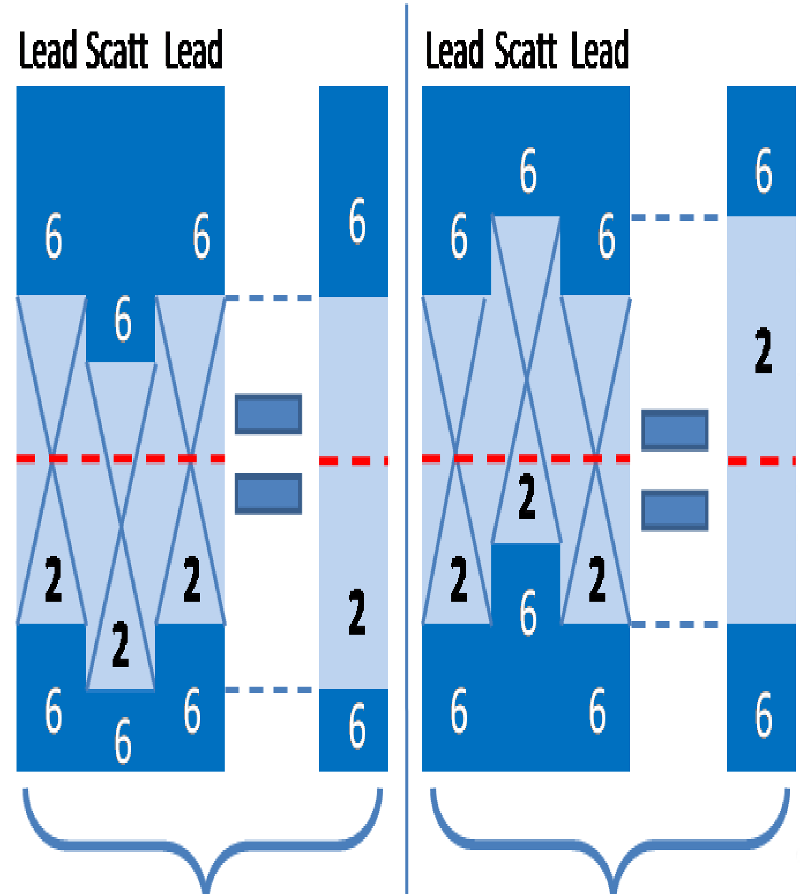
Transport properties



Transmittance



Number of channels is reduced (incrased)



Available number of electronic states (2 or 6)

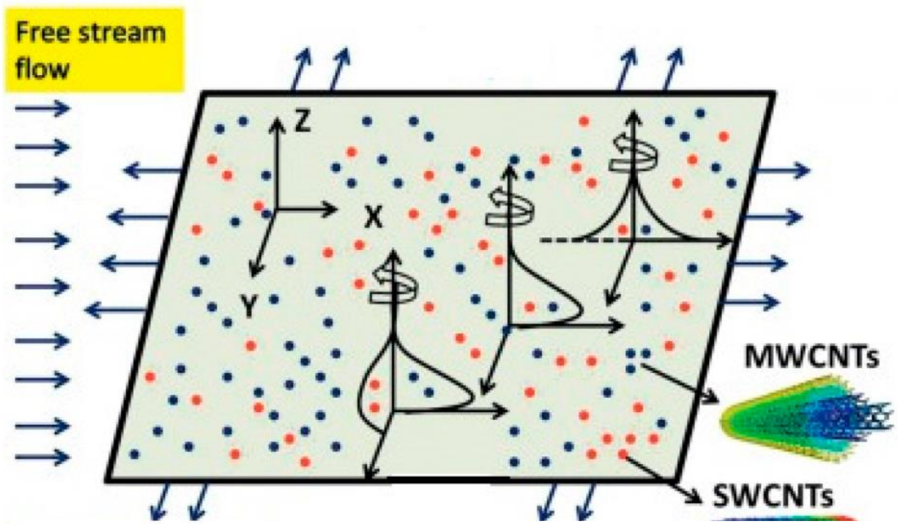
Cations

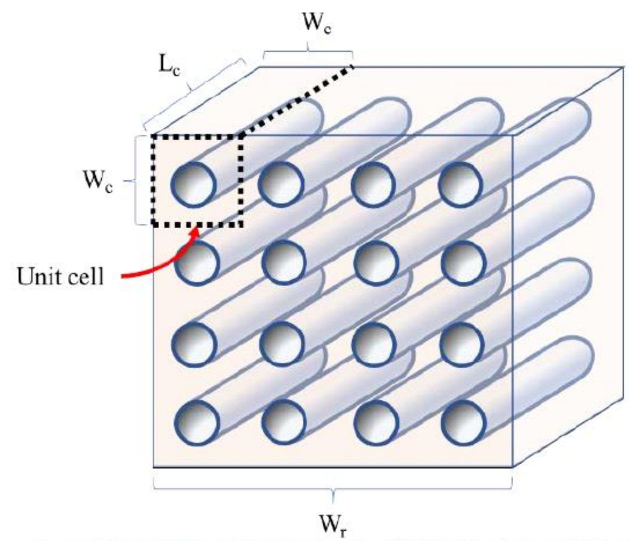
Anions

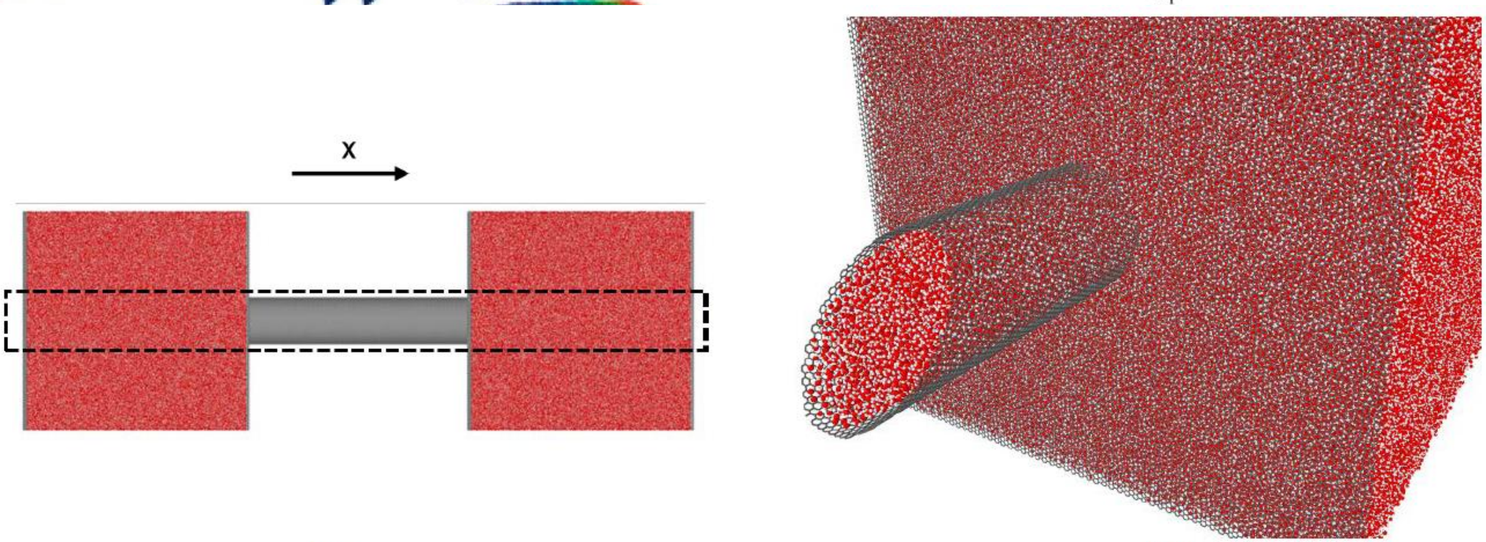
A Kirch, JM de Almeida, CR Miranda - Journal of Chemical Theory and Computation, 2018

What Happens to Permeability at the Nanoscale? A Molecular Dynamics Simulation Study
Velasco,Raul et al. Proc. of the 5th Unconventional Resources Tech. Conf. (2017)

Permeability @ nanoscale



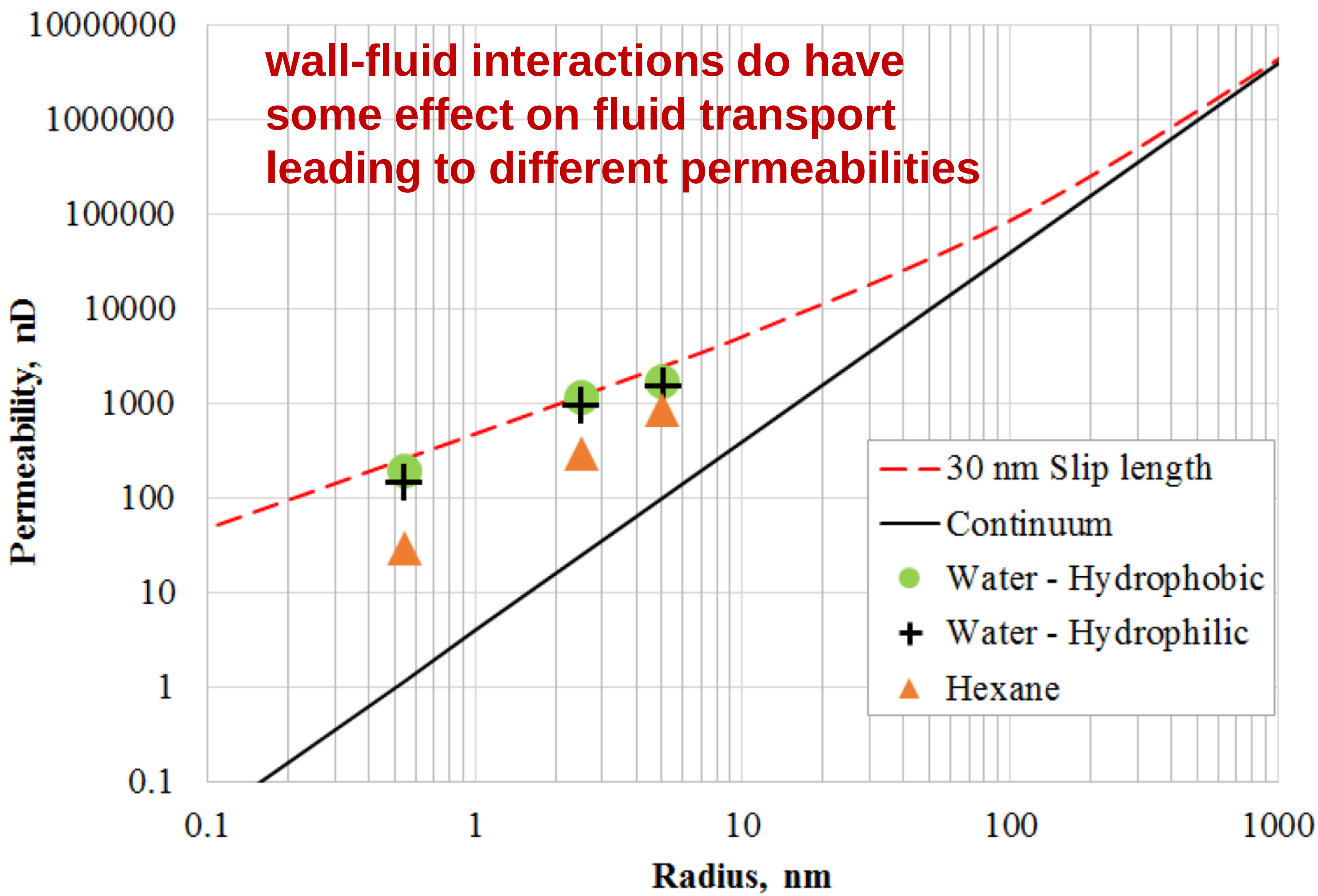




(A) (B)

What Happens to Permeability at the Nanoscale? A Molecular Dynamics Simulation Study
Velasco,Raul et al. Proc. of the 5th Unconventional Resources Tech. Conf. (2017)

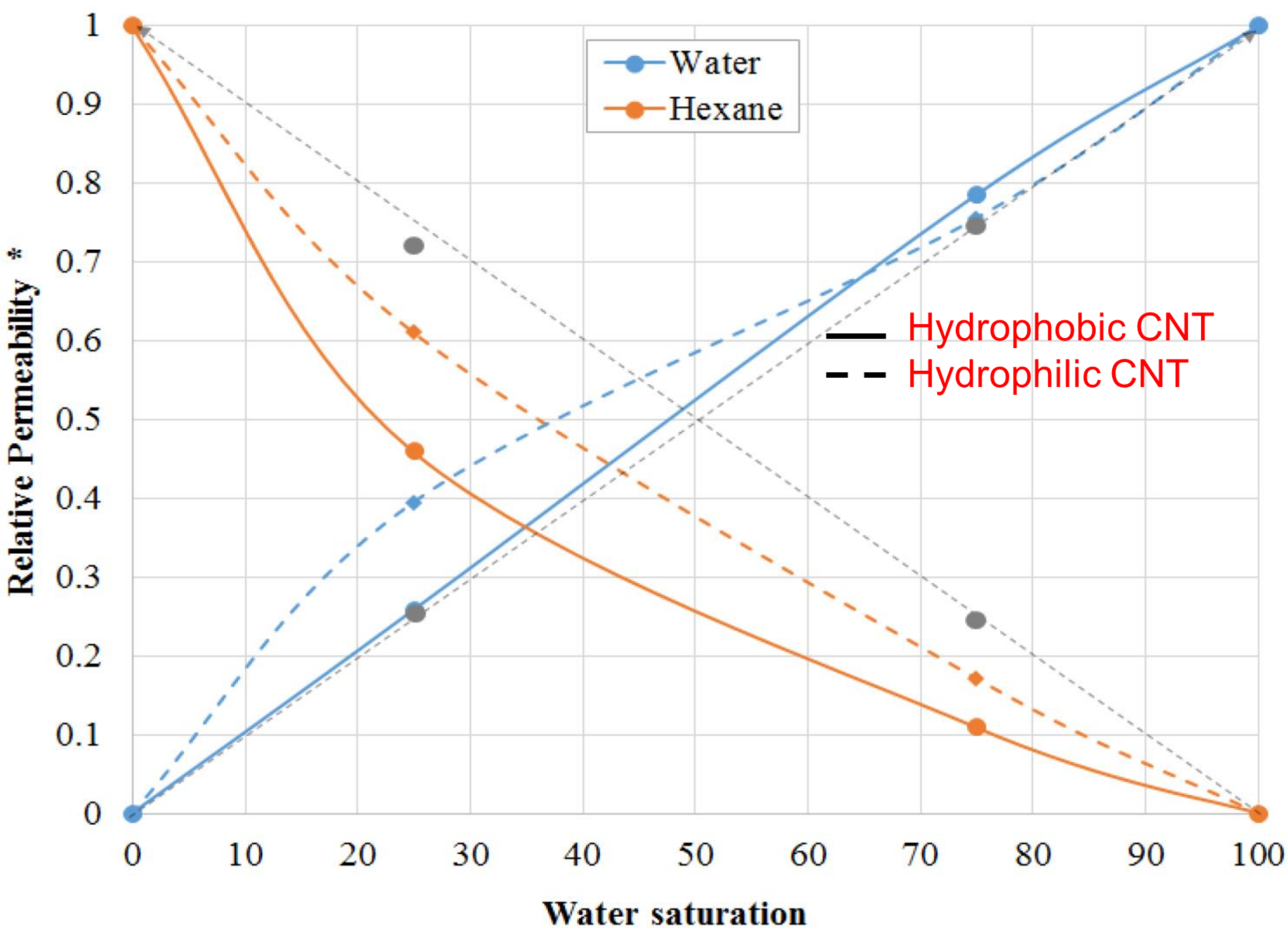
Darcy's law ?



What Happens to Permeability at the Nanoscale? A Molecular Dynamics Simulation Study
Velasco,Raul et al. Proc. of the 5th Unconventional Resources Tech. Conf. (2017)

Permeability @ CNT

"Nanopore permeability is no longer fluid independent."



Gas flow through micro/nano porous medium

$$U_s = -\frac{K}{\mu}\nabla p,$$

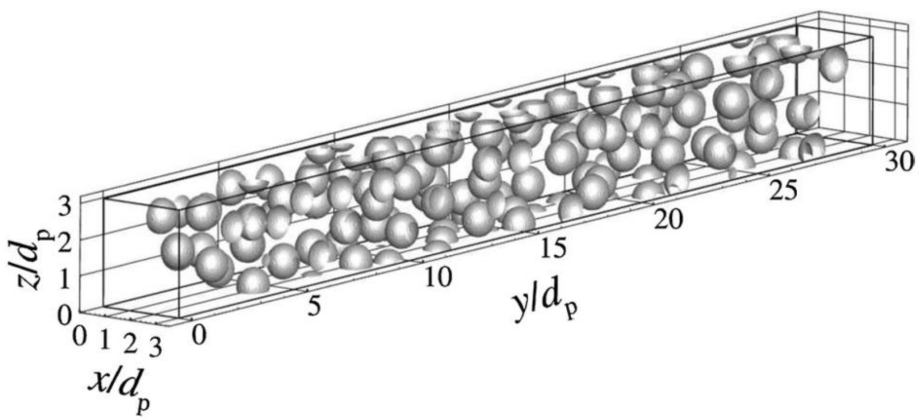
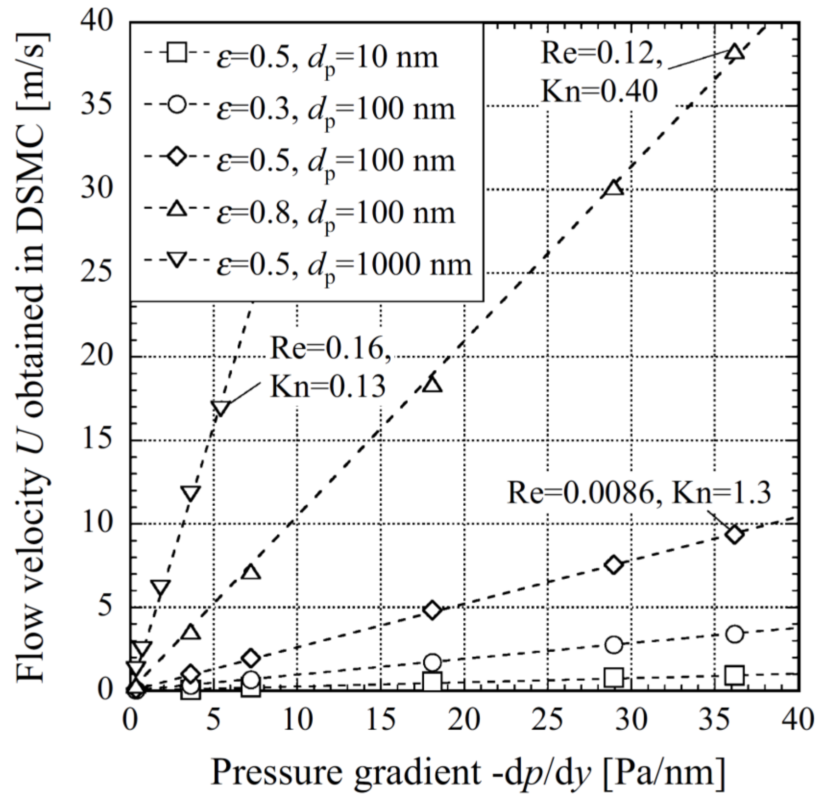


Fig. 1 Porous medium represented by randomly arranged solid spherical particles



Low density fluid flow:

Microfluid Nanofluid (2016) 20:162
DOI 10.1007/s10404-016-1829-8

"Darcy's law holds even in the case of a porous medium with micro-/nanoscale pores."

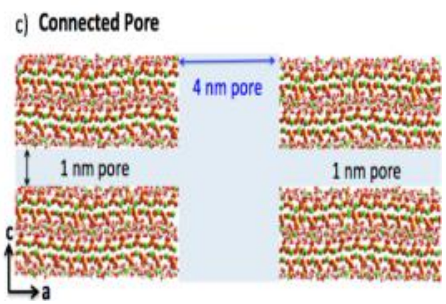
FLUID FLOW AT ROCK'S NANOPORE

James M. de Almeida, Alexsandro Kirch, and Sylvia Mutisya

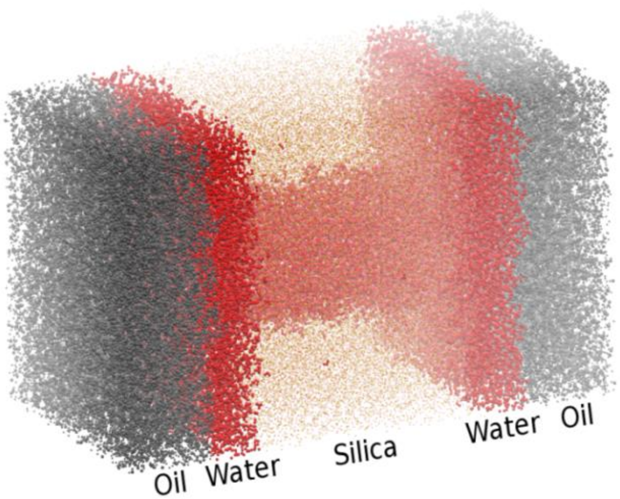
In collaboration with Sylvia Multisya, A. Kirch
J. M. de Almeida, V. M. Sanchez.

Nanofluidics: pressure driven flow

Water and CO2 in Cement

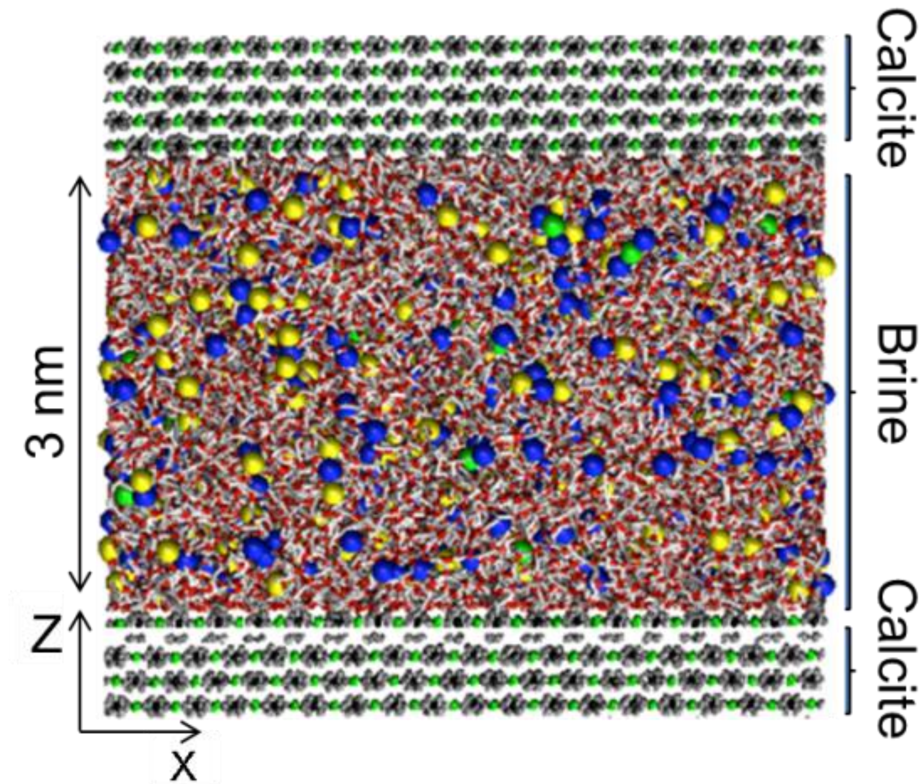


Sylvia Mutisya, PhD Thesis



Almeida and Miranda
Scientific Reports (2016), P.R. Fluids (2020)

Water confinement



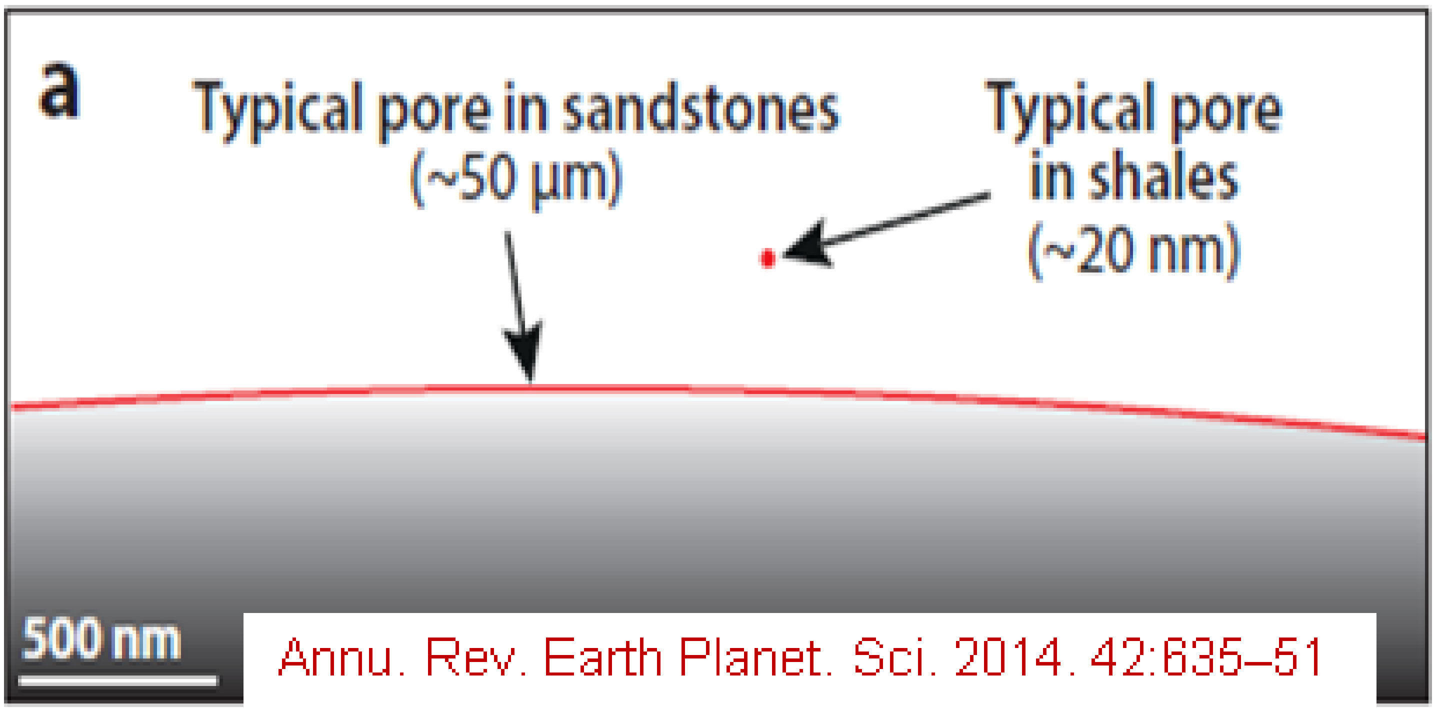
- SMART WATER – Low salt EOR “Água esperta”
- Structural properties of water/brine in calcite pores

NANO-IOR
PRESSURE DRIVEN FLOW

- Explore the water and oil flow through silicates and carbonates 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.

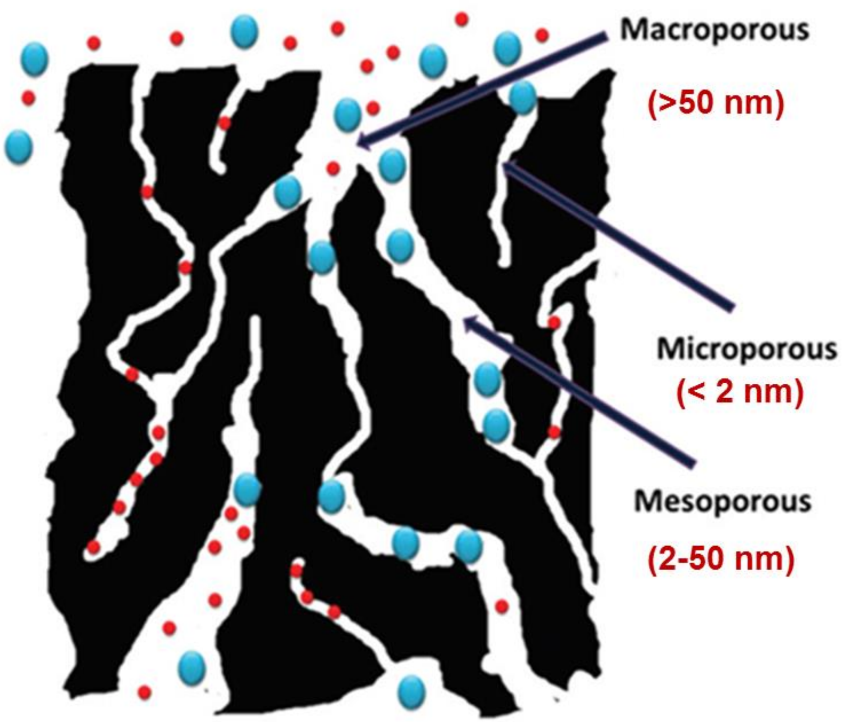


Annu. Rev. Earth Planet. Sci. 2014. 42:635–51

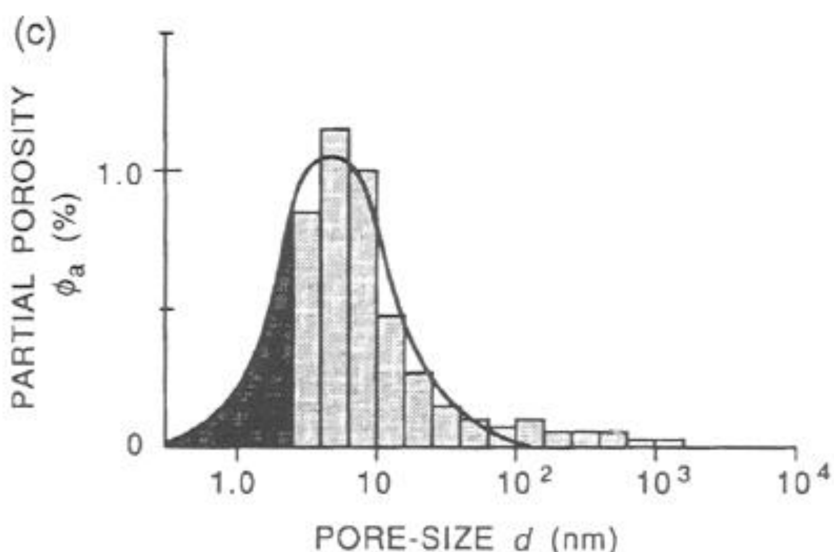
Fluid flow through nanoporous

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**

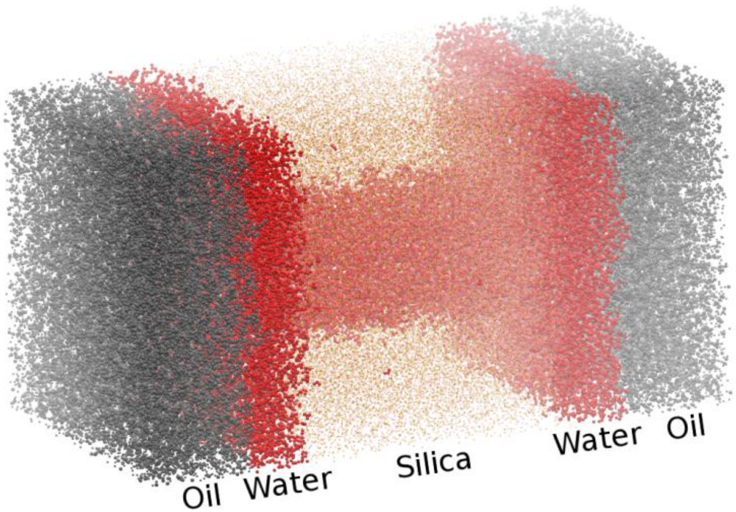


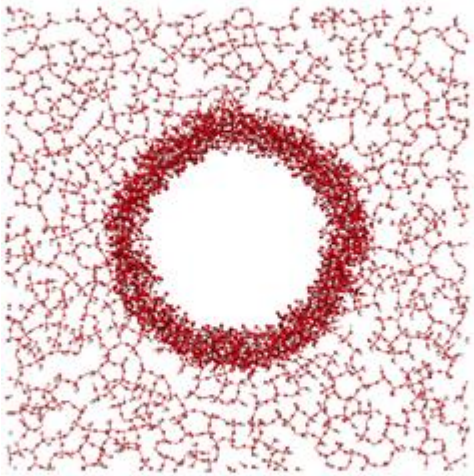
Clay Minerals (1994) **29**, 451–461



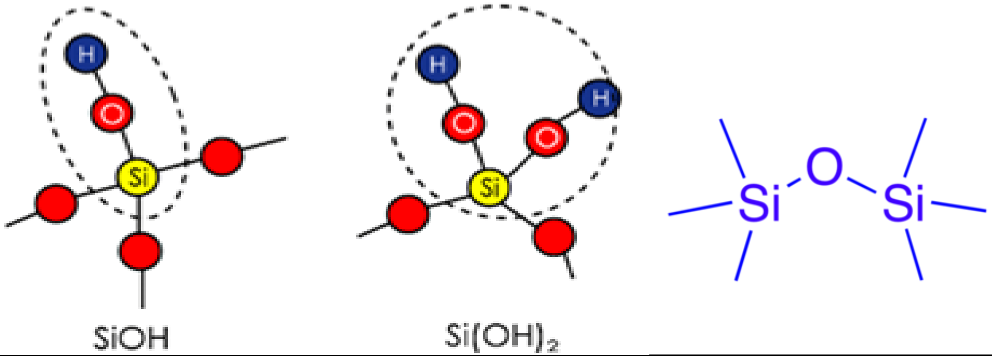
Nano IOR - Fluid infiltration in silicate nanoporous through MD

Diameters
1 nm 2 nm 3 nm 4 nm





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



Higher hydrophilicity

Lower hydrophilicity

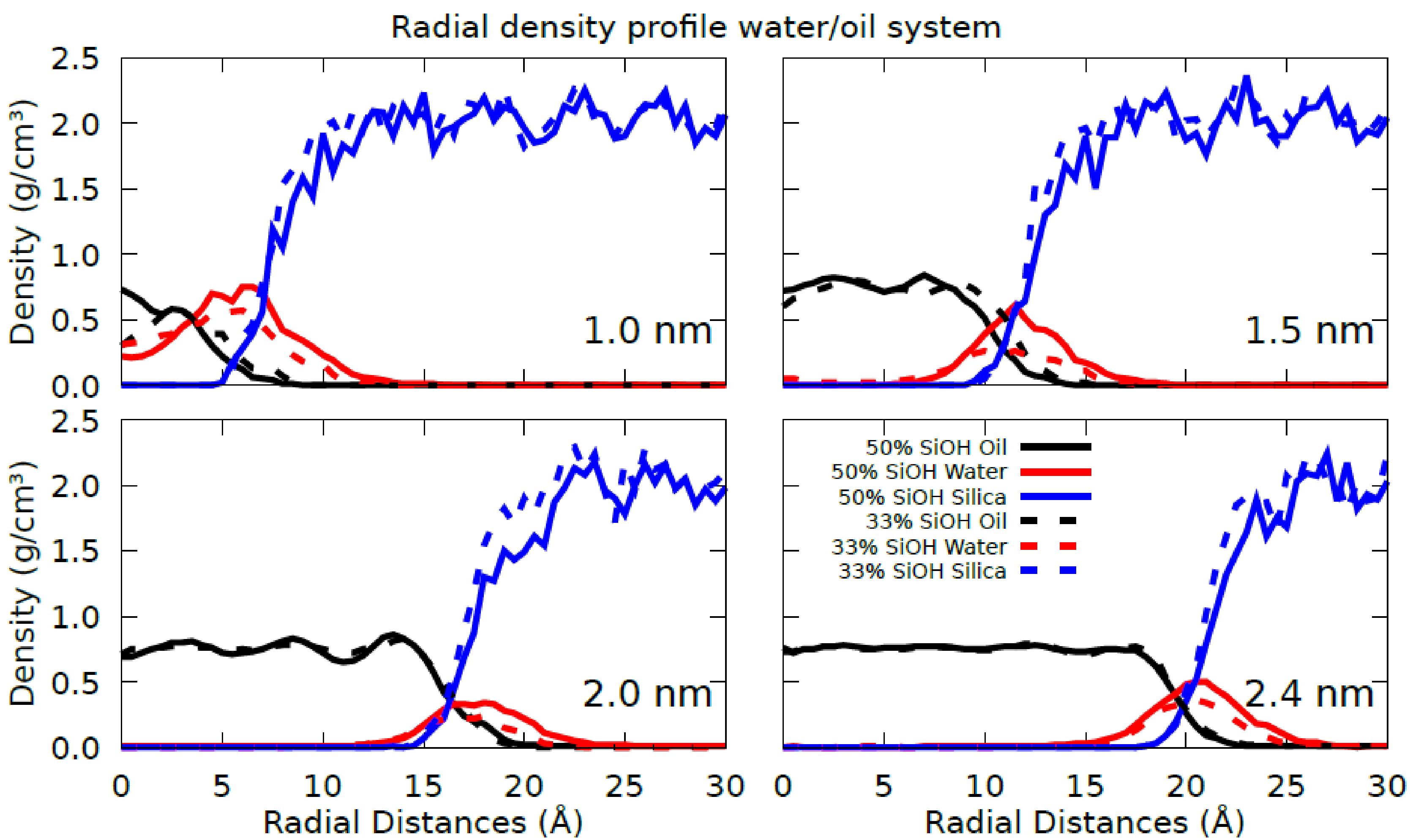
Label	Diameter (Å)	SiOH terminations	$Si(OH)_2$ terminations	SiOSi terminations
SiOH-Rich	39.42	6.65%	44.50%	48.86%
SiOSi-Rich	36.45	30.76%	4.60%	65.71%

Confinement and hydrophilicity effects on geologically relevant fluids in silica nanopores

James M. de Almeida and Caetano R. Miranda

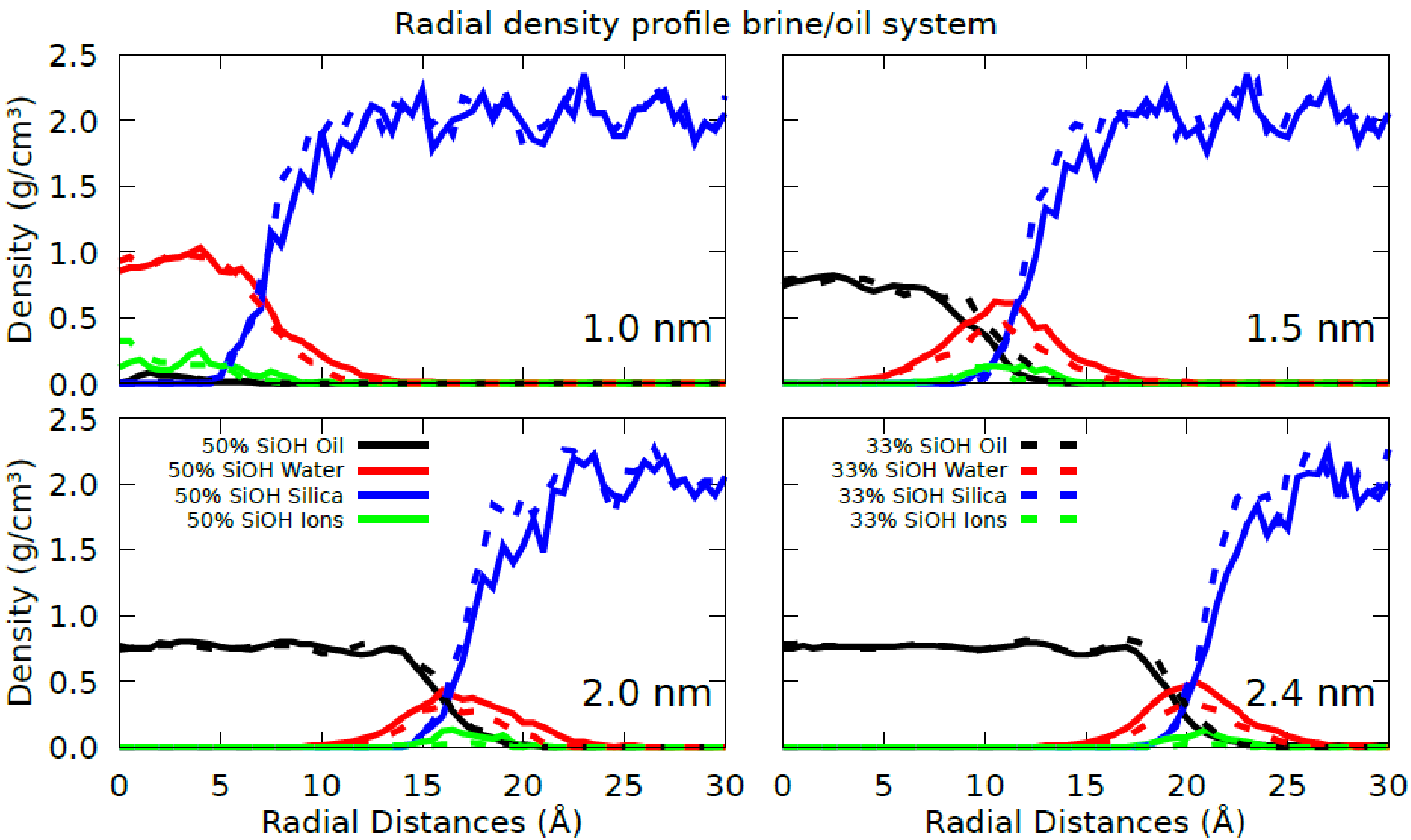
Work under review

Radial density profiles for the pore with an adsorbed water layer and oil.



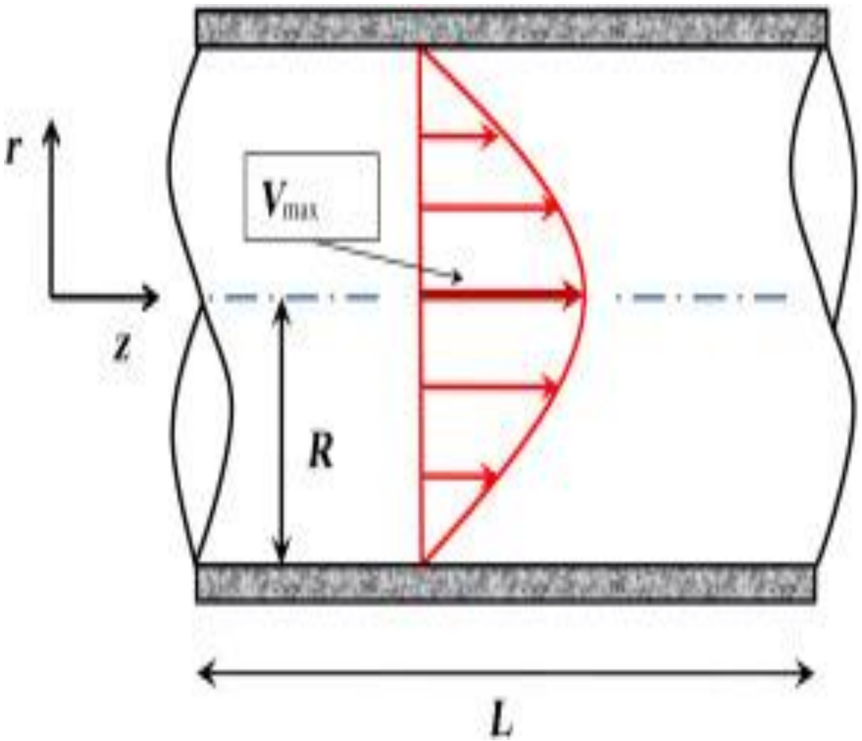
Physical Review Fluids, submitted (2020)

Radial density profiles for the pore with brine-oil.

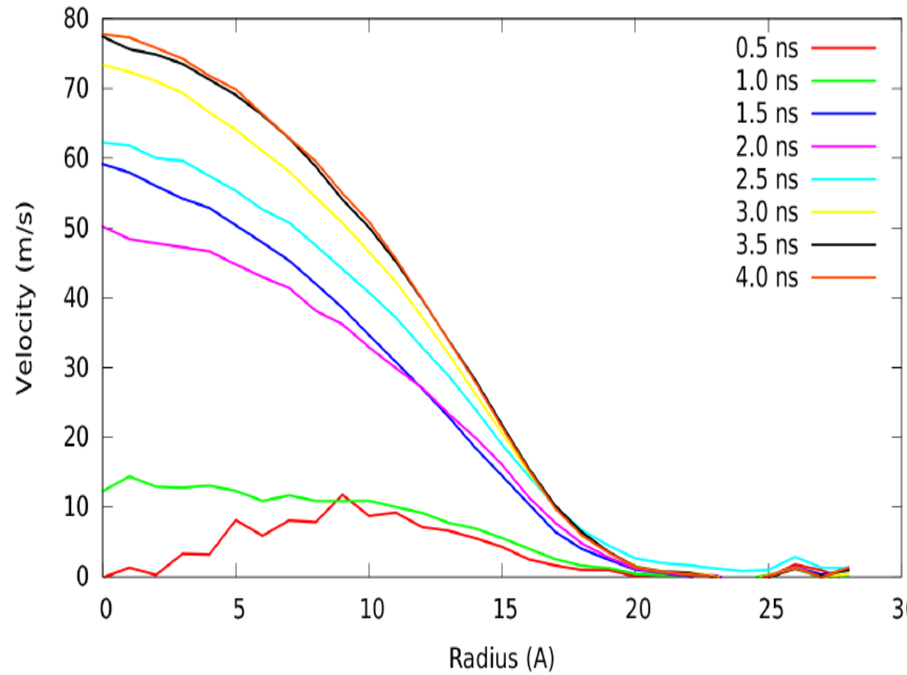


Physical Review Fluids, submitted (2020)

Hagen–Poiseuille equation



$$u(x) = \frac{3g\left[(d/2)^2 - (x - x_{max})^2\right]}{2(\tau - 1/2)}$$



$$\eta = -\frac{\vec{a}\rho}{\left(\frac{d^2 v(\vec{r})}{dr^2}\right)},$$

Applied acceleration ← $\vec{a}$

ρ → **Density, constant region has to be taken**

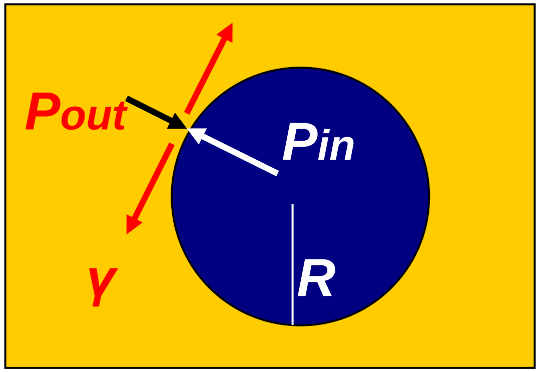
Denominator → **Second derivative of the parabolic velocity profile**

Fluid-Fluid interface

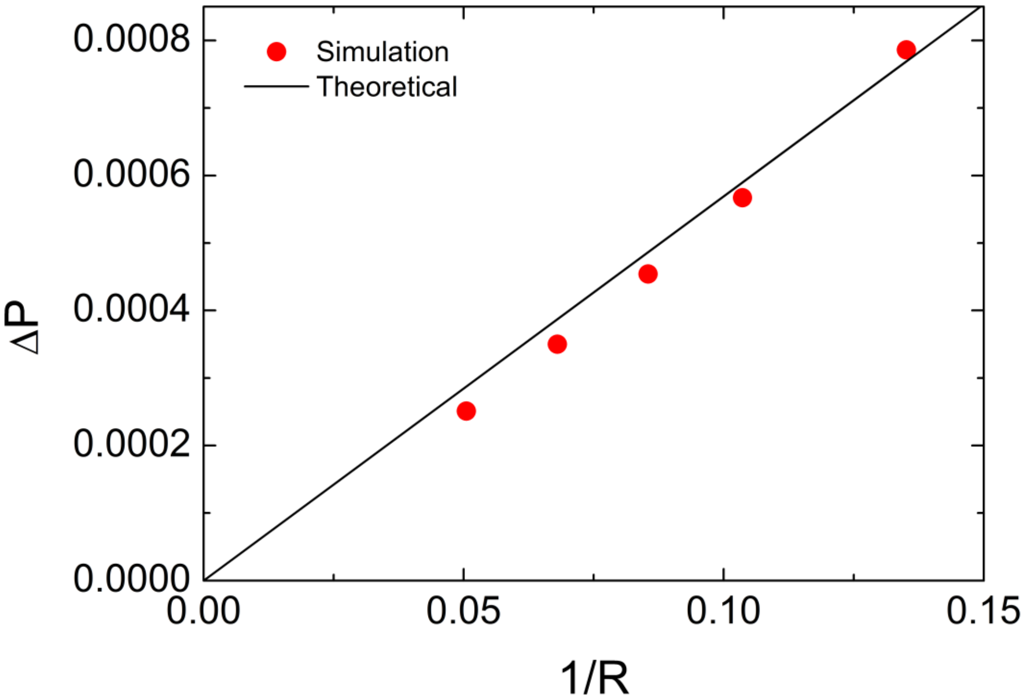
$\Delta P = P_{in} - P_{out}$

Laplace's Law:

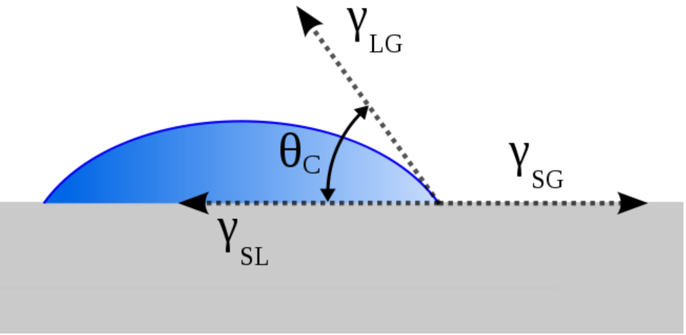
$$\Delta P = \frac{2\gamma}{R},$$

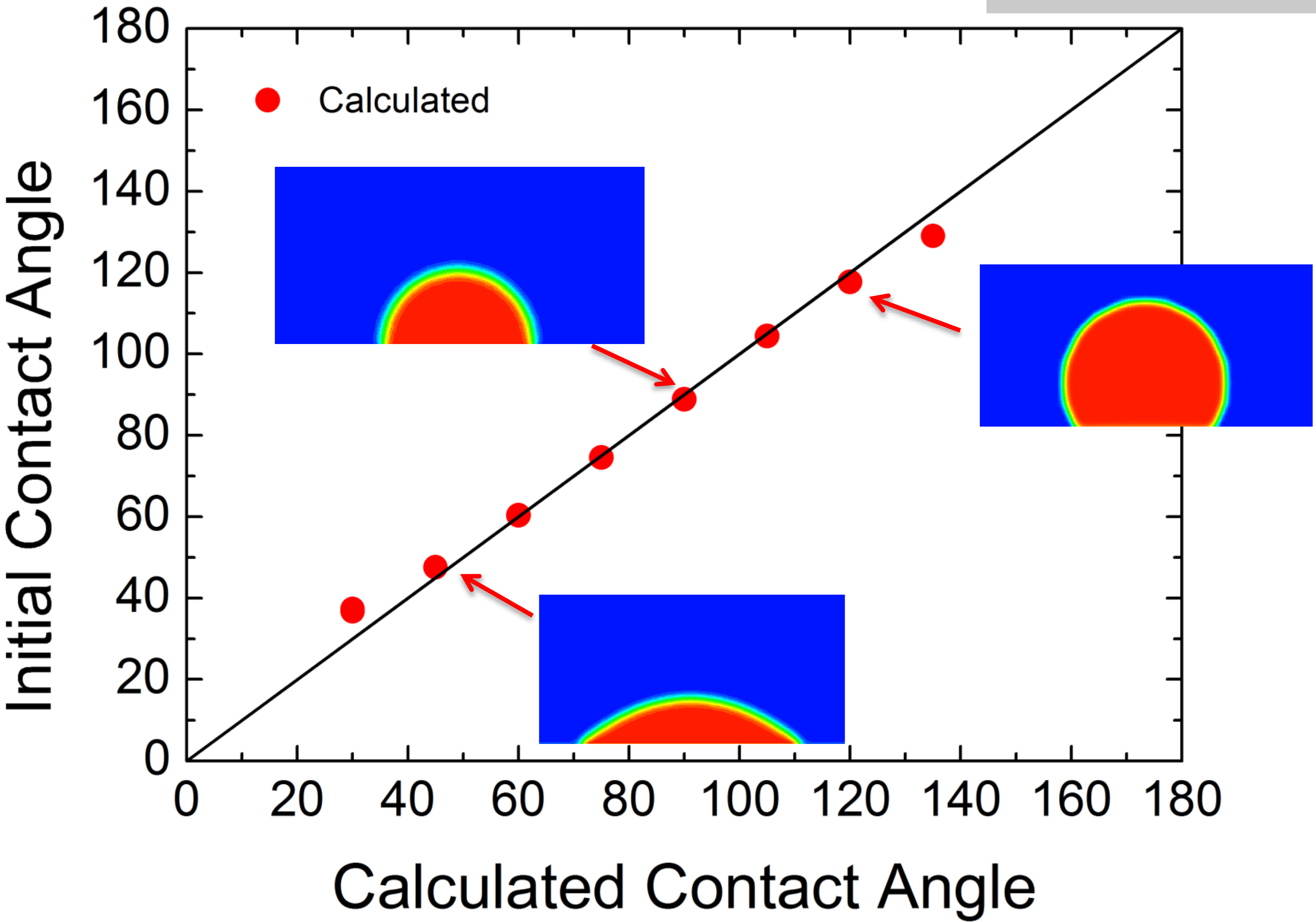


The *Laplace's law* indicates that dP is linear with respect to the curvature of bubbles or drops



Young-Laplace equation
Solid-fluid-fluid interface





Critical Infiltration Pressures

- From the bulk densities one can obtain the critical infiltration pressures, with the Young-Laplace relation:

$$\Delta P = \frac{2\gamma}{R},$$

- Which gives us the following:

Radius (Å)	ΔP Water (atm)	ΔP Brine (atm)
1.0 nm	925	989
1.5 nm	636	680
2.0 nm	456	487
2.4 nm	390	417

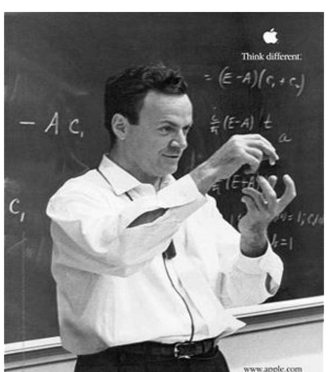
The predicted pressures would imply that we should have observed infiltration for all the systems

→ 600 atm on simulation

- The critical pressure for the 1.0 nm predicted 1000 atm. No infiltration is observed for up 3000 atm.
- We notice a limitation of ***Young-Laplace*** relation to obtain the critical infiltration pressures on nanopores,

Summary: "There is Plenty of Room at the Bottom" and the Ground

- The properties of fluids confinement at nanoscale differ from bulk → remarkable properties
- Hagen–Poiseuille equation deviates from quadratic behavior at nanopores (< 2nm)
- Young-Laplace is not valid for the studied nanochannels.
- Darcy's law also may not be valid
- Plethora of dynamics in nanoporous media observed (Cavitation, bubble formation, fluid flow)
- Reactive and control theory at nanoscale

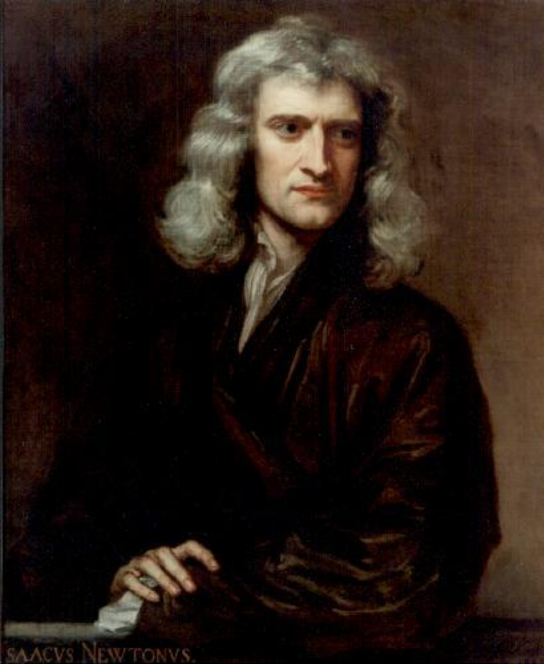


HOW TO CHARACTERIZE A FLUID FLOW AT MOLECULAR LEVEL ?

WHAT IS A LIQUID ?

<u>THE</u> question:

"Can we predict the macroscopic properties of (classical) from microscopic systems?"



NEWTON: F=m a

LAPLACE:

Nous devons donc envisager l'état présent de l'universe comme l'effet de son état antérieur et comme la cause de delui qui va suivre. Une intelligence qui, pour un instant donné, connaîtrait toutes les forces dont la nature est animée et la situation respective des êtres qui las composent, si d'ailleurs elle était assez vaste pour soumettre ces données à l'Analyse, embrasserait dans la même formule les mouvements des plus grands corps de l'univers et ceux du plus lèger atome : rien ne serait incertain pour elle, et l'avenir, comme le passé, serait présent à ses yeux.

"Translation" In principle "Yes".

Provided that we know the position, velocity and interaction of all molecules, then the future behavior is predictable,…BUT

…. There are so many molecules.

This is why, before the advent of the computer, it was impossible to predict the properties of real materials.

What was the alternative?

1. Smart tricks ("theory")

   Only works in special cases

2. Constructing model ("molecular lego")…

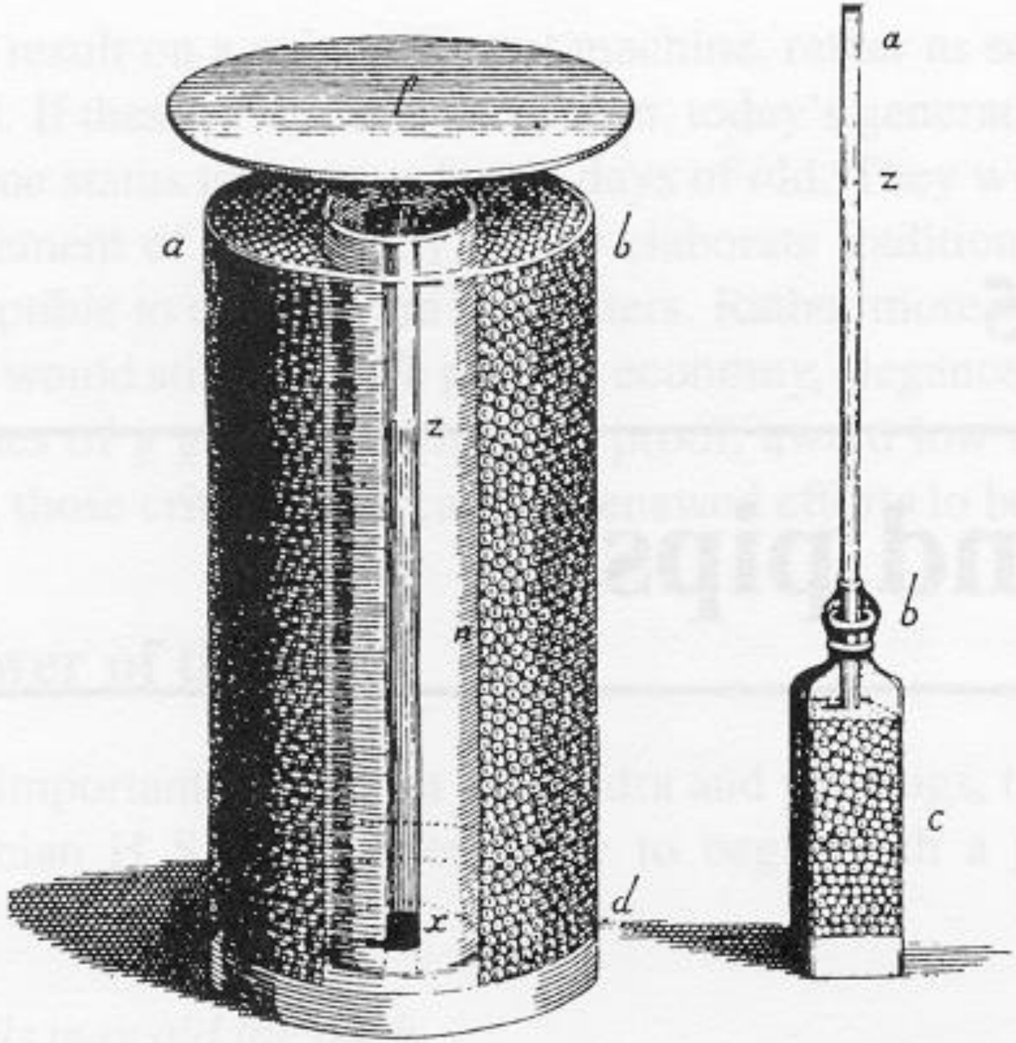
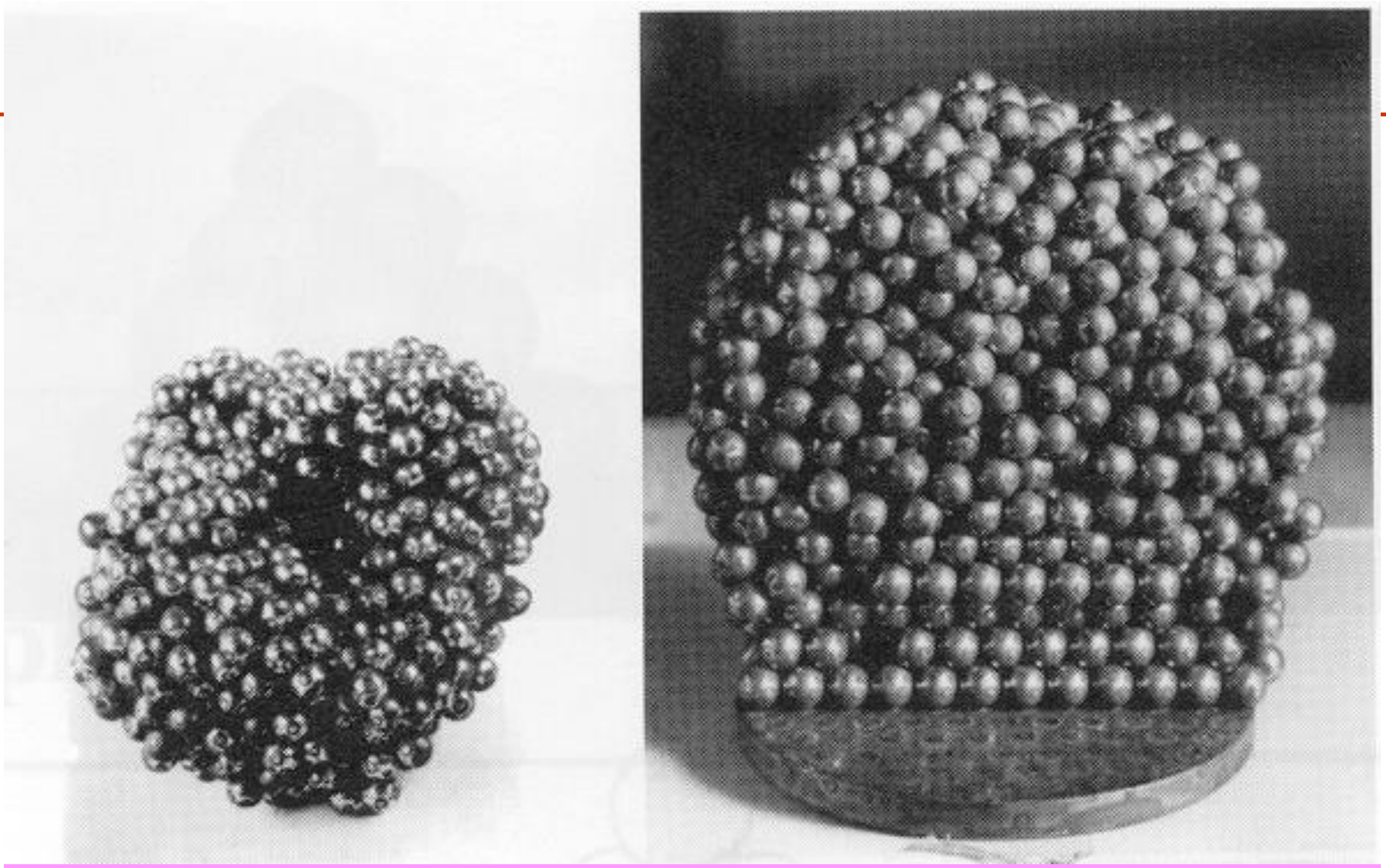
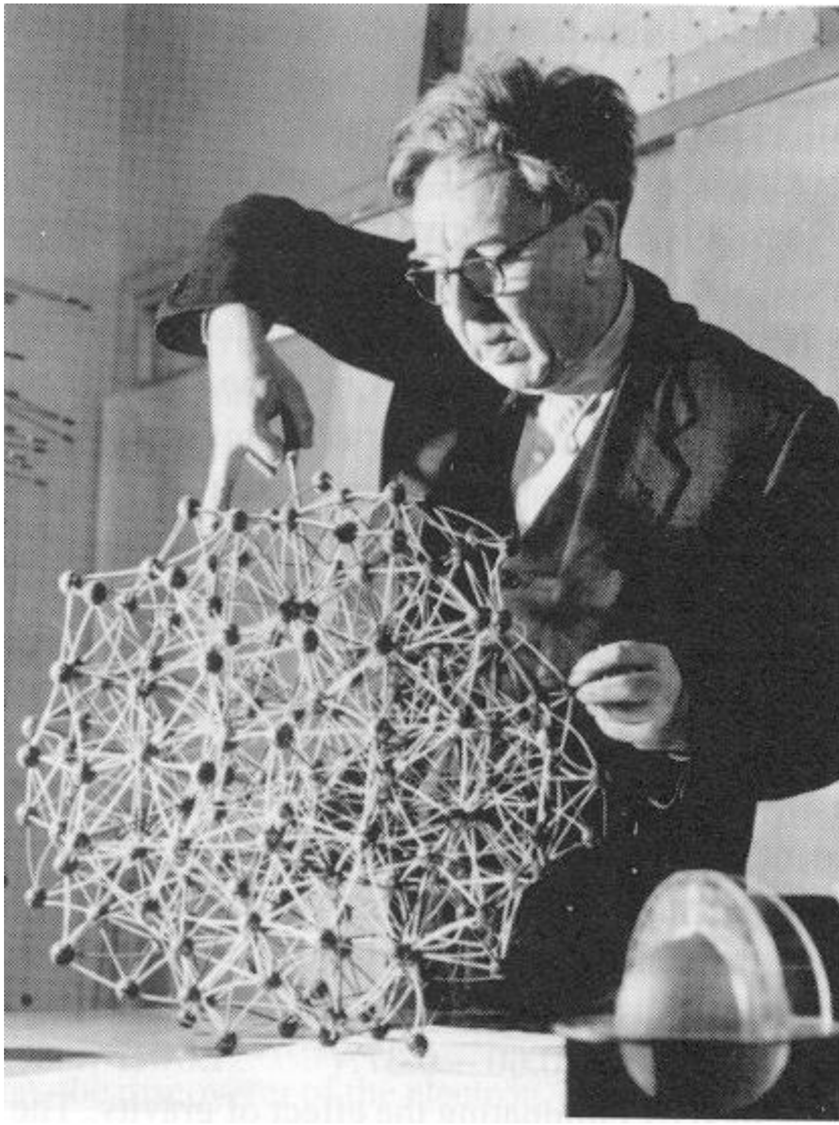


Figure 5.1. The experimental apparatus used by Hales to demonstrate the force exerted by dilating peas. When the lid was loaded with a weight, the dilated peas fill the interstices, developing polyhedral forms.



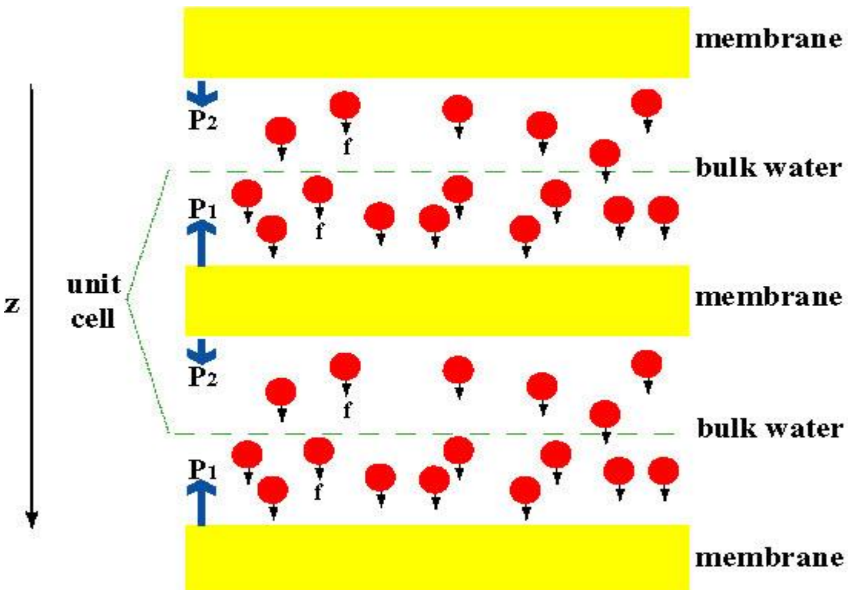
J.D. Bernal's "ball-bearing model" of an atomic liquid…

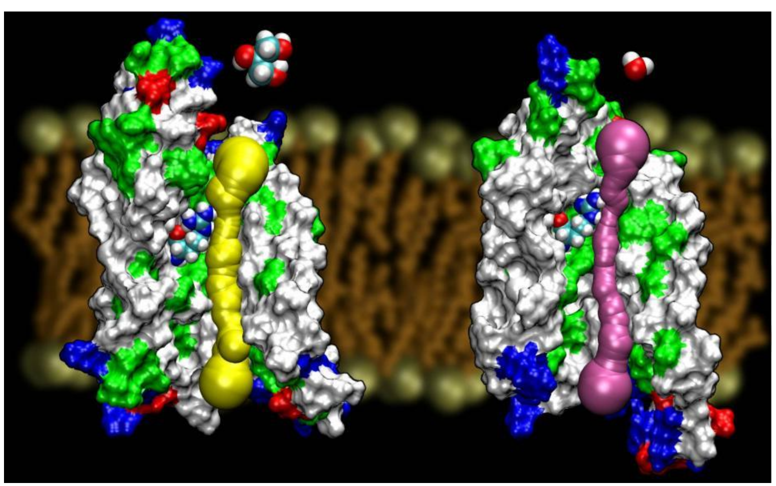


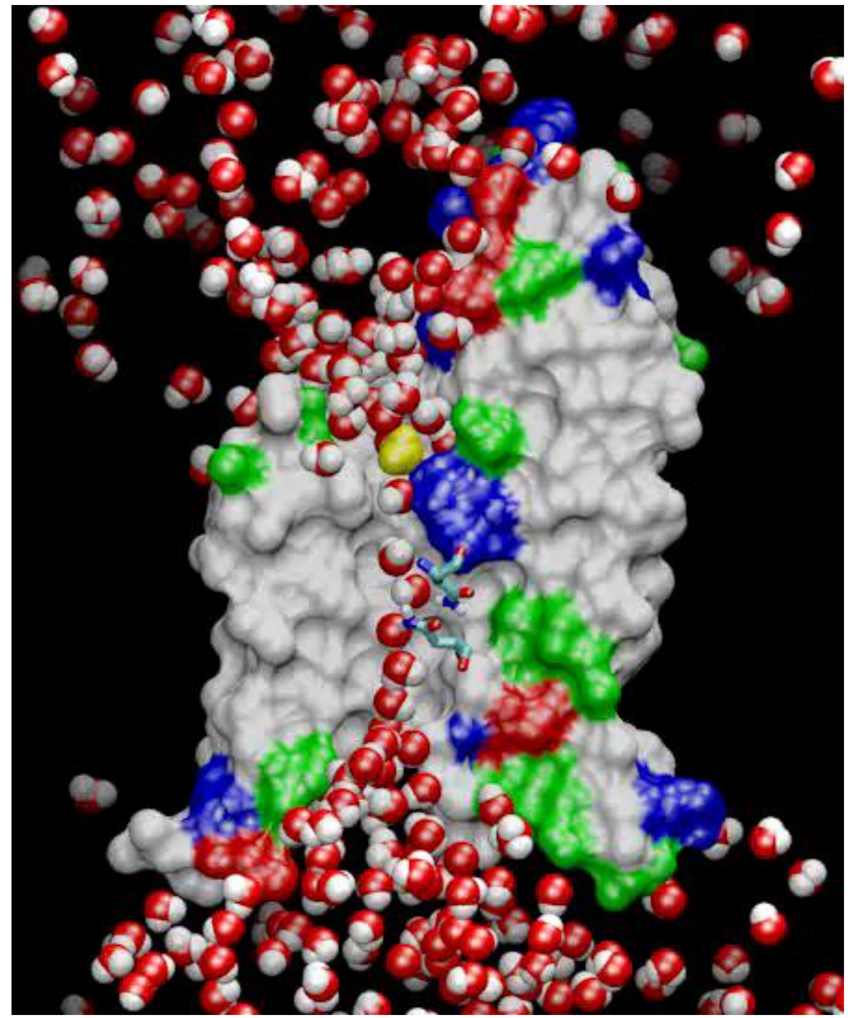
J.D. Bernal constructs a model of a liquid… (around 1950)..

I took a number of rubber balls and stuck them together with rods of a selection of different lengths ranging from 2.75 to 4 in. **I tried to do this in the first place as casually as possible, working in my own office,
being interrupted every five minutes or so and not remembering what I had done before the interruption.** However, ...

Water - membrane ionic channels







Função de distribuição radial g(r)