Applications on multiscale computational nanoscience for energy technologies:

a pathway towards carbon-neutral cycle

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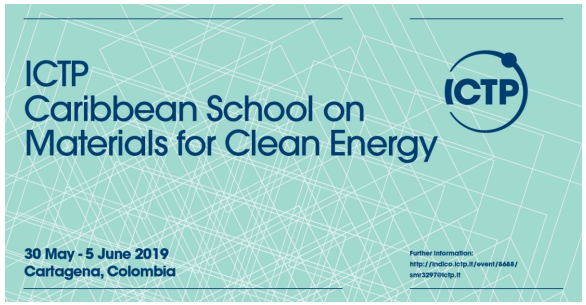

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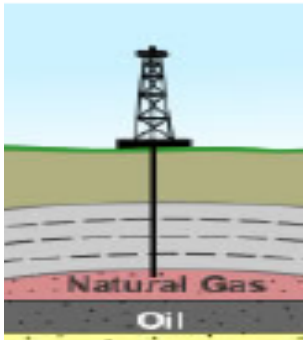
Nanopetro

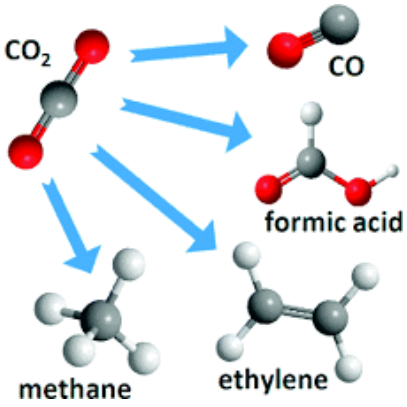
Research Group

Outline

- Perspectives and Challenges
- Computational Nanoscience Design towards sustainable decarbonization process on our energy matrix :

I. Oil & Gas
II. Carbon neutral cycles
III. Ethanol catalysis





My daily basis Brazilian jungle (São Paulo)

20.3 Million inhabitants – 6 Million cars and 1 million motorcycles – 500 new cars a day.

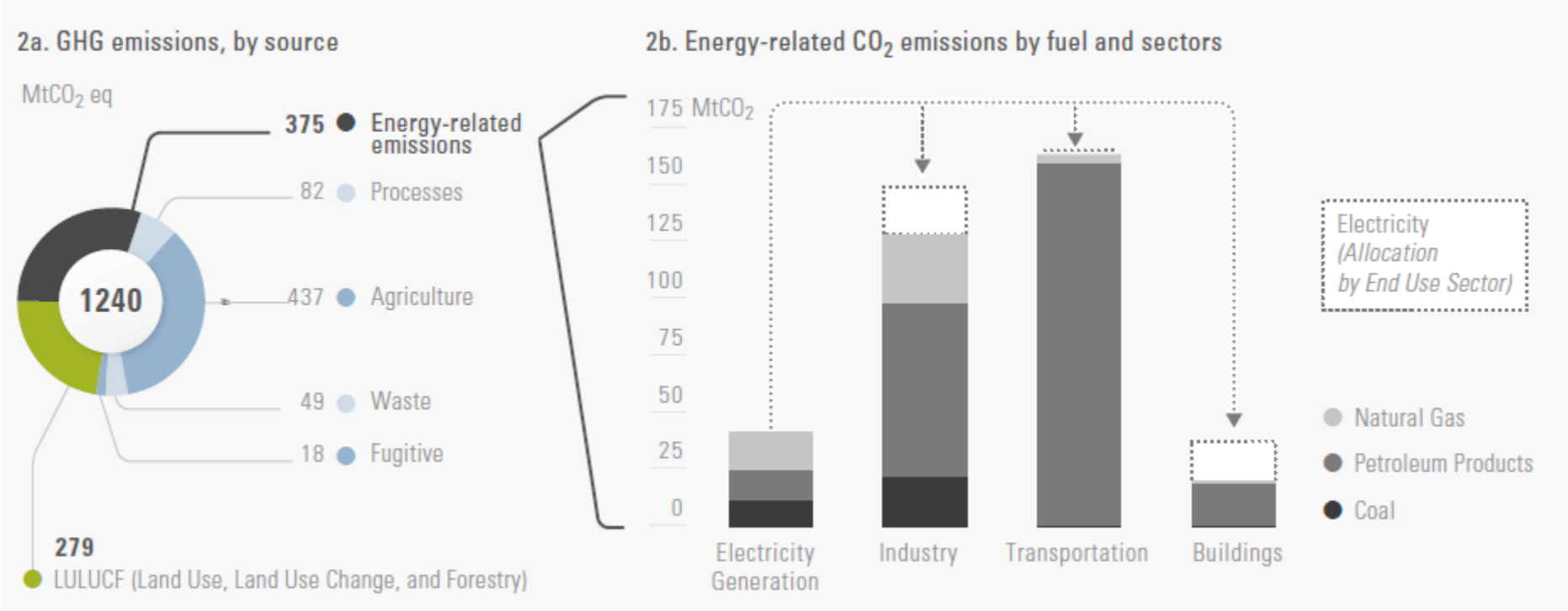
Typical filling station in Brazil

- ***APPLICATIONS ON ENHANCED OIL RECOVERY***
- ***NATURAL GAS & CO2 MANAGEMENT***
- ***ETHANOL CATALYSIS***

Decarbonization of energy sources

Satisfy the Paris Conf. milestones:

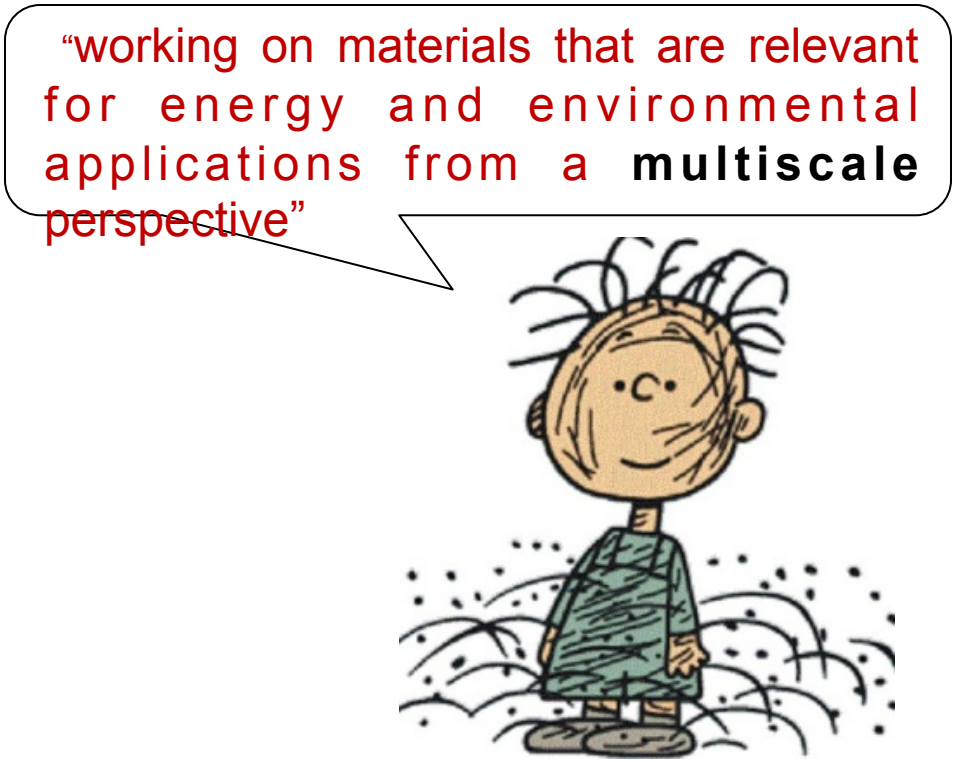
- **zero net anthropogenic greenhouse gas emissions**
- **limiting global warming to less than 2°C compared to pre-industrial levels**



From: Pathways to deep decarbonization in Brazil (2015) E. Lèbre La Rovere, C. Gesteira, C. Grottera and W. Wills

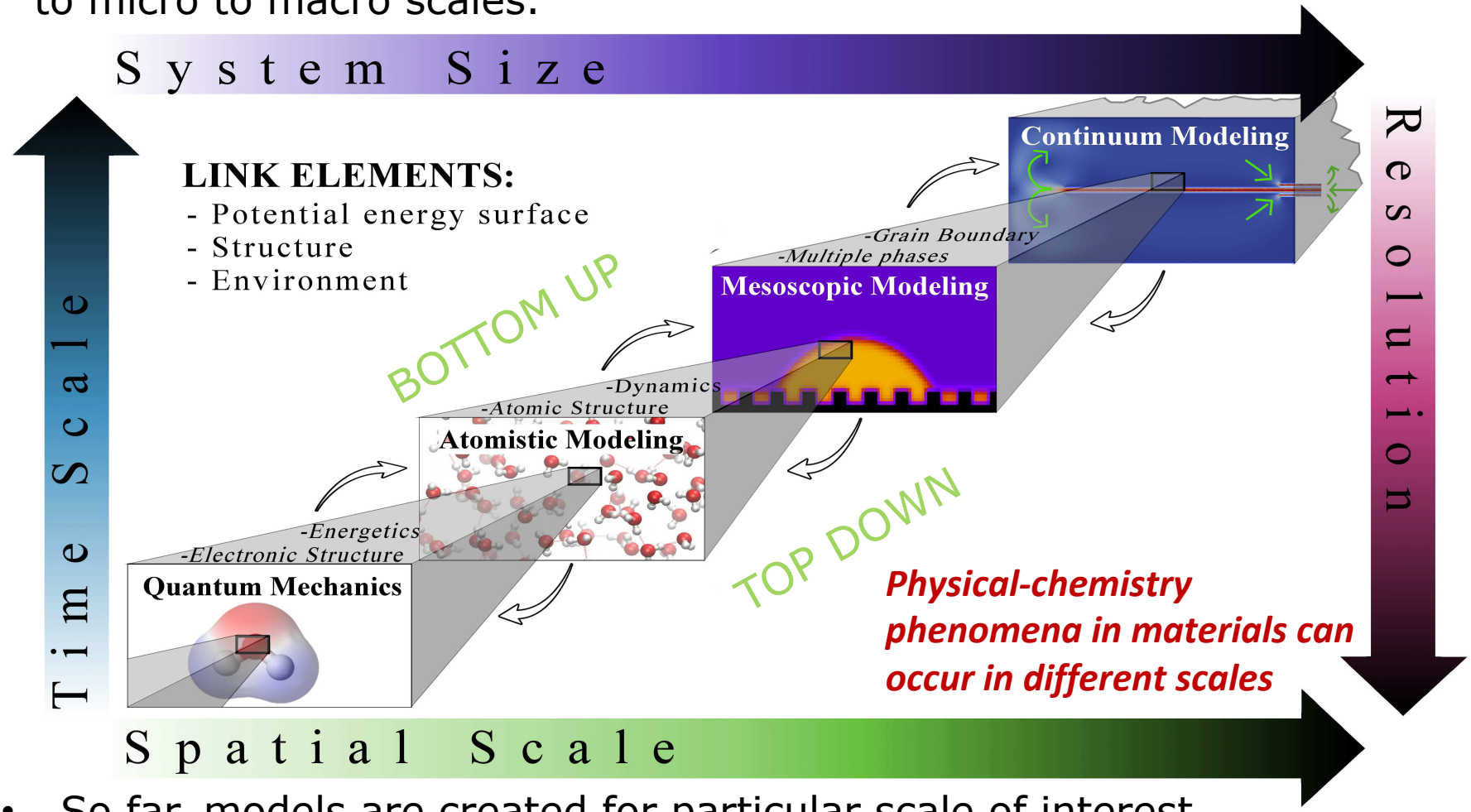
- ***APPLICATIONS ON ENHANCED OIL RECOVERY***
- ***NATURAL GAS & CO2 MANAGEMENT***
- ***ETHANOL CATALYSIS***

Is this clean ?



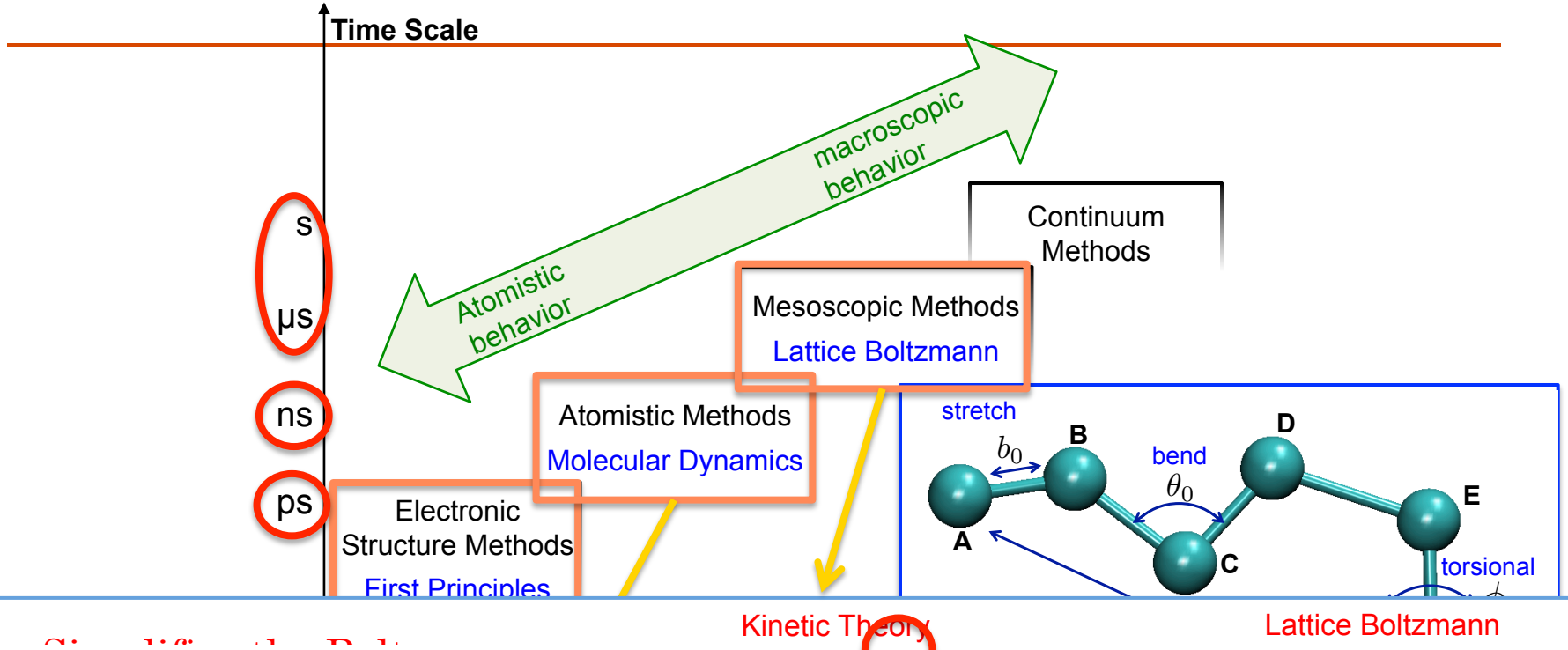
Multiscale approaches

- ***Challenge:*** modeling a physical phenomena ranging from molecular to micro to macro scales.



- So far, models are created for particular scale of interest

Multiscale computational approach



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

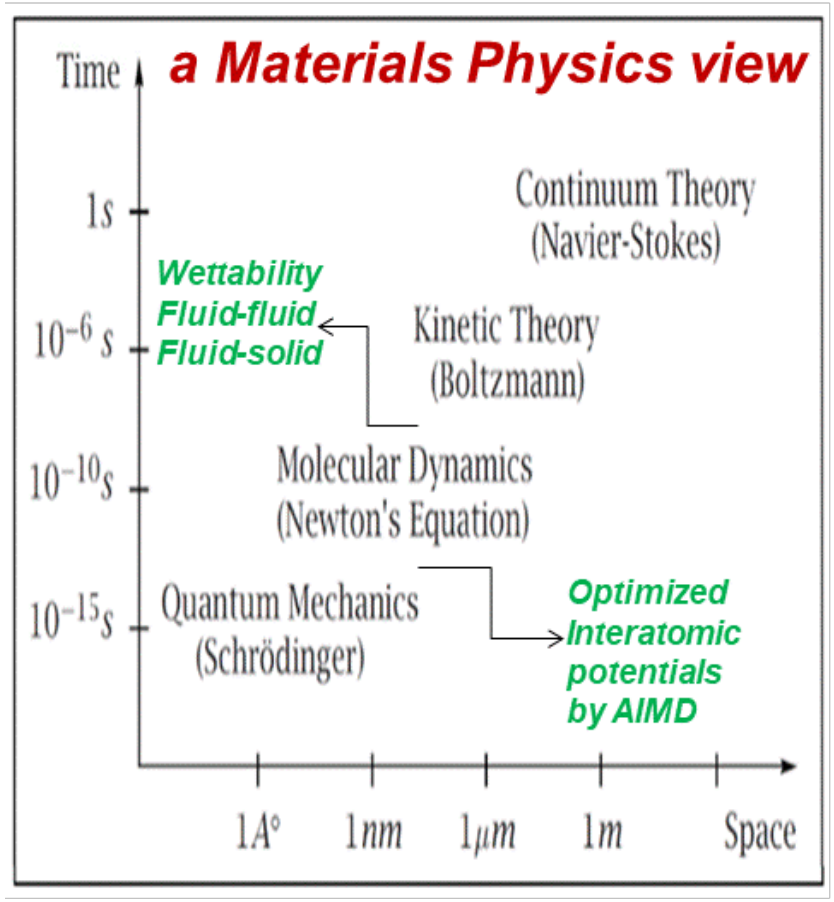
a similarly discretizing time into distinct steps

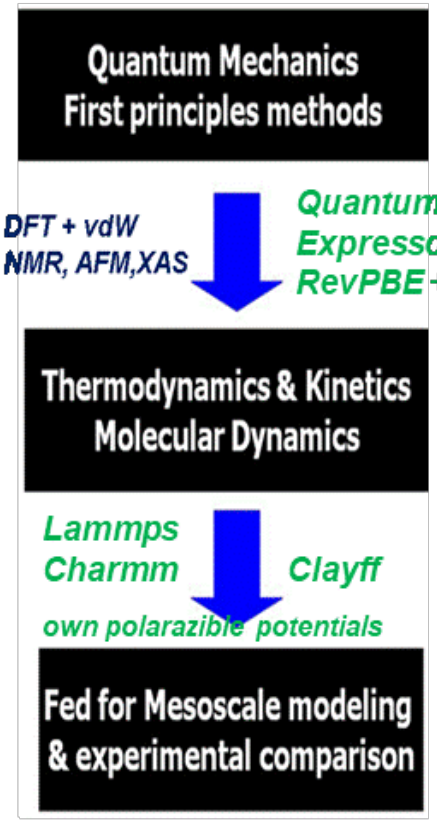
$$\mathbf{v}\nabla_{\mathbf{x}} f + \mathbf{F}\nabla_{\mathbf{p}} f + \frac{\partial f}{\partial t} = \Omega$$

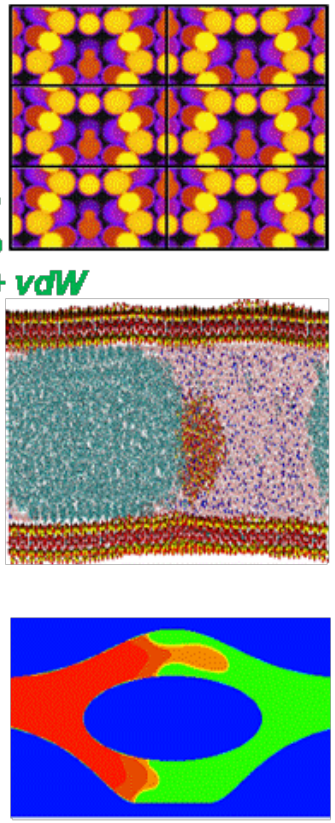
$$f_i(\mathbf{x} + \mathbf{e}_i \Delta t, t + \Delta t) = f_i(\mathbf{x}, t) + \Omega_i(\mathbf{x}, t)$$

Multiscale molecular simulations BOTTOM-UP

Complex systems and controled conditions over scales



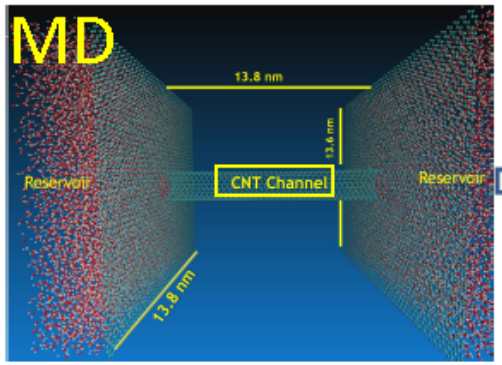




More efficient ?

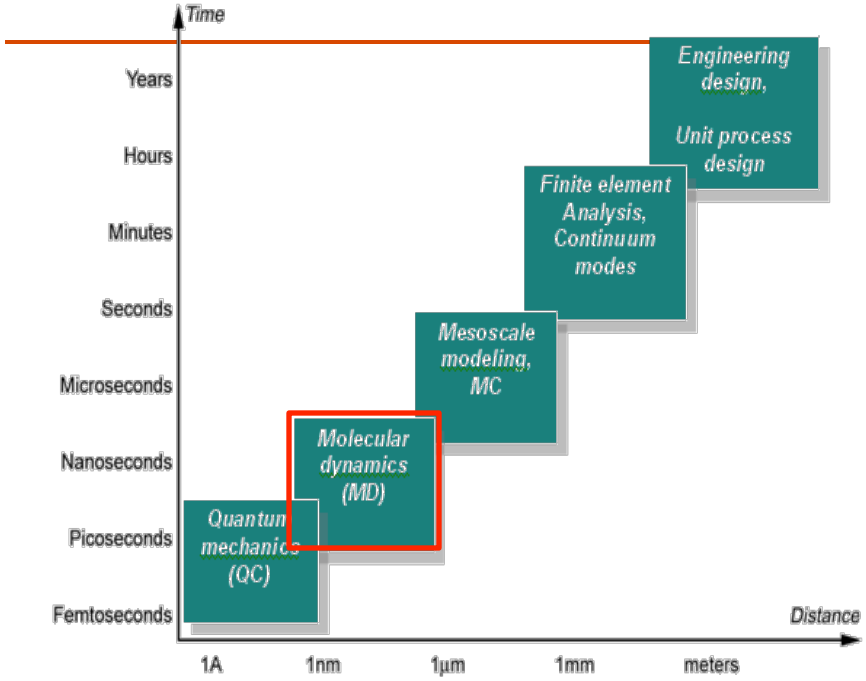
Big Data and Machine Learning

Multiscale molecular simulations
UP-DOWN



Atomic configurations

- Lammps code;
- Flexible water potential;
- Van der Waals interactions with 10 Å cutoff;
- Coulomb potential.
- NPT ensamble (200 atm, 300 K)

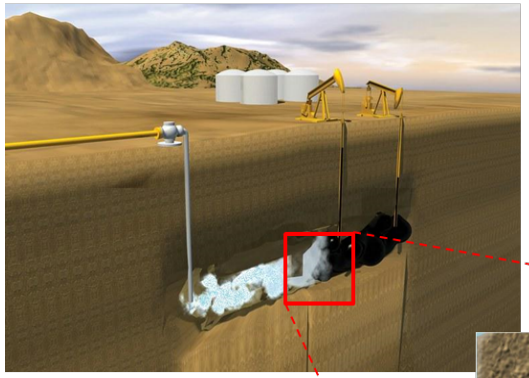


NANO-EOR

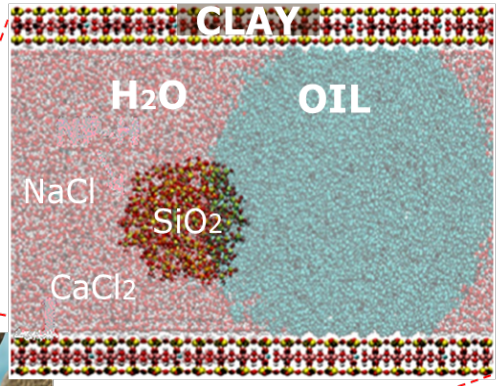
AN INTEGRATED WAY TO APPROACH THE PROBLEM

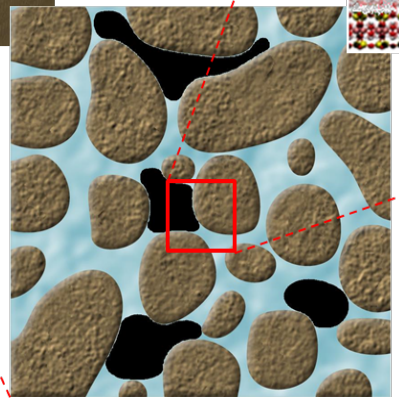
Enhanced Oil Recovery processes

MACROSCALE

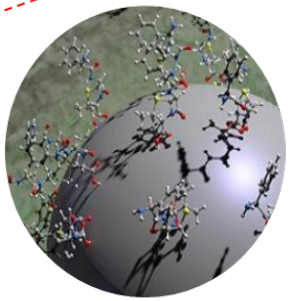


NANOSCALE





MICROSCALE



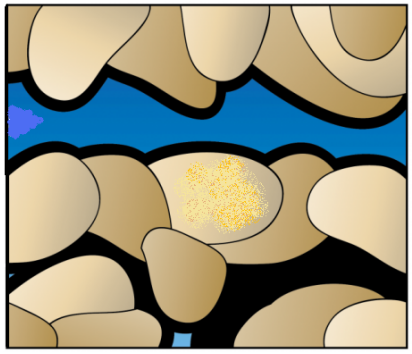
Nanostructures

A. Porous media

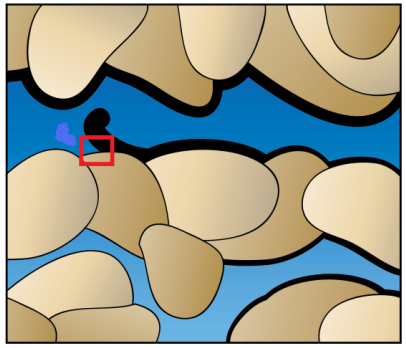
1. Shape
2. Size
3. Distribution

1. Without NP
2. NP-H
3. NP-SA
4. NP-PEG2

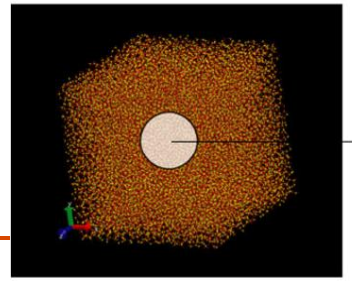
A. Geometry - Effect

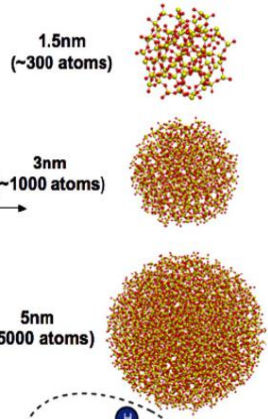


B. Wettability- Effect

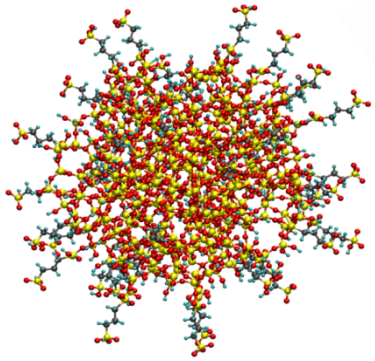


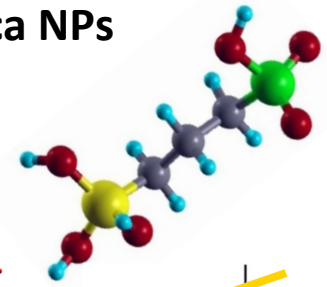
Nanoparticles @ oil/brine/rock interfaces

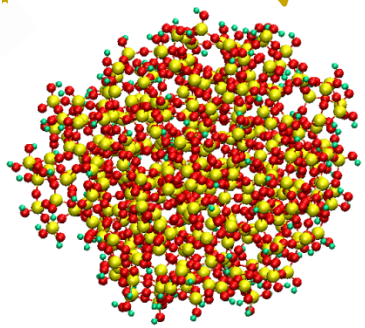


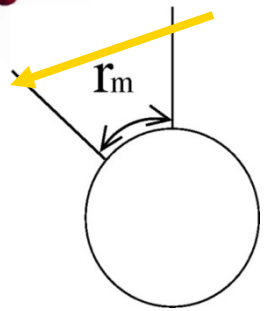


Functionalized Silica NPs (3 – 10 nm)

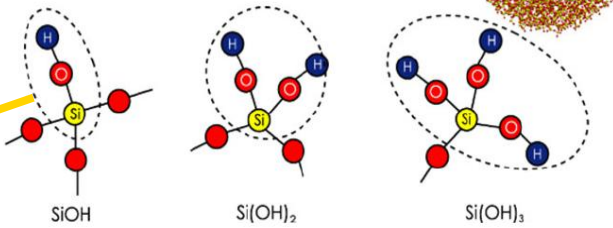








Hydroxilated NP

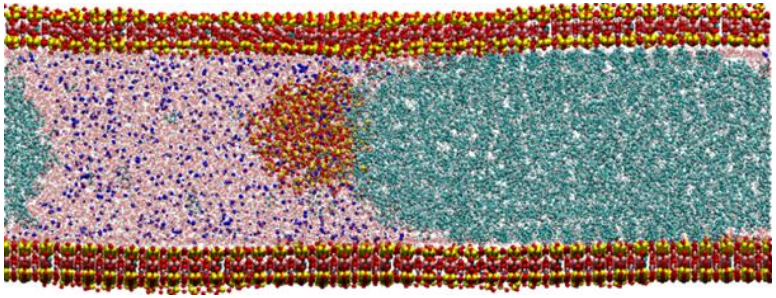


Hydroxylated Poliethylene glycol (Hydrophilic) -CH_2-CH_2-Sulfonic acid (Hydrophobic)

Functionalization based on First Principles interactions

Miranda et al., J. of Mat. Sci., 45, 5084 (2010)
Miranda et al.,Applied Surface Science, 292,742 (2014).

NP – rock interaction:
Silicates / Carbonates / Clays
Montmorillonite (MMT)
$(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$.



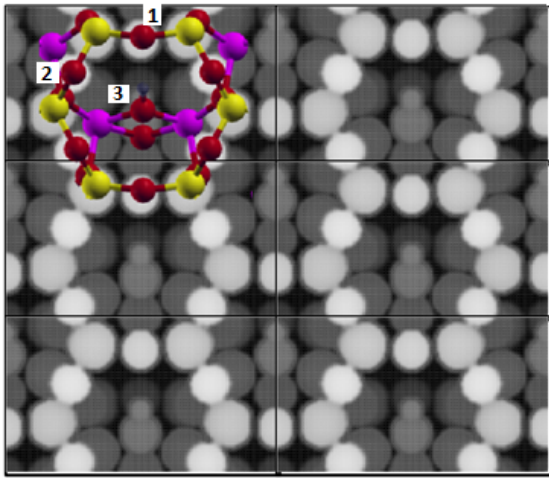
MMT is naturally hydrophilic and it is used as drilling mud.

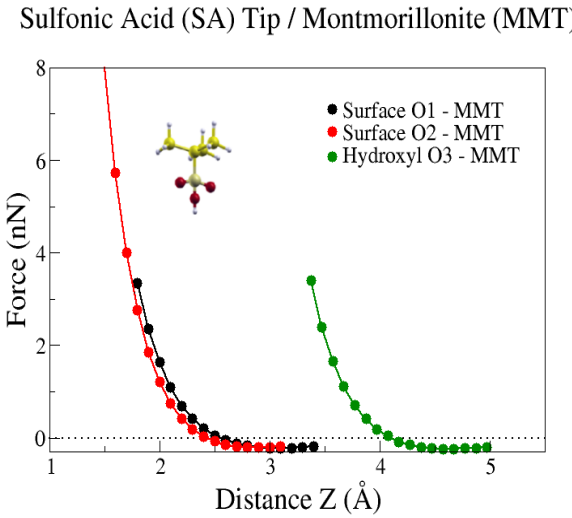
NANO-EOR

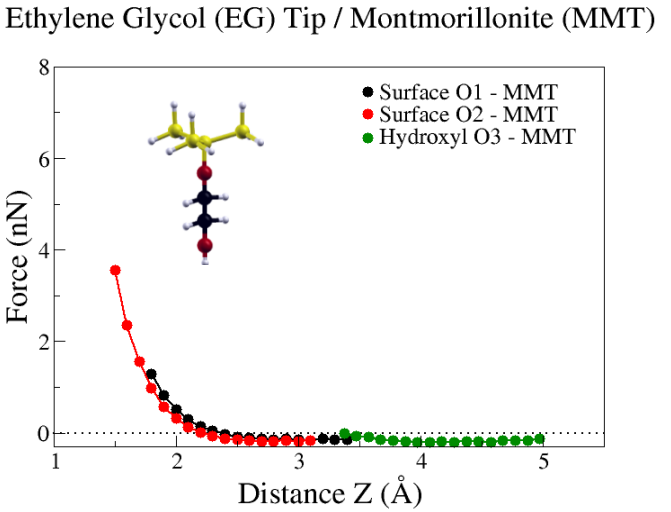
Alvim and Miranda, J. Phys. Chem. C, 120, 13503(2016)
Alvim and Miranda, Phys. Chem. Chem. Phys.,17, 4952 (2015)

Surface driven flow

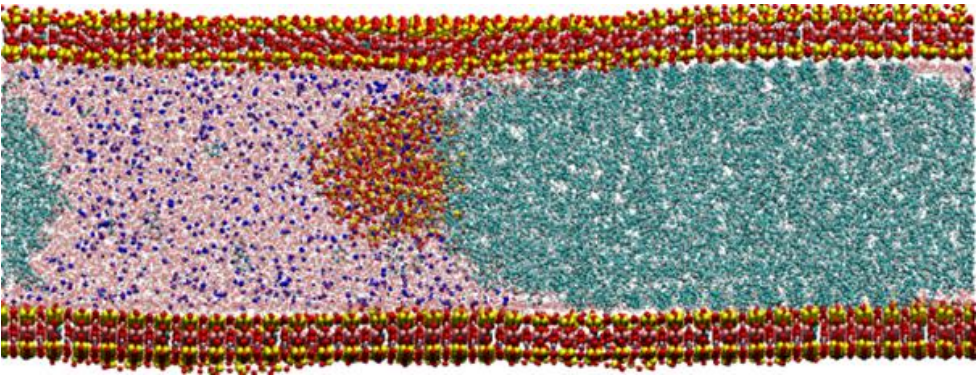
AFM Simulations Functional groups with Clay surfaces – DFT + vdW

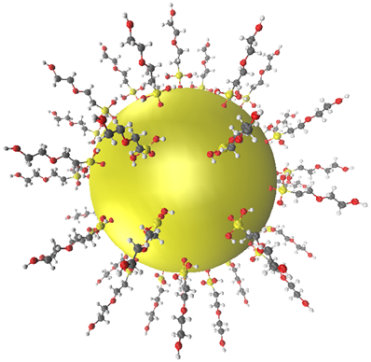


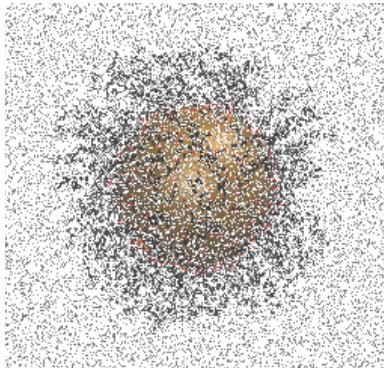




Molecular models of OIL and ROCKS

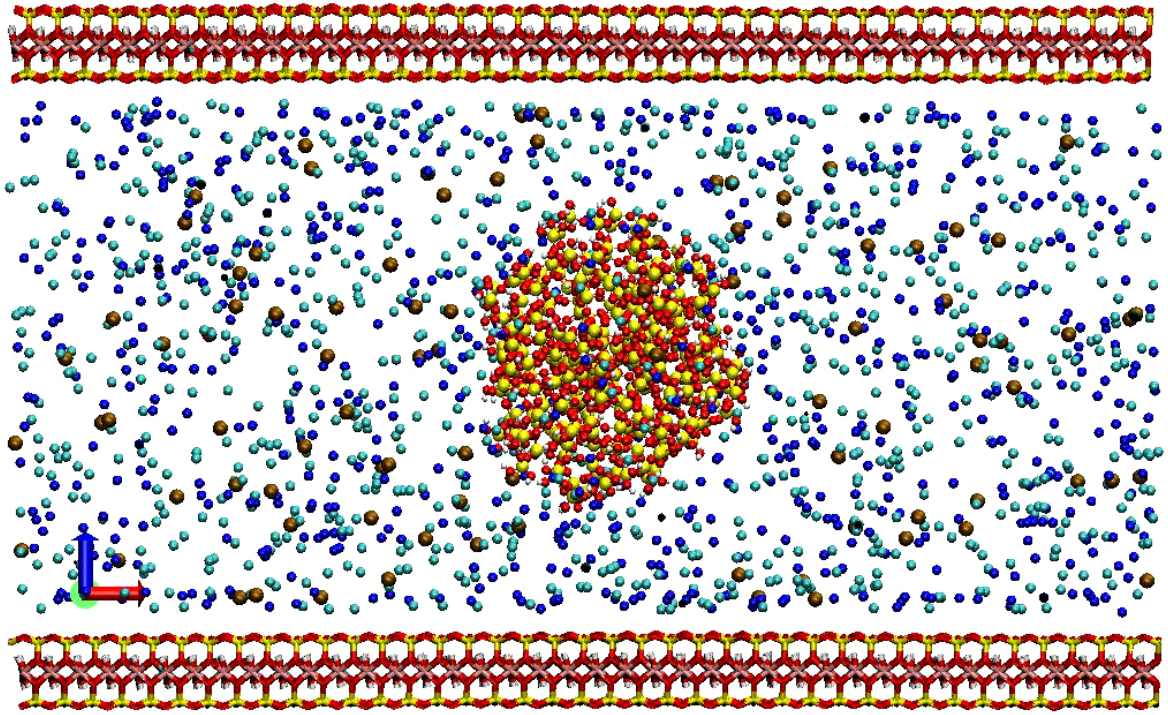


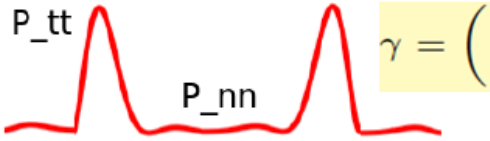




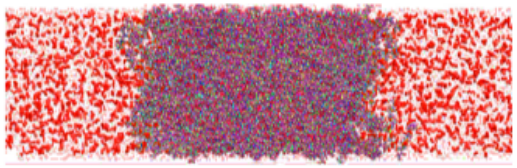
Fully atomistic to hybride models: Larger and magnetic NPs systems

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





$$\gamma = \left(\frac{\partial F}{\partial A}\right)_{N,V,T} = \left(\frac{\partial G}{\partial A}\right)_{N,P,T}$$

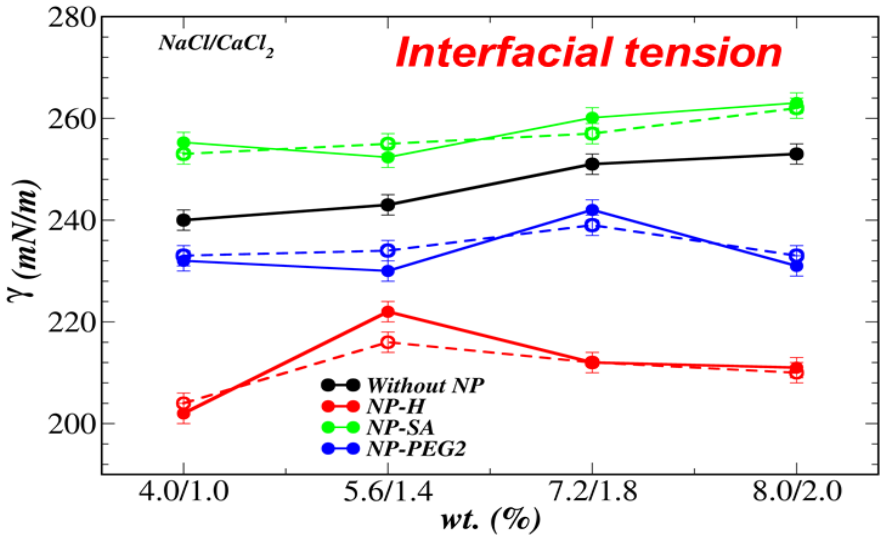


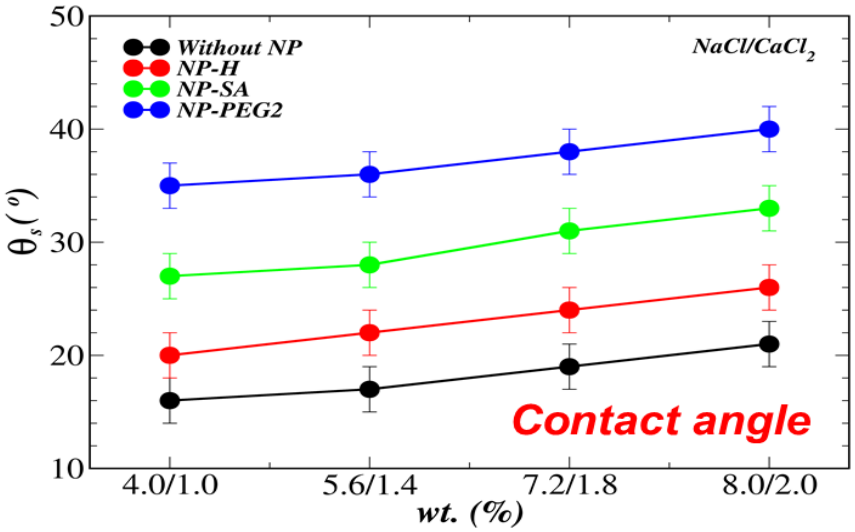
$$\gamma_{ij} = \int \Delta pdz$$

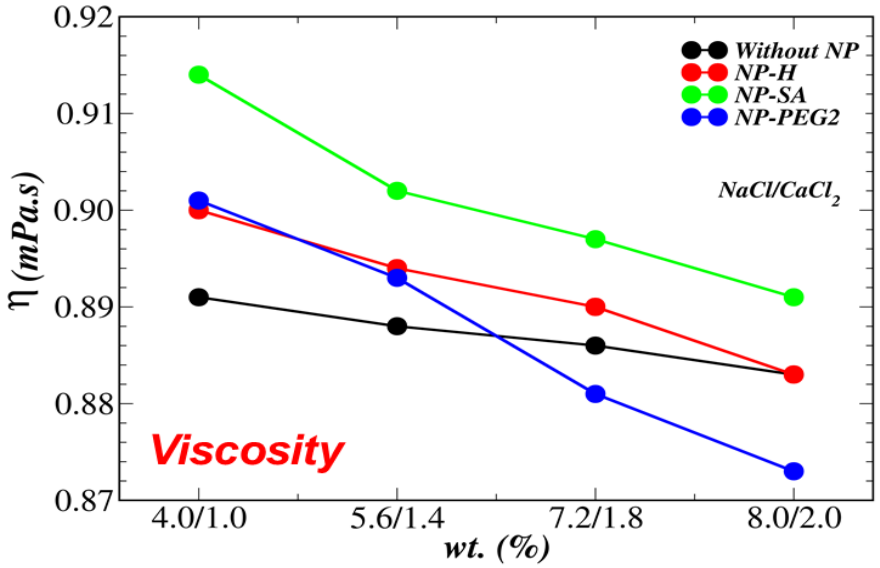
Miranda et al., J. Phys. Chem. C, 120, 6787, (2016)
Miranda et al., J. Phys.: Condens. Matter 27 325101 (2015)
Miranda et al.,Eur. Phys. J. B 88,261 (2015)
Miranda et al.,Applied Surface Science, 292,742 (2014)

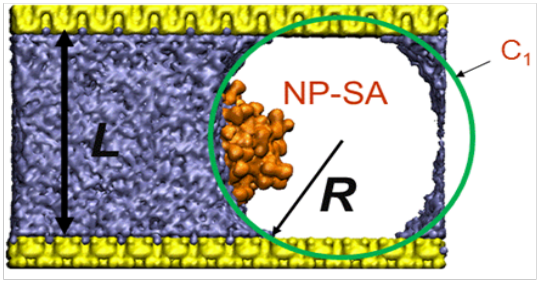
Interfacial phenomena
Bottom-up approach

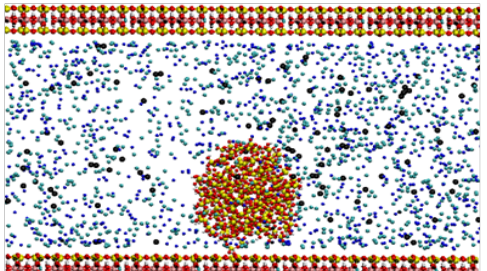
Miranda et al.,Applied Surface Science, 292,742 (2014).
Miranda et al., J. Phys. Chem. C, 120, 6787, (2016)
Miranda et al., J. Phys.: Condens. Matter 27 325101 (2015)
Miranda et al.,Eur. Phys. J. B 88,261 (2015)









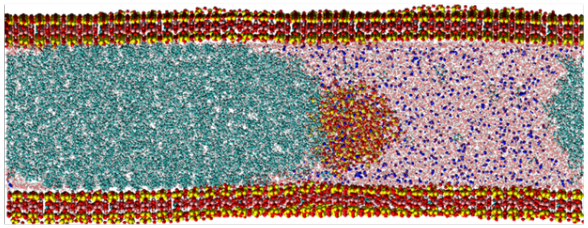


T=300K – 400K and P=1 to 200atm

MD : nm ns
LBM : µm/mm µs/ms

Going beyond MD

Hierarchical Computational Protocol: Molecular Dynamics + LBM



MD physical properties
ρ_o=0.81 g/cm³; ρ_b=0.96 g/cm³;
η_o=3.60 mPa-s; η_b=0.88 mPa-s;
γ_{ob}=38 mN/m; θ_w= 21°

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

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

Characteristic Scale for LBM simulations
l_0, t_0 and m_0

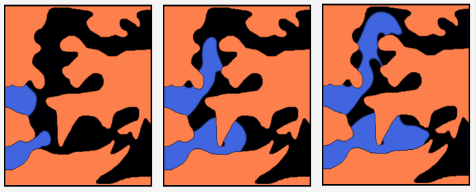
Computational parameters
Relaxation time, fluid-fluid and fluid-mineral interactions

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 2, 20 (2016)

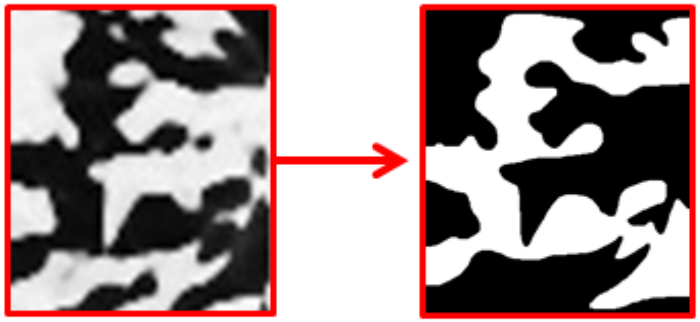
Exploring Oil Extraction by Nanofluids in Clay Coated Pore Network Models

Oil displacement by Brine+NP-PEG2: First Injection

$C_a = 3.7 \times 10^{-2}$

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

Image treatment



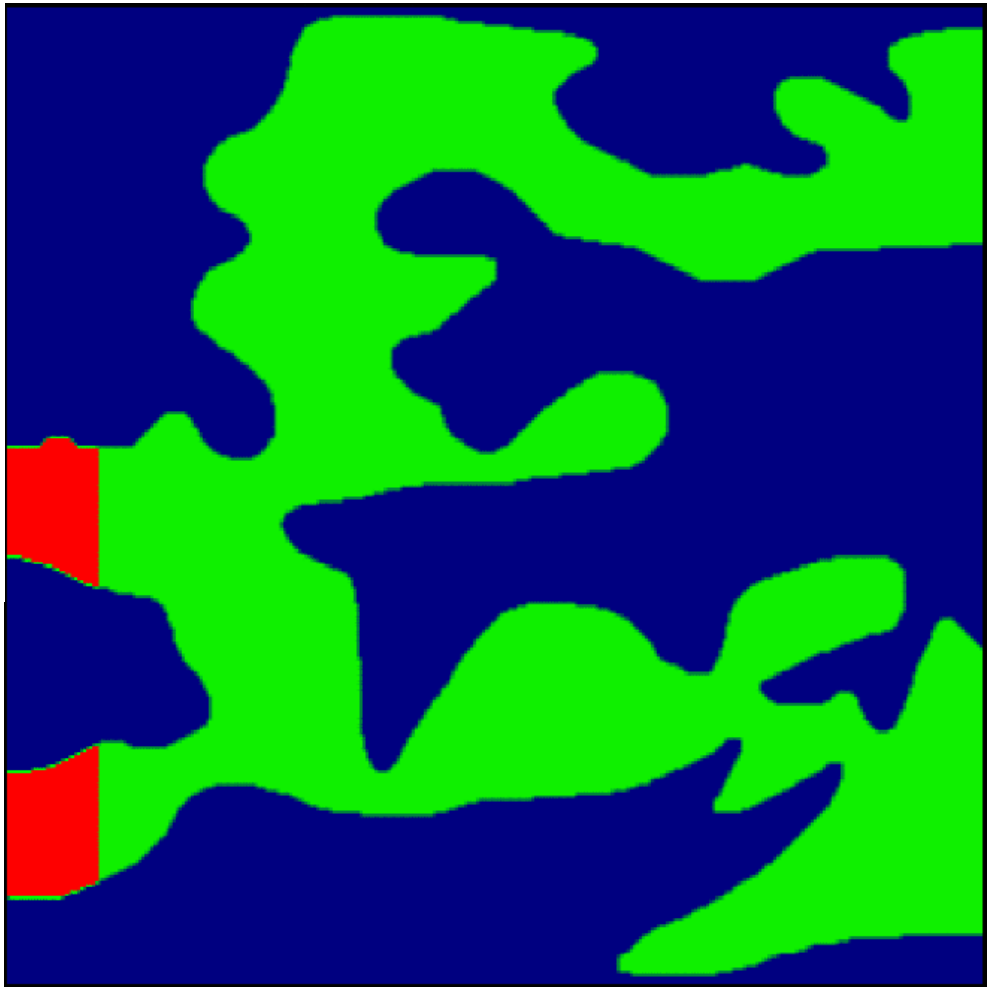
Computational Rock Model

Characteristic Scale

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

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

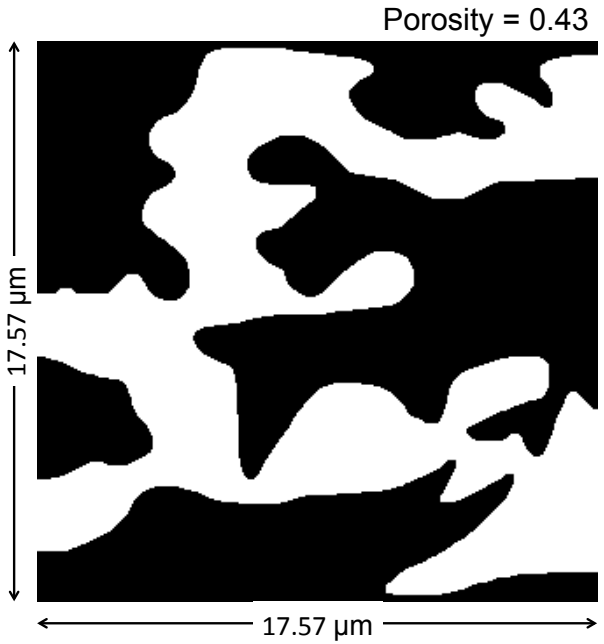
$m_0 = 1.50 \times 10^{-10}$ kg



Rock Brine Oil

Exploring Oil Extraction by Nanofluids in Clay Coated Pore Network Models

LBM Simulations: Oil displacement at the pore-size scale

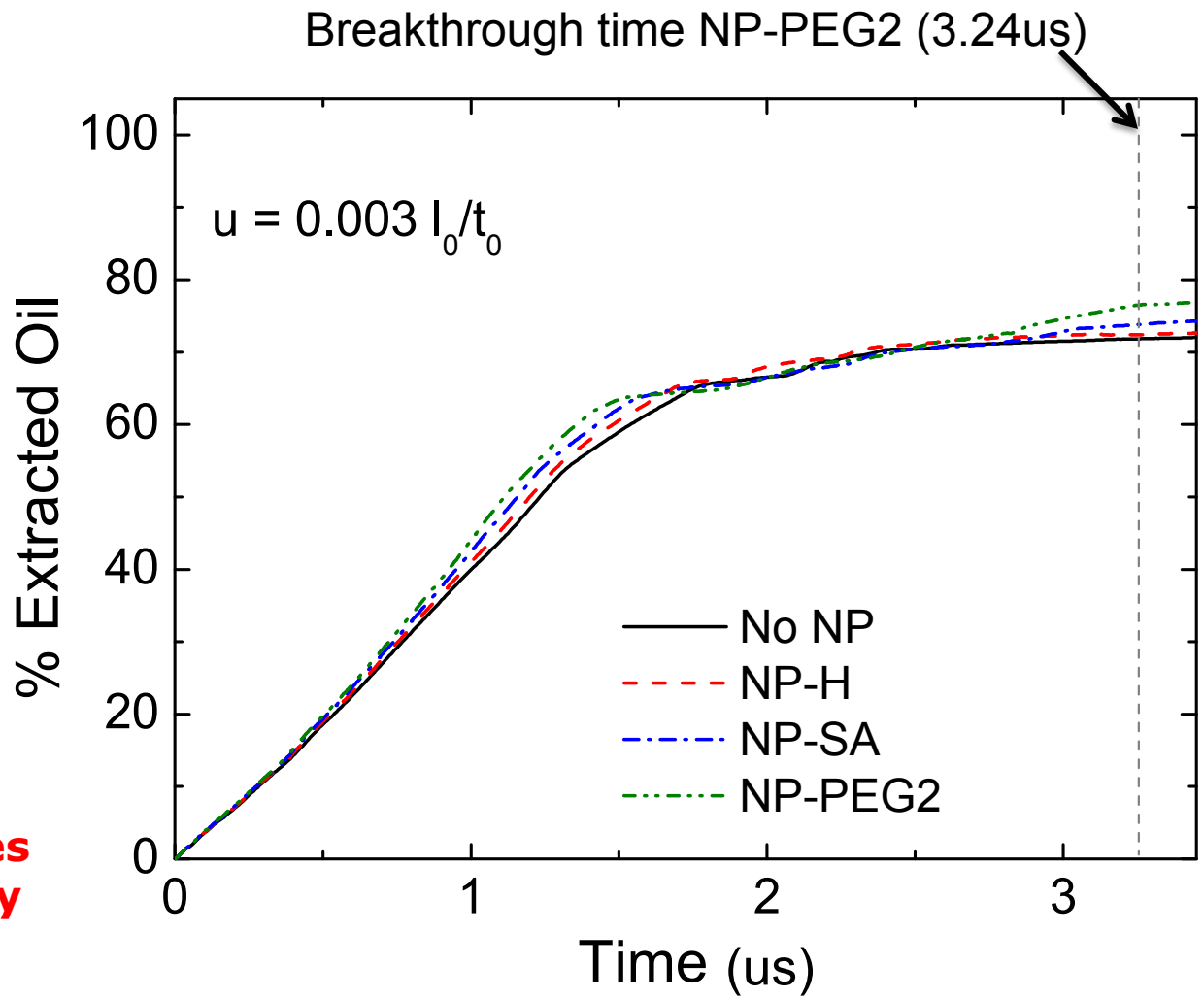


l_0=5.49x10^{-8} m

t_0 =5.91x10^{-10} s

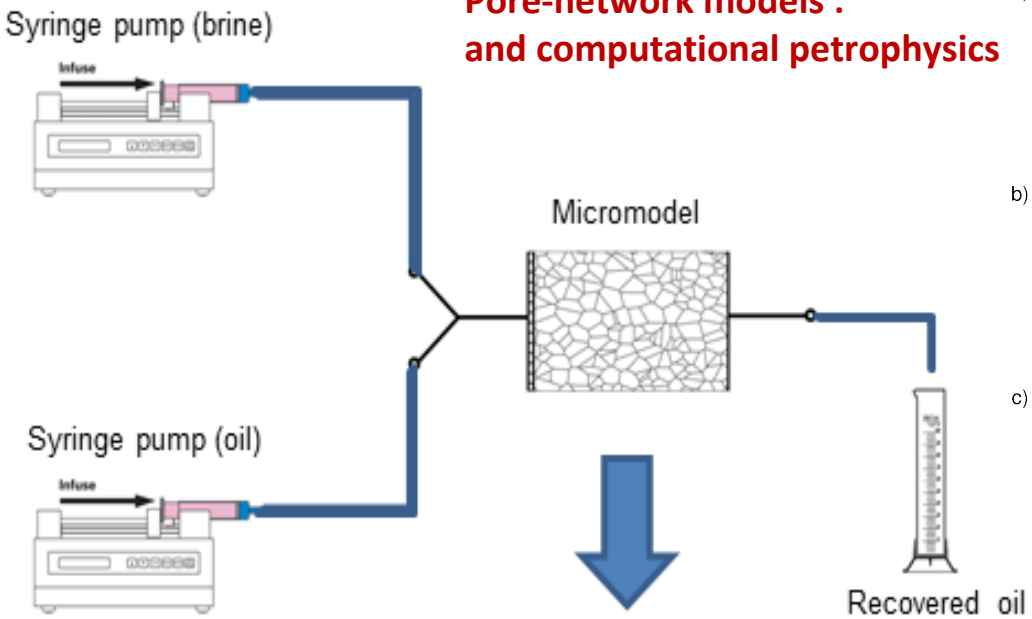
m_0=1.50x10^{-19} kg

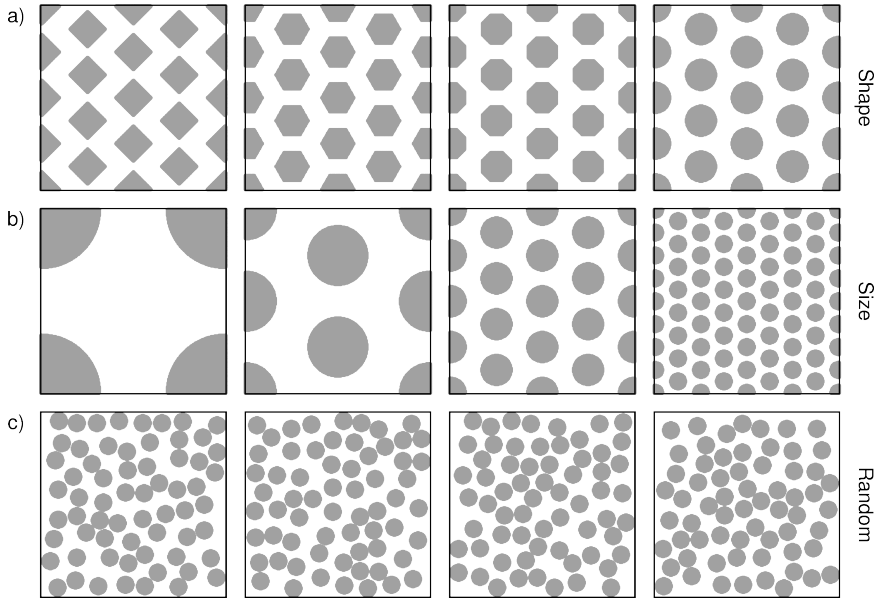
Addition of nanoparticles improve the oil recovery process



Enhanced Oil Recovery On Chip Setup

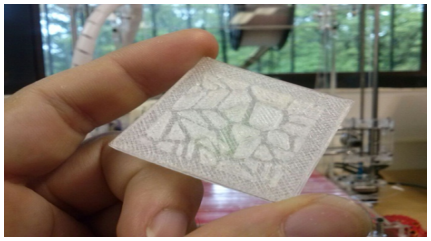
Pore-network models :
and computational petrophysics

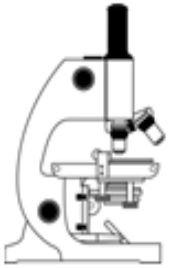


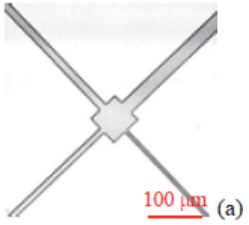


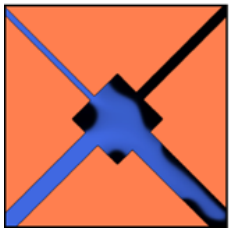
Porosity: 0.69 **Tortuosity:** 1.12

Porous 3D print



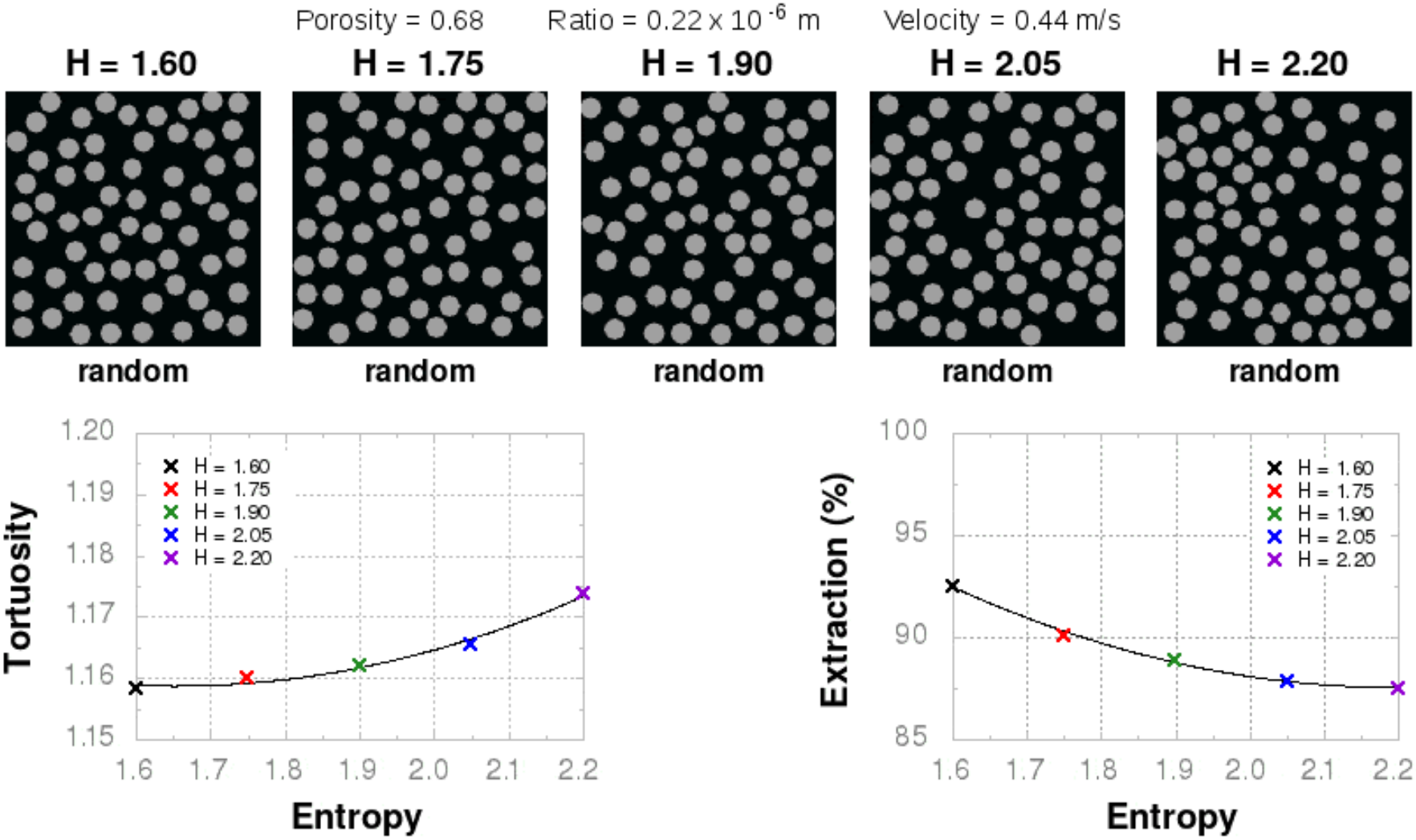






Porosity vs Permeabiability
Benchmark Experiment vs LBM

Pore models | Results - Variation-Entropy (r,ϕ: const.)



Summary

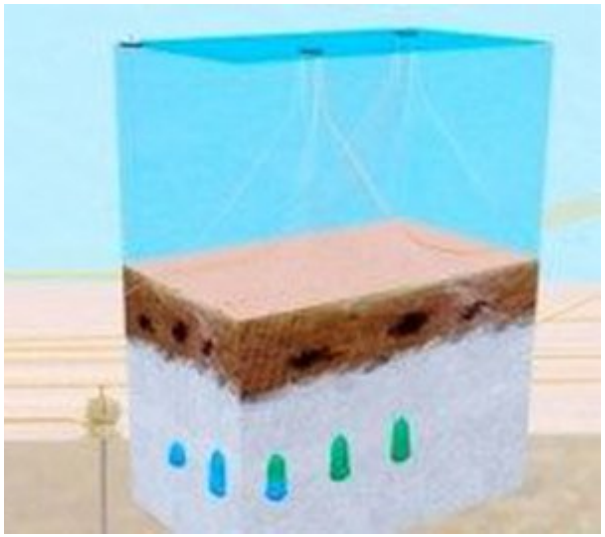
- Hierarchical multiscale approach
- Understanding the underlying molecular mechanisms of phenomena at nanoscale
- Cost effective way to explore nanostructures under controlled, realistic and operational conditions.
- Materials design over a broad portfolio of energy technologies (***batteries***, ***fuel cells***, …)
- Big data and Machine Learning can provide insightful information for Energy Materials design.

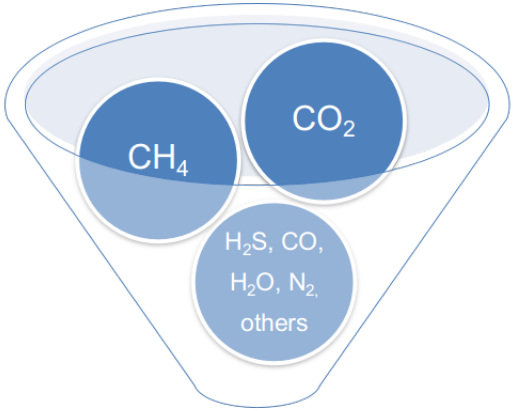
NANOFLUIDICS

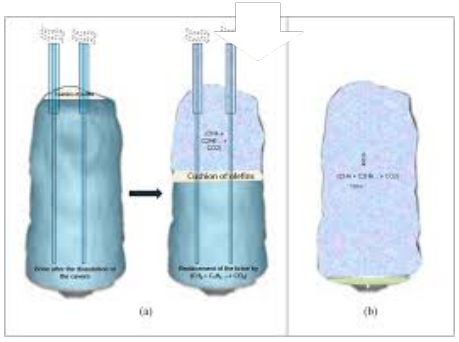
In collaboration with:
Alexsandro Kirch (USP)
James Moraes de Almeida (UFABC)

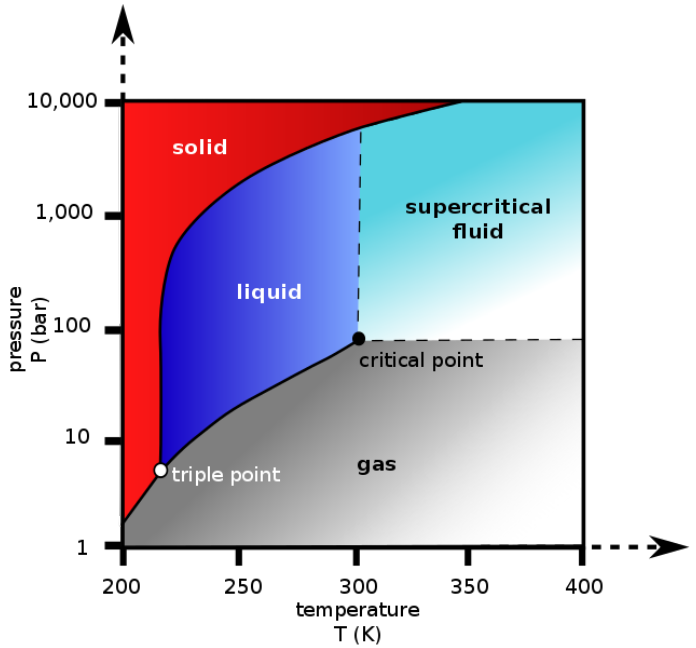
Natural gas

- **Lack of experimental data** describing gas mixture properties;
- **Molecular dynamics simulations** (MD) are more accurate than predictions supported by semi-empirical state equations.



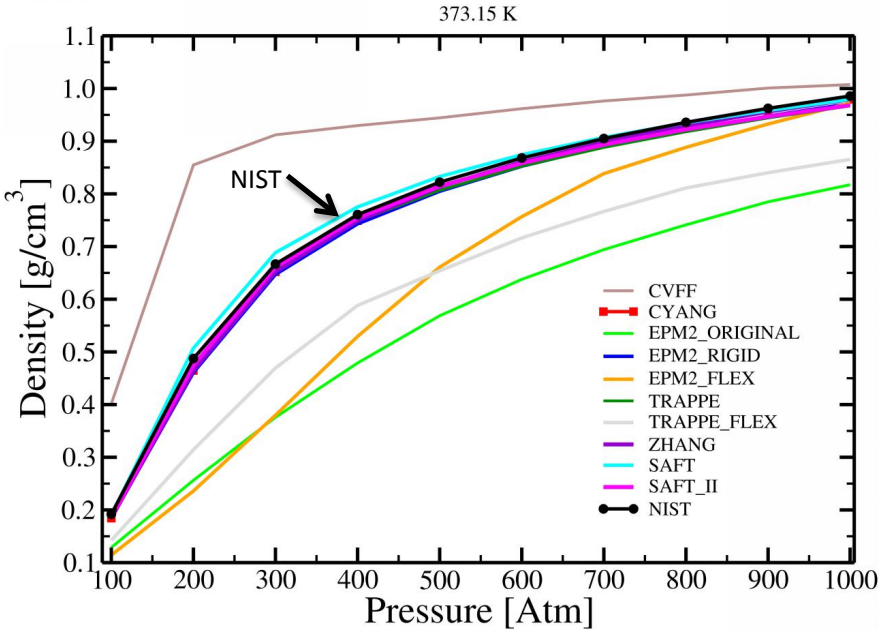




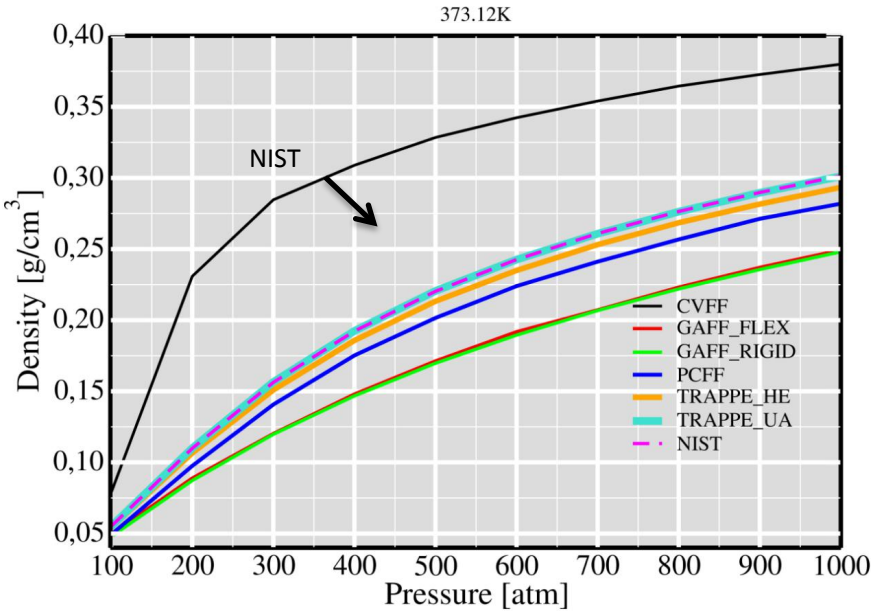


Force Field Benchmark

CO_2

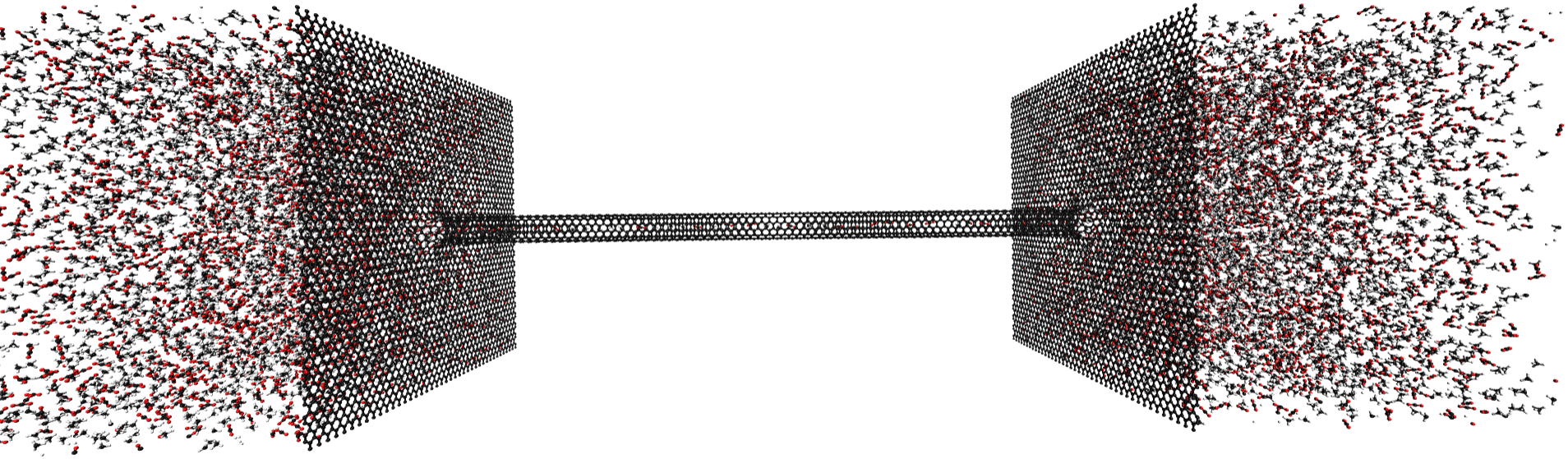


CH_4

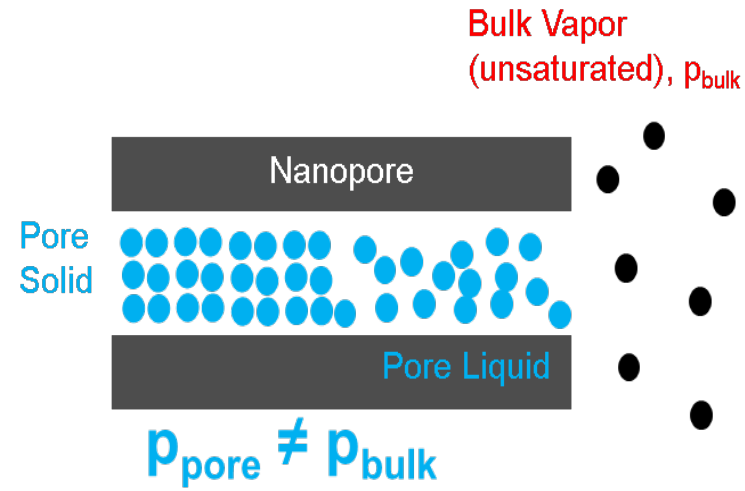


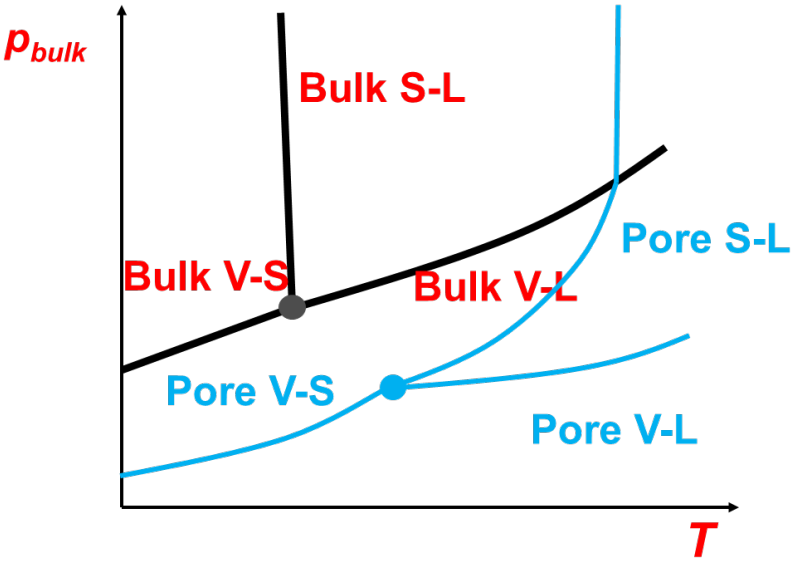
T=313.15K and 100 atm	**Density g/cm^3**	**Viscosity Pa.s**
Pure CH_4	0.07	1.42×10^{-5}
Pure CO_2	0.63	4.88×10^{-5}
80% CH_4, 20% CO_2	**0.08**	**1.66×10^{-5}**

Natural gas mixture bulk properties and confined @ CNTs

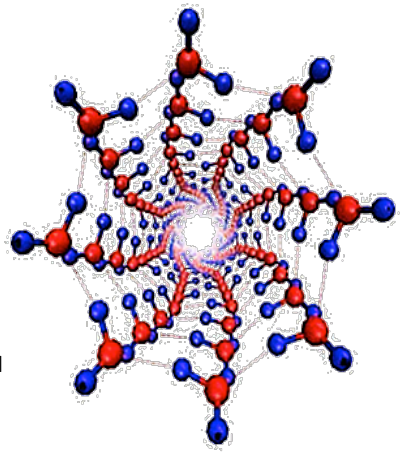


Fluids confined at nanoporous



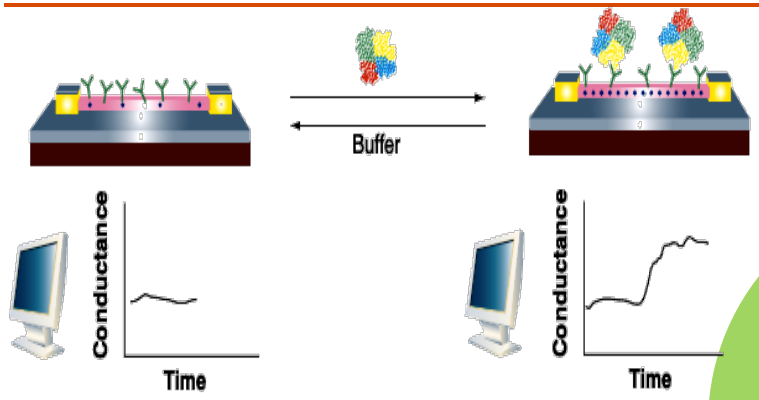


- **Under confinement, the structuring is frustrated by surface effects, that disrupts the hydrogen bond networks.**
- **New phenomena can emerge, as *new phase transitions*, *layering near the interface*, eg. *first layer of immobile water*.**
- **At nanoscale, the continuum models for fluids may not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

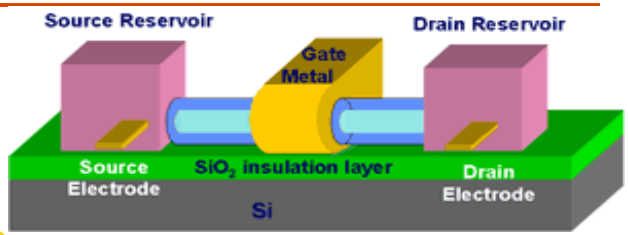


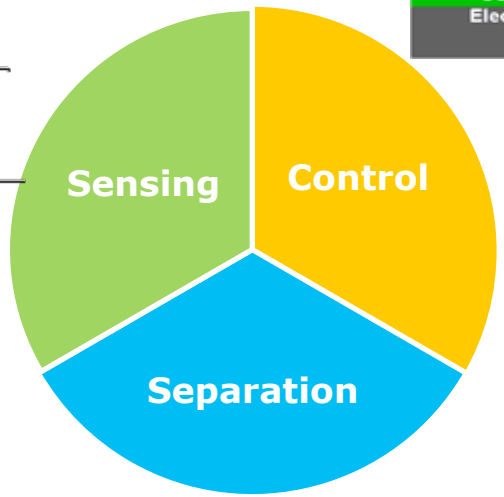
Li, Shujuan & Schmidt, Burkhard (2015). Molecular dynamics simulations of proton-ordered water confined in low-diameter carbon nanotubes. *Physical Chemistry Chemical Physics, 17*, 7303-7316.

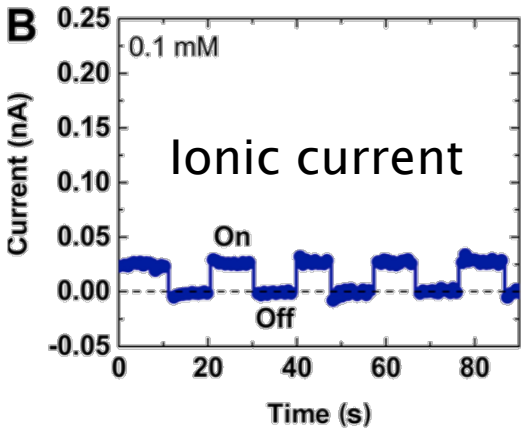
Nanofluidics



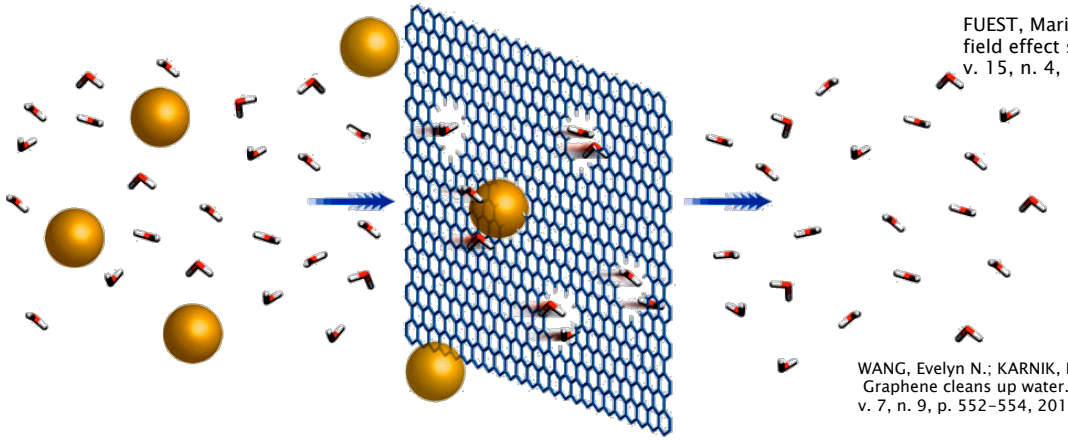
PATOLSKY, Fernando; ZHENG, Gengfeng; LIEBER, Charles M. Nanowire sensors for medicine and the life sciences. 2006.





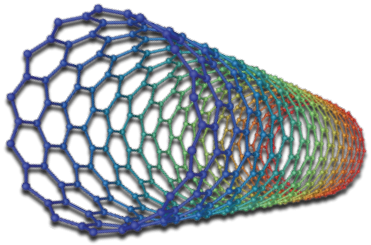


FUEST, Marie et al. A three-state nanofluidic field effect switch. **Nano letters**, v. 15, n. 4, p. 2365-2371, 2015.

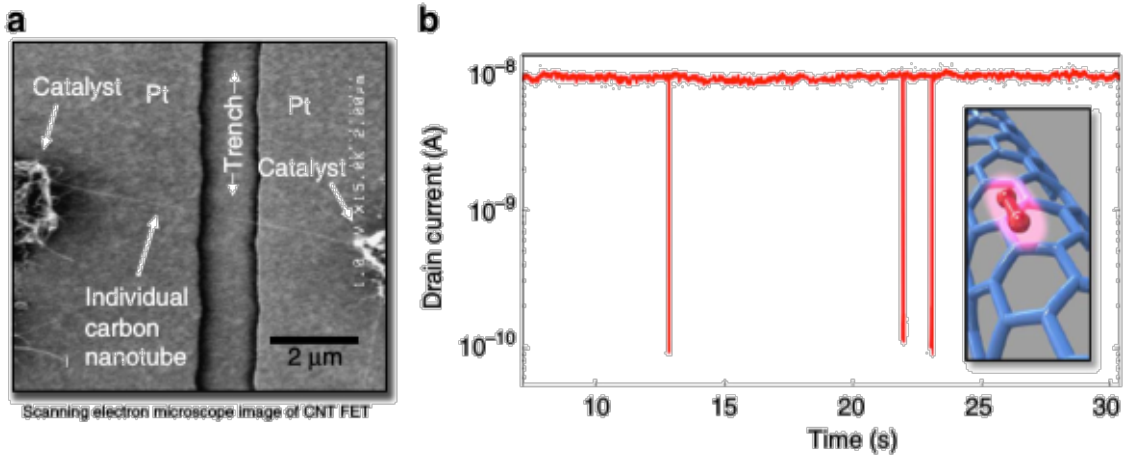


WANG, Evelyn N.; KARNIK, Rohit. Water desalination: Graphene cleans up water. **Nature nanotechnology**, v. 7, n. 9, p. 552-554, 2012.

Single molecule sensor
Why CNTs?



1. **Geometric properties**: hydrophobic wall and well defined nanometric openings enable ultrafast transport of water and gas;
2. **Electronic properties**: highly susceptible to changes in charge states in contact with the ions/molecules.



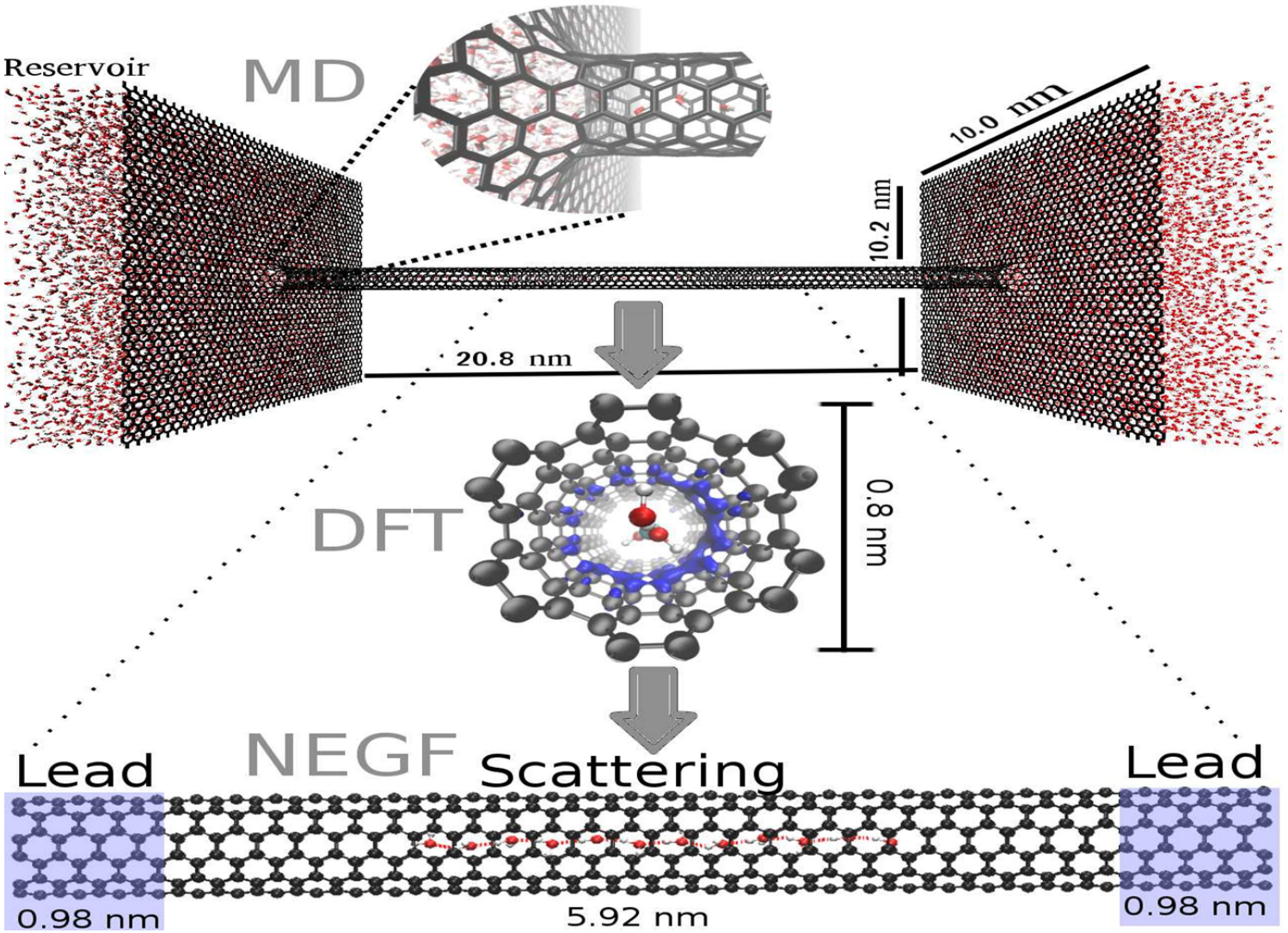
Scanning electron microscope image of CNT FET

Bushmaker, A. W. *et al*. Single-ion adsorption and switching in carbon nanotubes. *Nat. Commun.* 7:10475 (2016).

Figure 1 | Device layout and switching transients caused by single-ion adsorption. (**a**) Scanning electron microscope image of CNT FET device and (**b**) plot of drain current versus time showing switching transients observed during ionized gas exposure. The inset shows a cartoon image of a gas molecule adsorbed on the surface of a carbon nanotube.

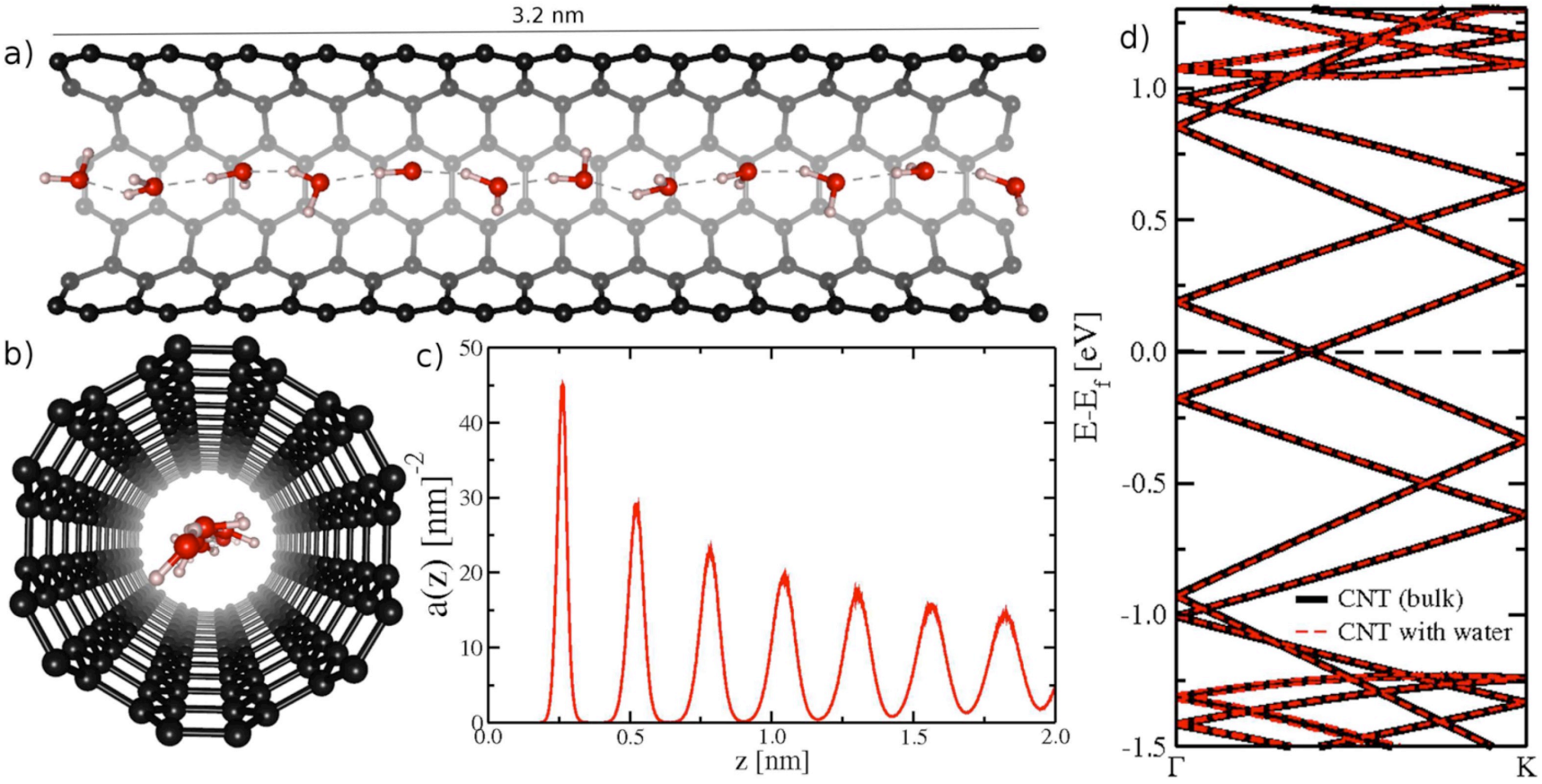
Kirch, Almeida and Miranda
(J. Chem. Theory and Comp. 2018)

Nanofluidics sensors



Kirch, Almeida and Miranda
(J. Chem. Theory and Comp. 2018)

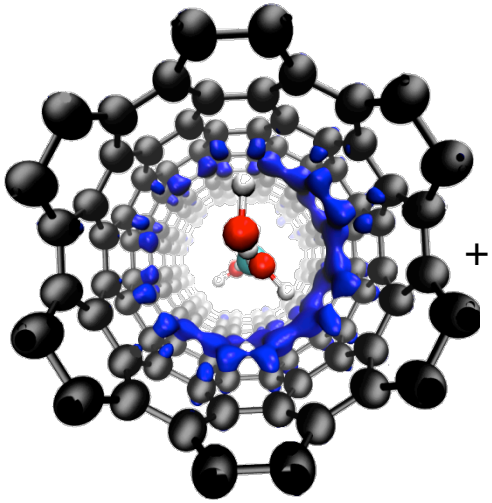
Atomistic



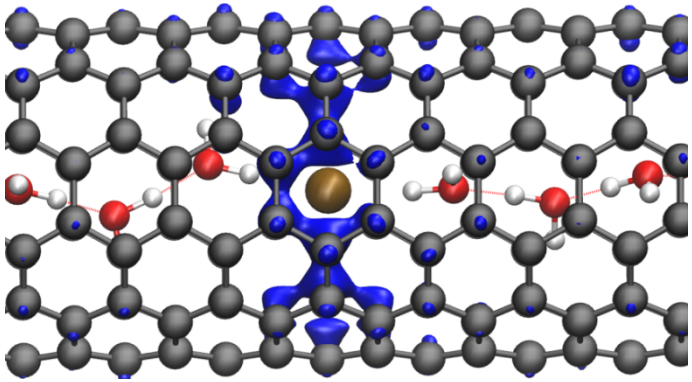
The interaction between water and CNT reveals ***weak binding energies*** and ***small charge transfer***, leading to its ***insensitivity*** to water exposure.

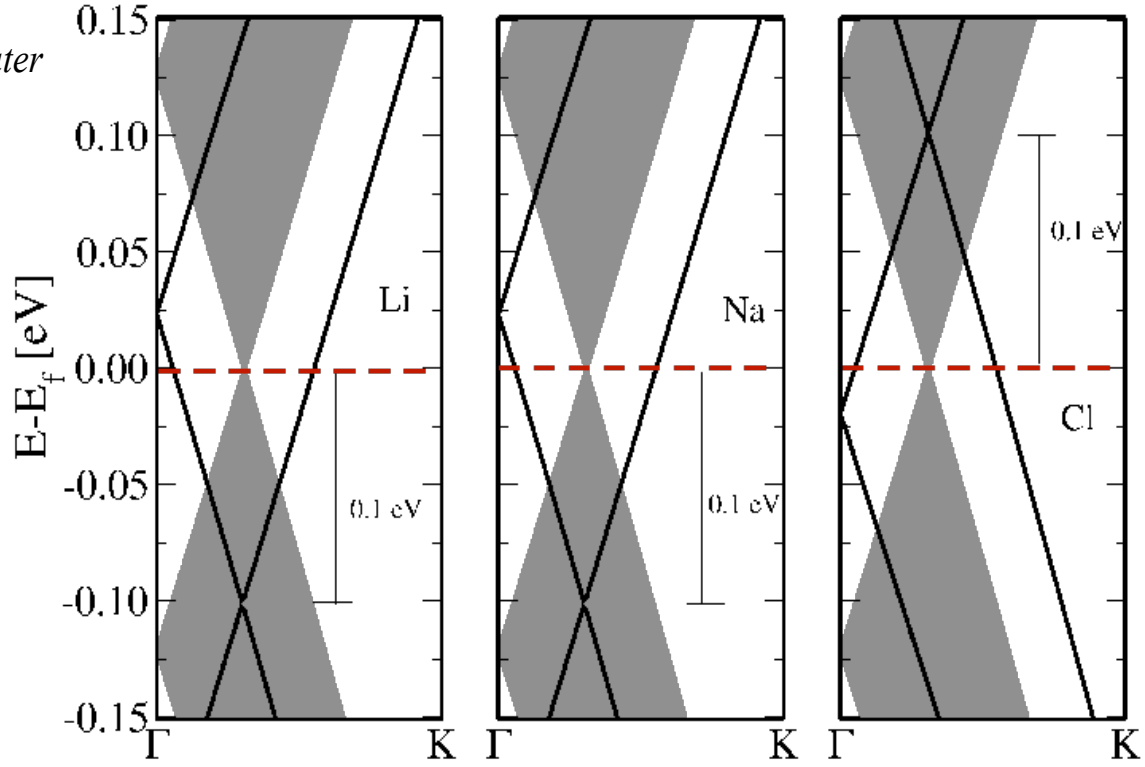
Electrolyte aqueous solution confined into (6,6) CNT

$$\Delta\rho = \rho_{Total} - \rho_{CNT} - \rho_{Ion} - \rho_{Water}$$



$$+0.01\frac{C}{Ang^3}$$

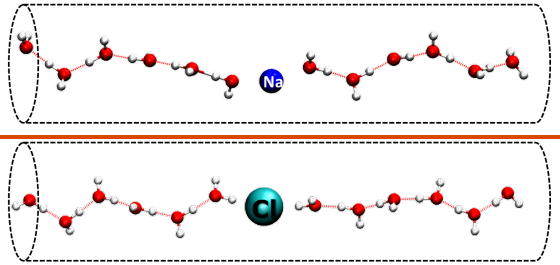


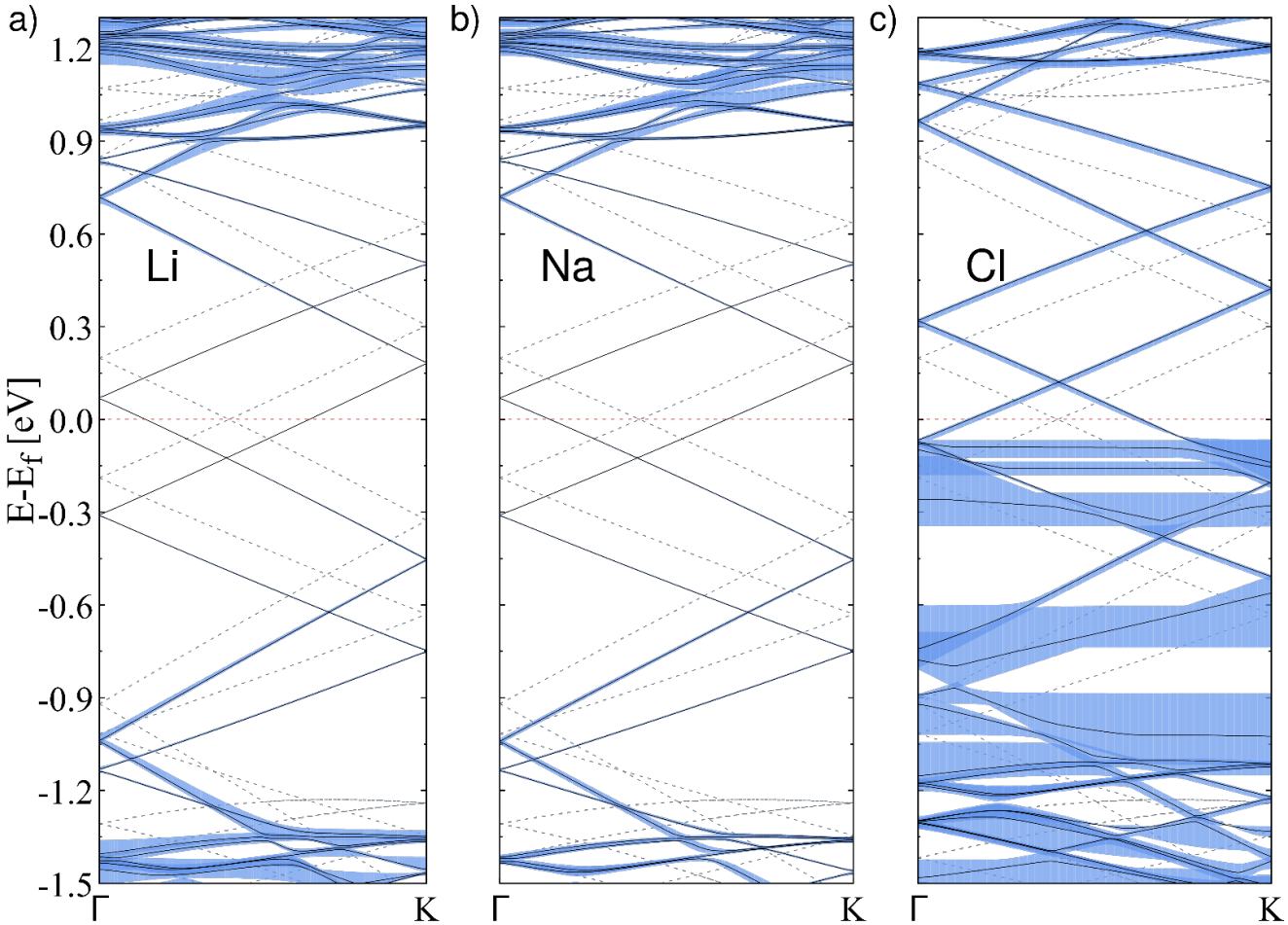


The ***band shift*** relative to the Fermi level is a consequence of the charge excess or absence on the CNT

Kirch, Almeida and Miranda
(J. Chem. Theory and Comp. 2018)

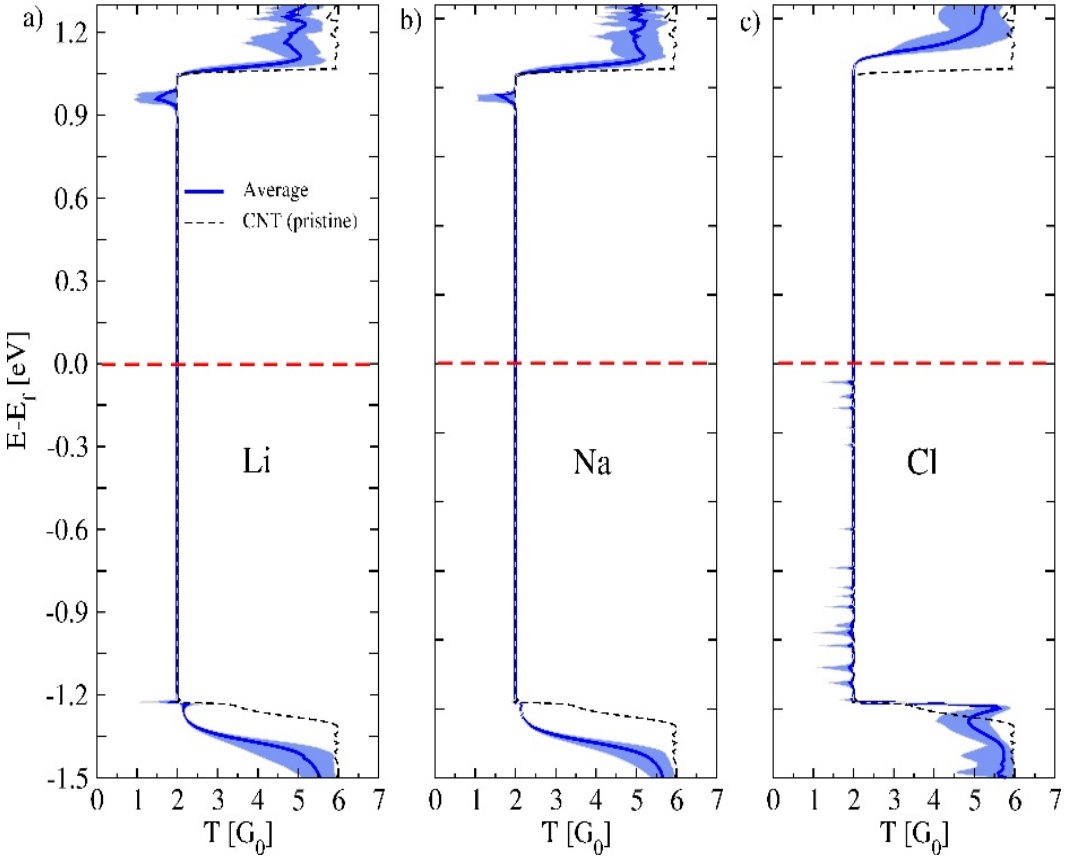
Electronic Structure

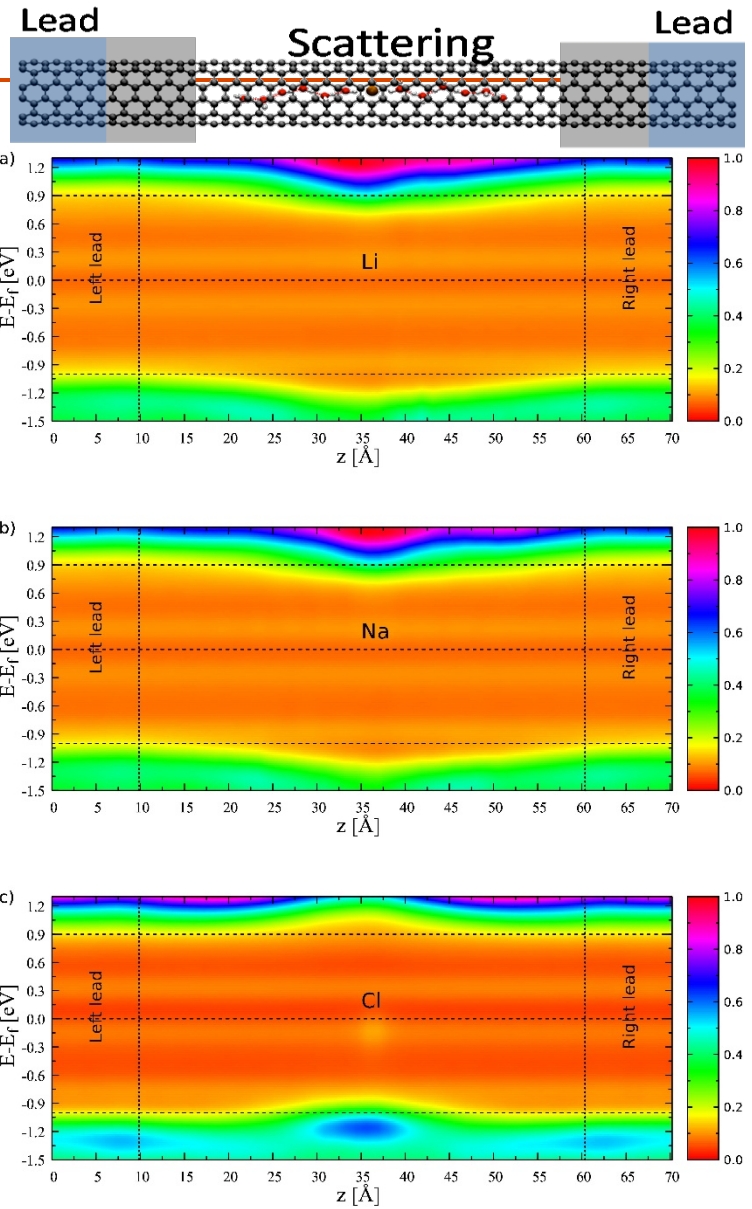




Kirch, Almeida and Miranda
(J. Chem. Theory and Comp. 2018)

Transport properties



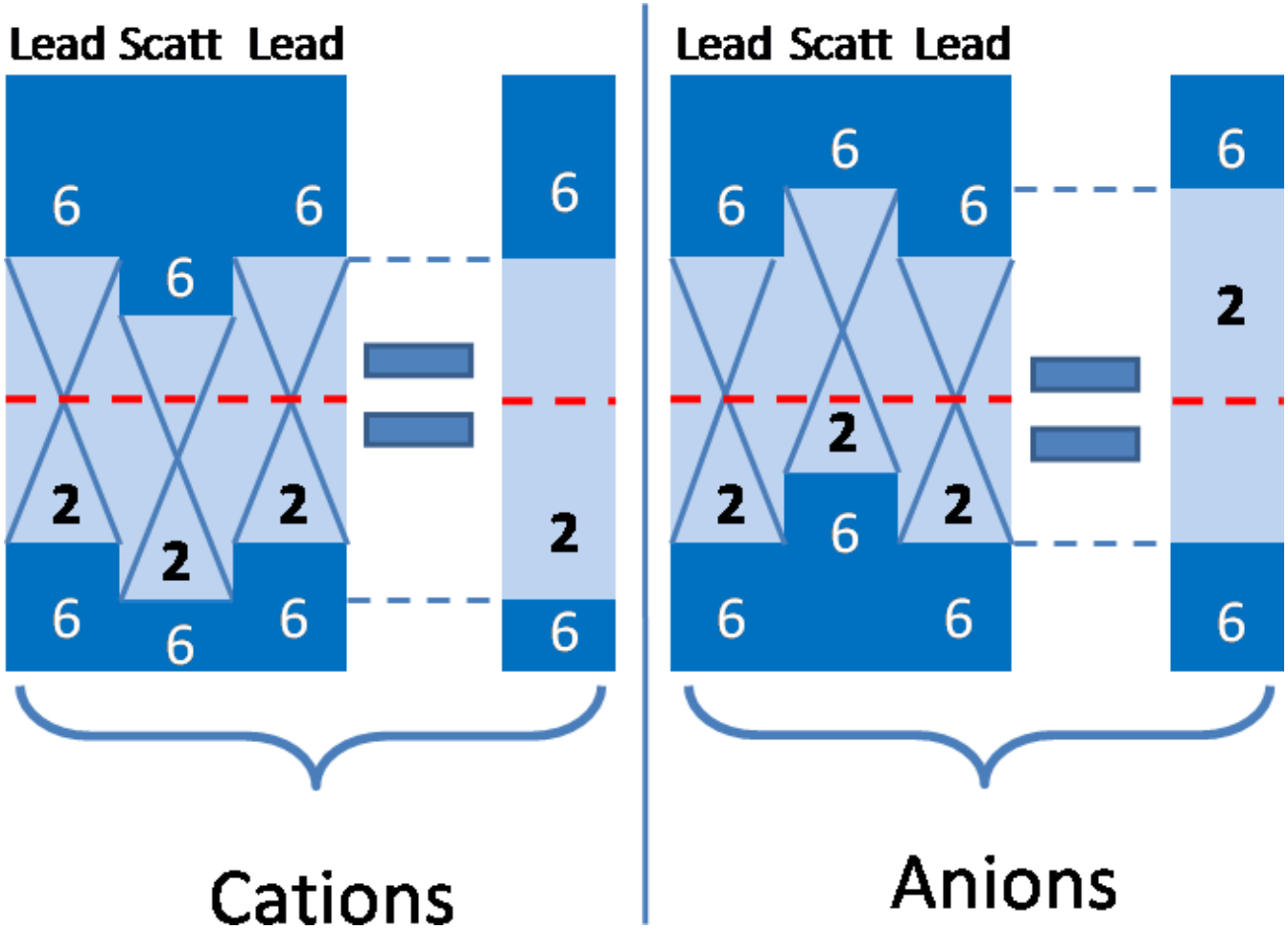


Two energy bands, $2G_0$ each spin, where $G_0 = e^2/h$. Above 1 eV from Ef, the electric conductance is higher (six channels, $6G_0$)

Kirch, Almeida and Miranda
(J. Chem. Theory and Comp. 2018)

Transport properties

Available number of conductance channels along the transport systems



# of channels is reduced (from 6 to 2) or increase (from 2 to 6).

there is a decrease in the # of channels for the anion (1.0 eV) , and for cation (-1.0 eV).

Cations and anions can be distinguished based on the transmittance

Summary

- Top-down (MD, FP and NEGF).
- Ions flow influences the CNT(6,6) electronic transport properties.
- The confinement on the CNT, favors the partially hydrated Na, Cl and Li ions to exchange charge with the nanotube.
- This leads to a change in the electronic transmittance, allowing to distinguish cations from anions.
- The top-down multiscale approach can be applied on the design of novel nanofluidic devices and sensors.

CO2 MINERALIZATION IN GEOLOGICALLY COMMON ROCKS FOR CARBON STORAGE

In collaboration with: Jihui Jia, Yunfeng Liang, Takeshi Tsuji, Yoshihiro Masuda, and Toshifumi Matsuoka

The Journal of Physical Chemistry C, 2019; 123 (8): 4938
DOI: 10.1021/acs.jpcc.8b12089

Introduction

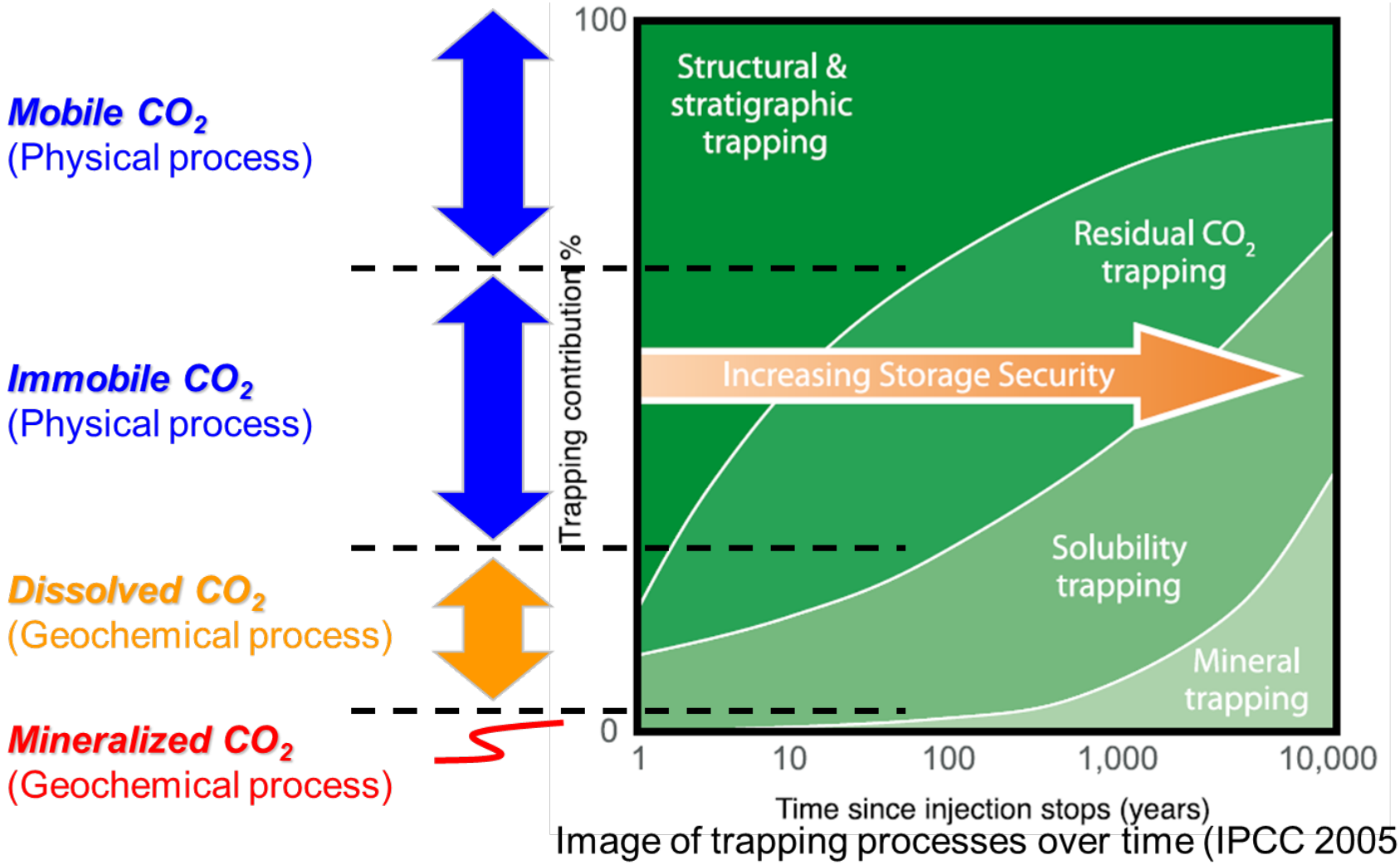


Image of trapping processes over time (IPCC 2005)

CO_2 Mineralization takes hundred years?

Motivation

Science

AAAS

Rapid carbon mineralization for permanent disposal of anthropogenic carbon dioxide emissions

Juerg M. Matter, Martin Stute, Sandra Ó. Snæbjörnsdottir, Eric H. Oelkers, Sigurdur R. Gislason, Edda S. Aradottir, Bergur Sigfusson, Ingvi Gunnarsson, Holmfridur Sigurdardottir, Einar Gunnlaugsson, Gudni Axelsson, Helgi A. Alfredsson, Domenik Wolff-Boenisch, Kiflom Mesfin, Diana Fernandez de la Reguera Taya, Jennifer Hall, Knud Dideriksen and Wallace S. Broecker (June 9, 2016)
Science **352** (6291), 1312-1314. [doi: 10.1126/science.aad8132]

Editor's Summary

Inject, baby, inject!

Atmospheric CO_2 can be sequestered by injecting it into basaltic rocks, providing a potentially valuable way to undo some of the damage done by fossil fuel burning. Matter *et al.* injected CO_2 into wells in Iceland that pass through basaltic lavas and hyaloclastites at depths between 400 and 800 m. Most of the injected CO_2 was mineralized in less than 2 years. Carbonate minerals are stable, so this approach should avoid the risk of carbon leakage.

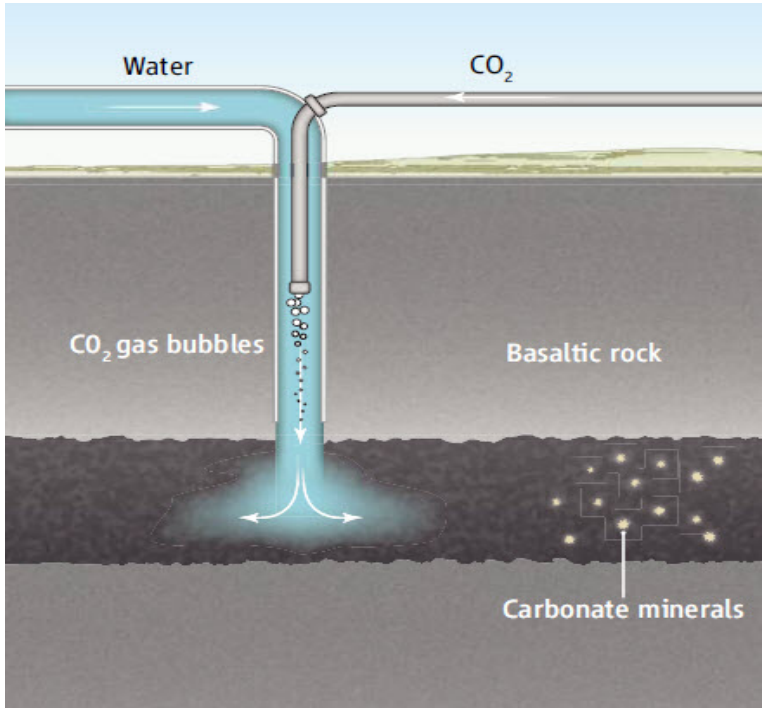
Science, this issue p. 1312

Why most of the injected CO_2 was mineralized in less than 2 years?

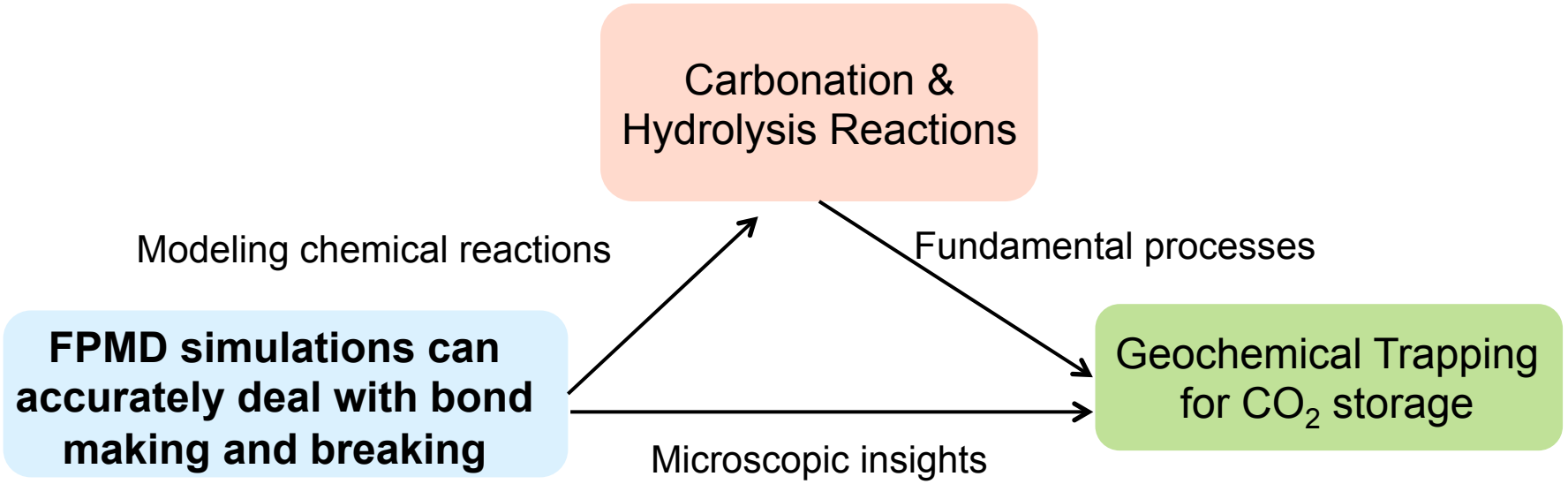
CO_2 mineralization

The proposed reactive parthways are:

- CO_2 firstly interacts with formation water, and this process can generate carbonic acid (H_2CO_3)
- This will dissociate into carbonate ion (CO_3^{2-}) or bicarbonate ion (HCO_3^-) and hydrogen ion (H^+).
- At given concentration of divalent cations (such as Ca^{2+}, Mg^{2+}, Fe^{2+}), carbonate minerals will precipitate in the pore space.
- Hundreds to thousands of years
  Iceland: 2 years !!!



Carbonation and Hydrolysis Reactions on Cleaved Quartz (001) Surface

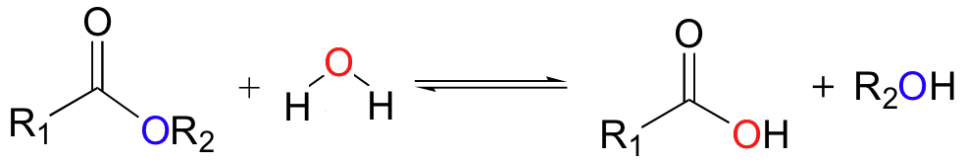


Carbonation

$$CO_2+H_2O=H_2CO_3=HCO_3^- +H^+=CO_3^{2-}$$

Source of Mg/Ca + $H_2CO_3 \rightarrow MgCO_3/CaCO_3$

Hydrolysis



Questions:

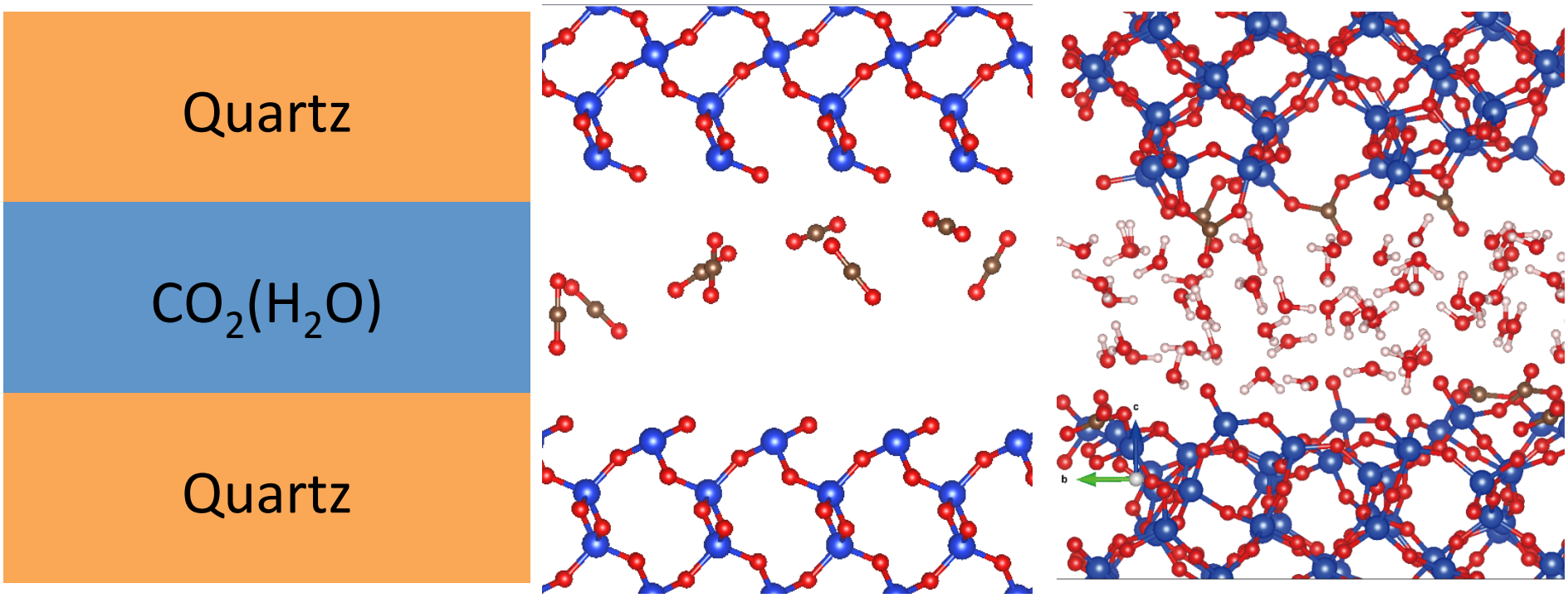
- What happened if CO_2 combines with quartz/basalt minerals?
- How will hydrolysis reaction influence the carbonation process?

Ab Initio MD - SiO2/CO2/H2O

Newly Cleaved Surface

1.Carbonation
8 CO_2 and **72 SiO_2**

2.Hydrolysis
7CO_2, **72 SiO_2** and **48 H_2O**

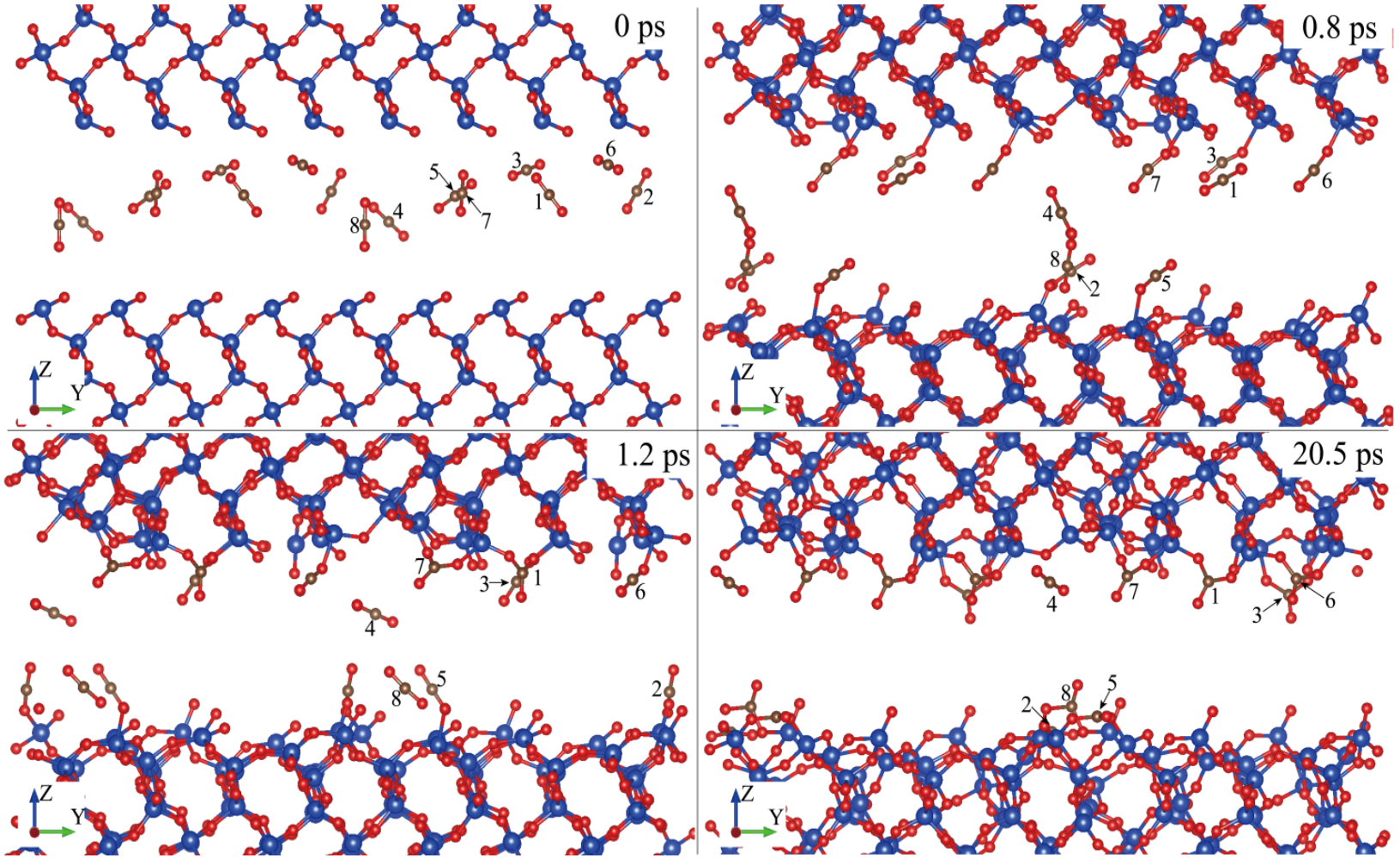


Blue: silicon, red: oxygen, Brown: carbon

Lattice Parameters: a=14.7 Å, b=17.0 Å, c=18.9 Å, $\alpha=\beta=\gamma=90°$

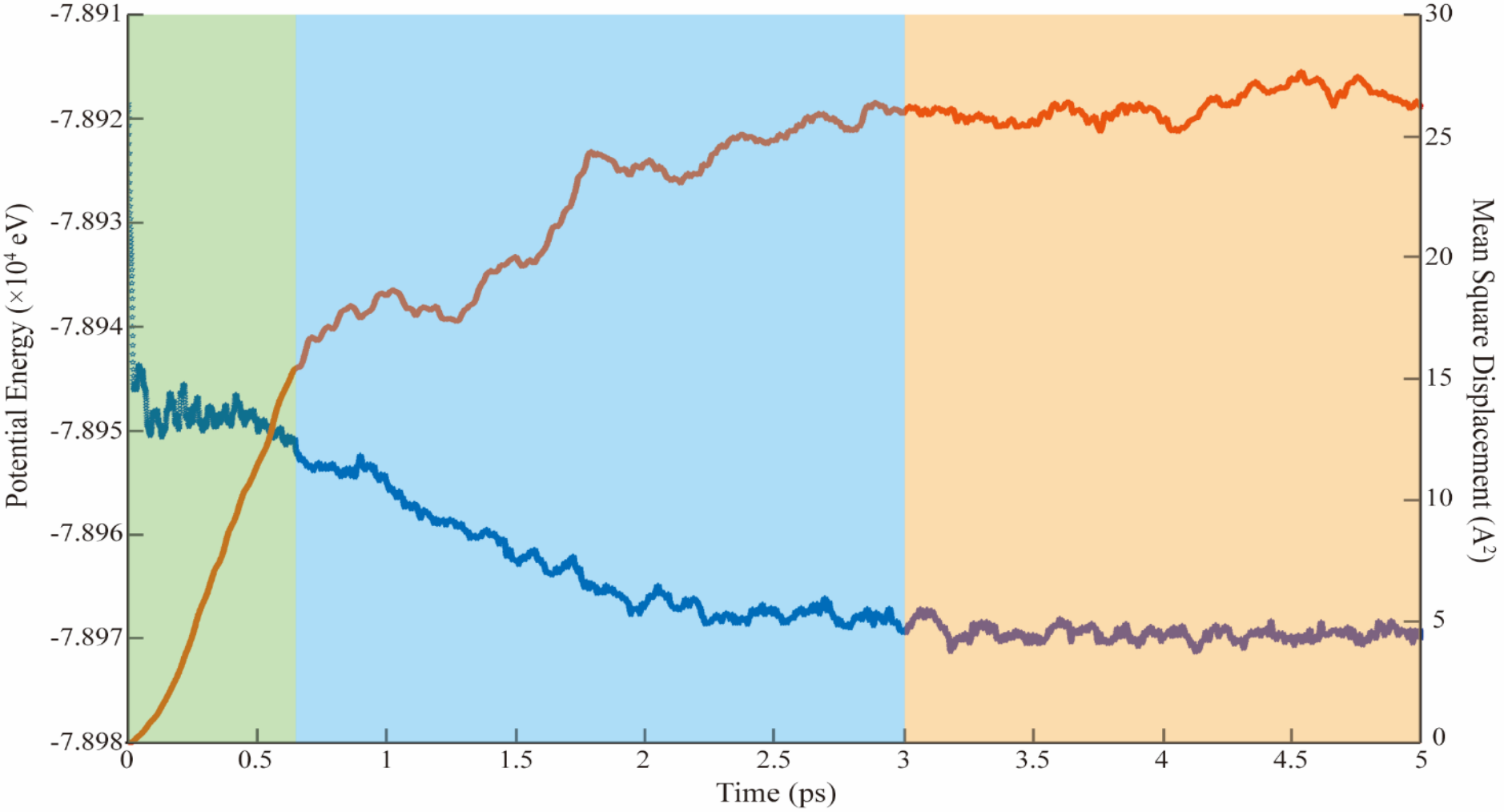
Calculated by CP2K package, PBE functional, Van der Waals corrections (Grimme's DFT-D3).
NVT ensemble; Temperature: 323 K; Time step: 0.5 fs; Cutoff value: 340Ry; PBC

AIMD – CO_2 @ quartz (001) surface

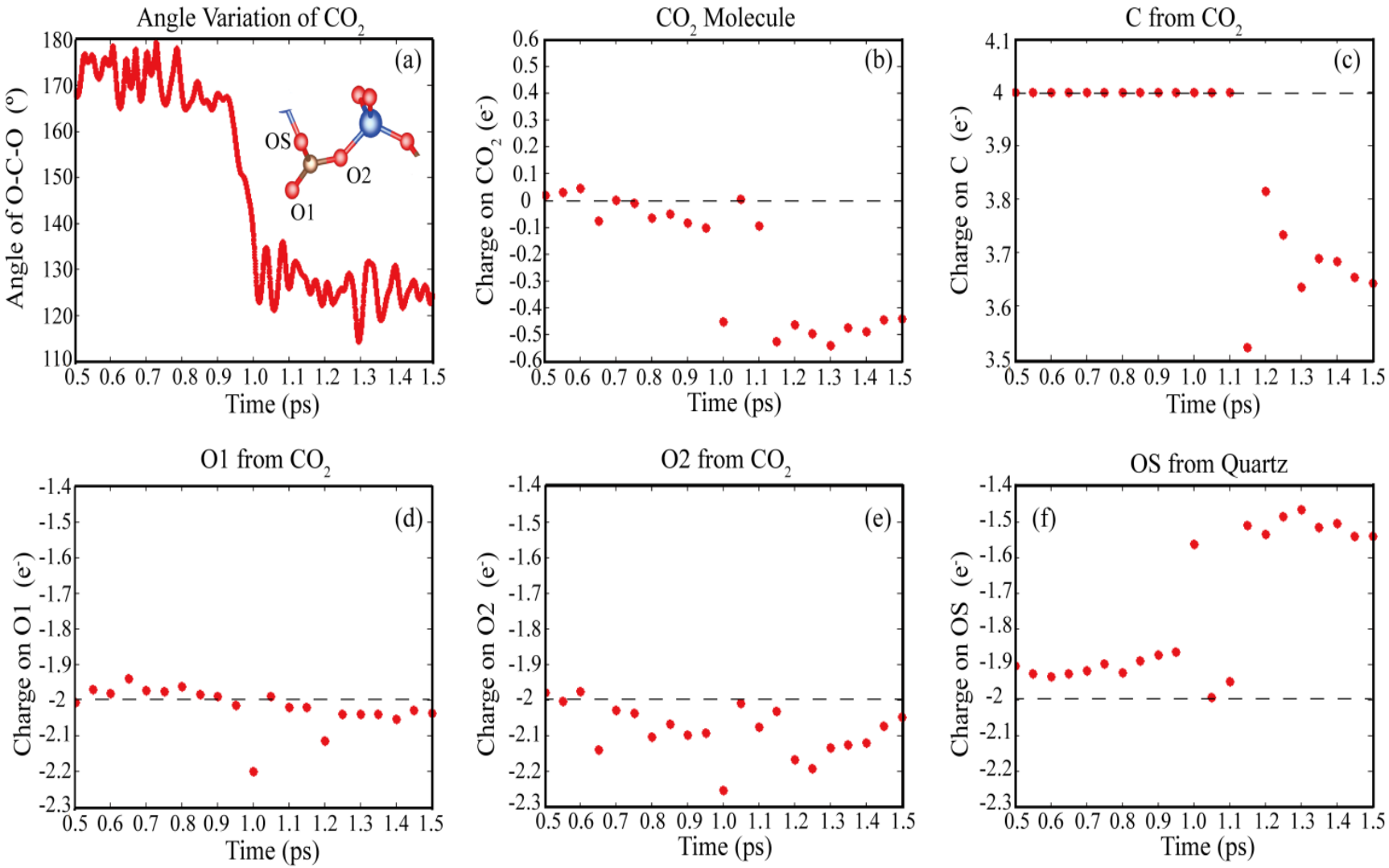


Energy and diffusion evolution

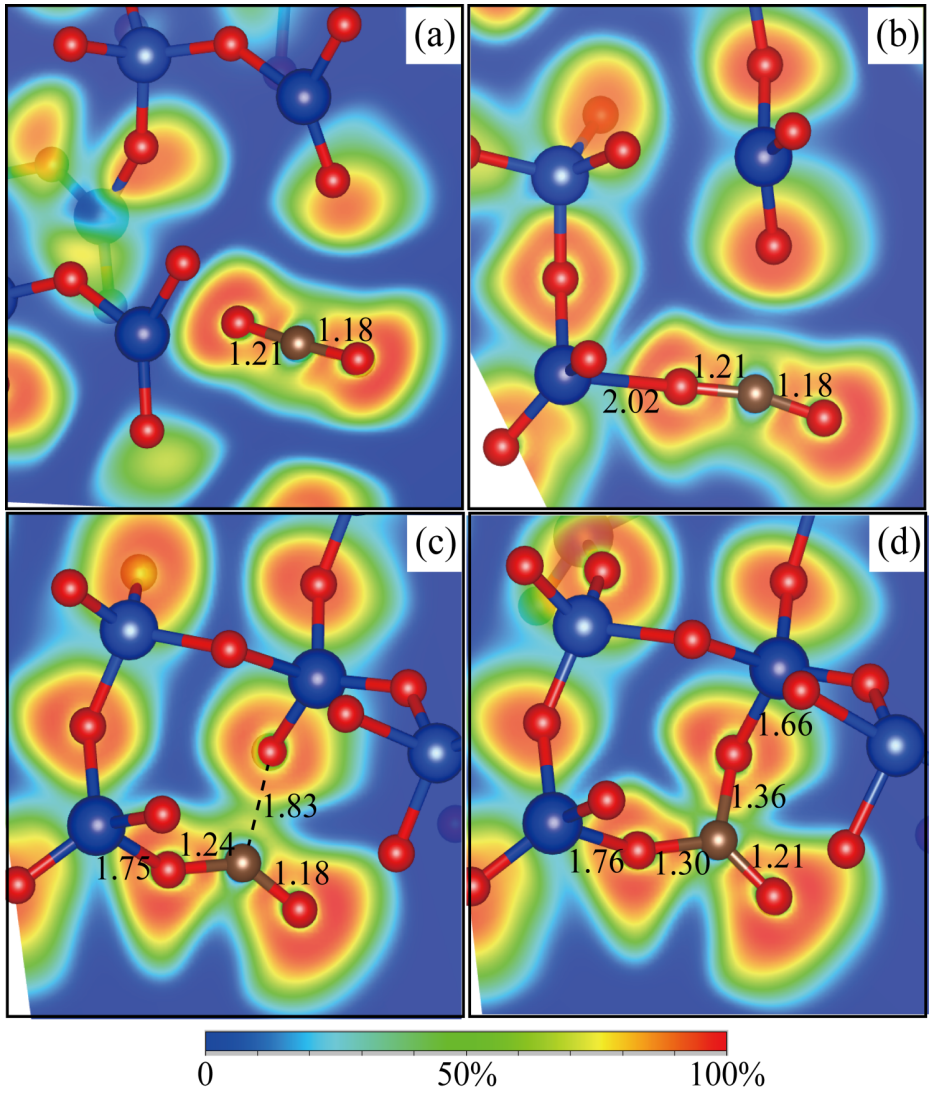
(1) free diffusion stage, (2) chemical reaction stage and (3) chemisorption stage.



Variation of atomic charges during carbonation process



Transforming from linear CO_2 molecule into planar CO_3 configuration (ELF)



Distribution of Electron Localization Function regarding transformation of CO_2 molecule into CO_3-like configuration.

Blue ball: Silicon atom (Si)

Red ball: Oxygen atom (O)

Brown ball: Carbon atom (C)

Length of C–O bond

For CO_2 molecule:

Experimental results: ~ 1.16 Å

(Glocker et al. J. Phys. Chem. 1958)

This study: ~ 1.18 Å *(Panel a)*

For CO_3^{2-} ion:

Experimental results: ~ 1.31 Å

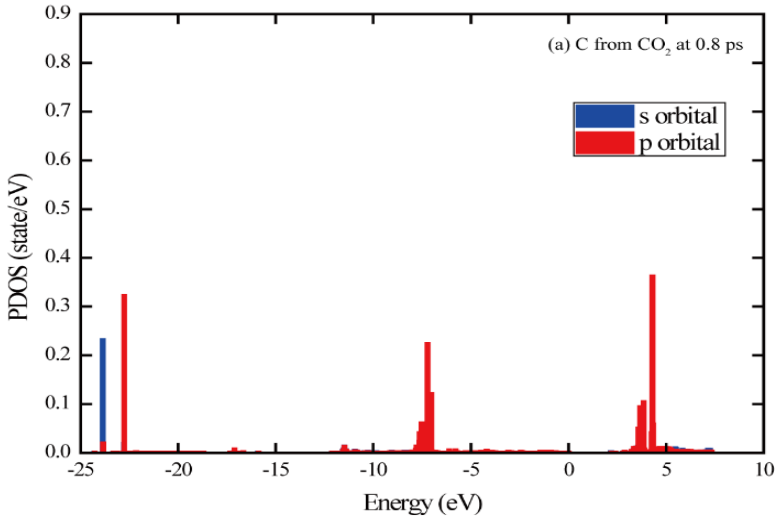
(Elliott et al. J. Am. Chem. Soc. 1937)

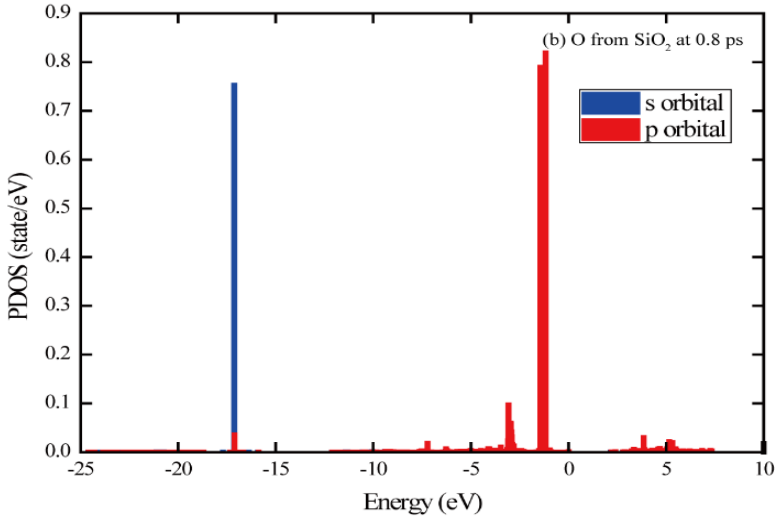
This study: ~ 1.29 Å

(average value from Panel d)

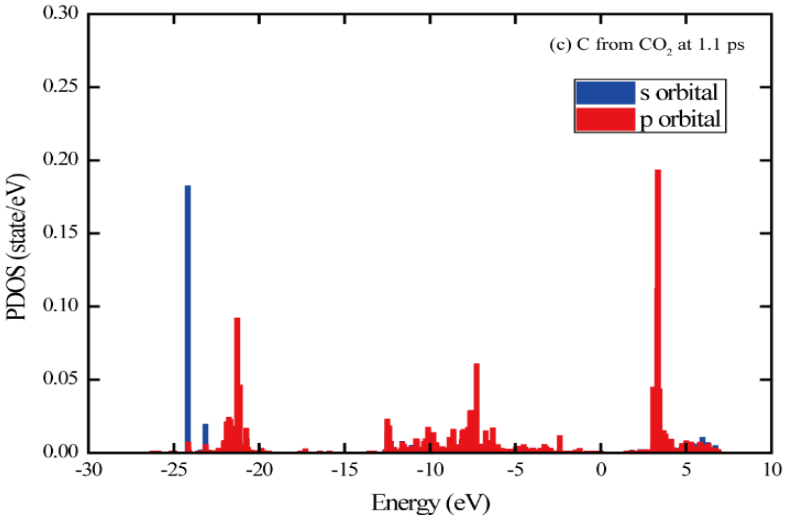
PDOS of relevant atoms in prior to and after chemical bonding.

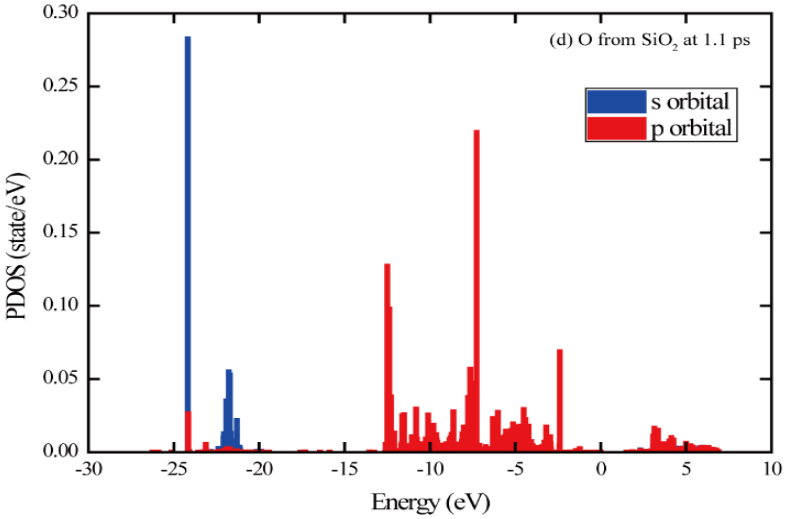
Before formation of C-O bond



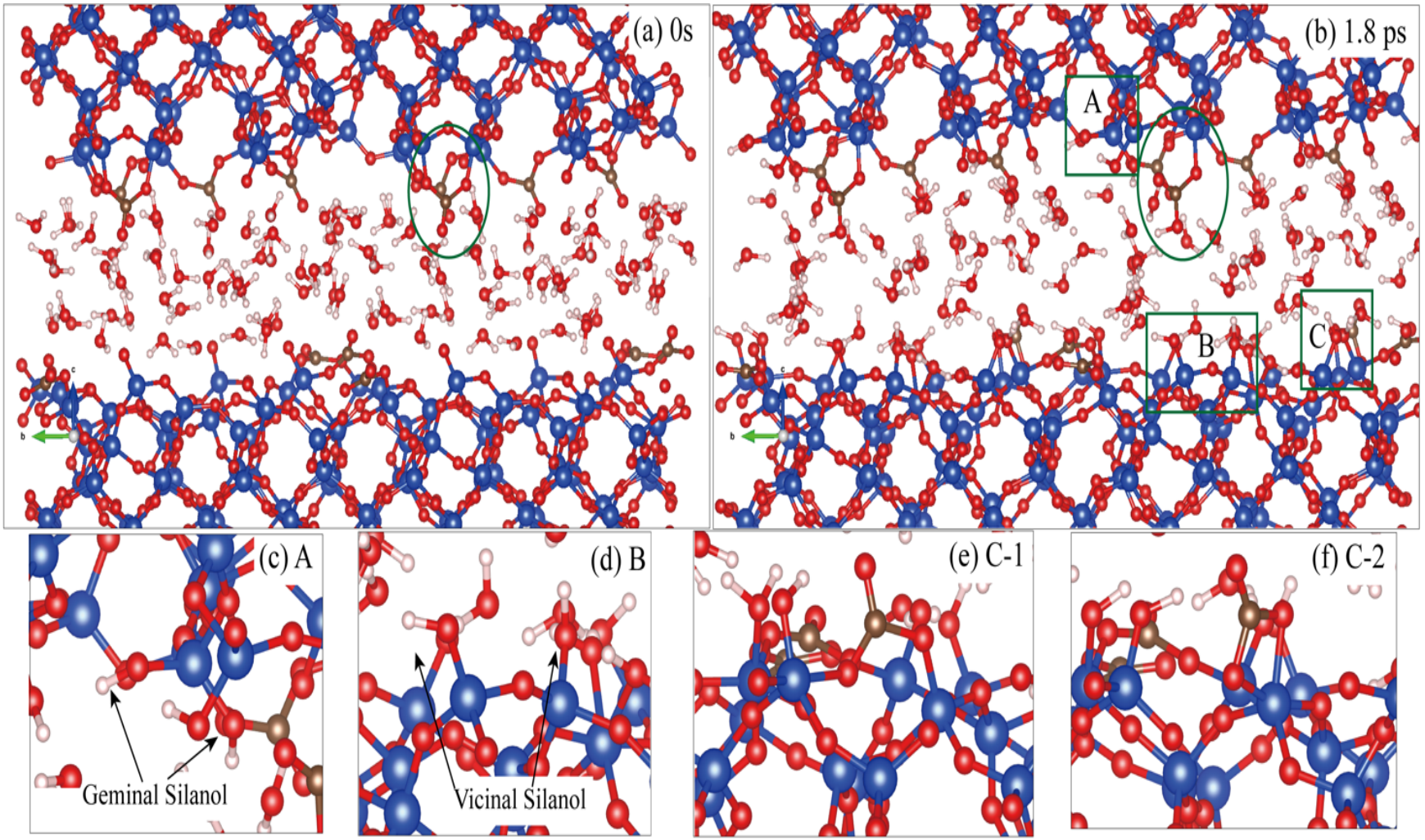


After formation of C-O bond

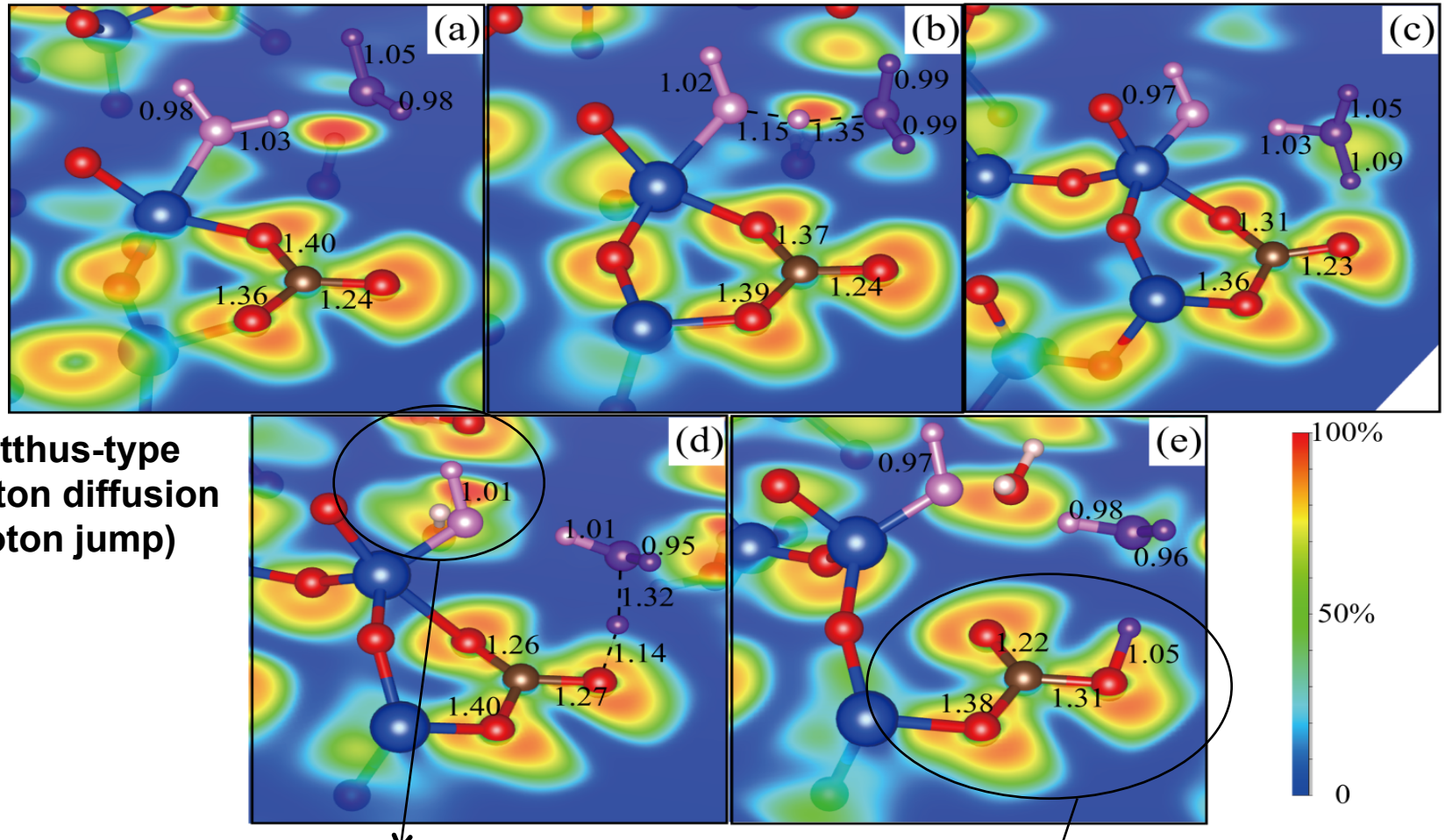




Hydrolysis reaction between carbonated SiO_2 surface (with CO_3 configuration) and H_2O.



Hydrolysis reaction with the formation process of bicarbonate species (HCO_3)



Grotthus-type proton diffusion (proton jump)

$>Si^{+} + OH^{-} \rightarrow >SiOH$

$CO_3^{2-} + H^{+} \rightarrow HCO_3^{-}$

Hydroxyl attached on the undercoordinated silicon while proton attached on the CO3 structure.

Summary

Answers to the Questions:

What happened if CO_2 combines with newly cleaved quartz surfaces ?

- ✓ CO_3-like configurations form, indicating carbonate ions are not necessarily from dissociation of H_2CO_3.

How will hydrolysis reaction influence the carbonation process?

- ✓ Hydrolysis reaction can alter CO_3-like configurations, and transform CO_3 to HCO_3.

In addition

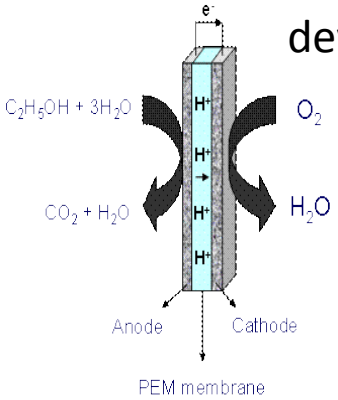
- ✓ CO_2 *mineralization* can be accelerated by *the reactive under-coordinated Si and O atoms* located on the mineral surface, which can exist under aqueous environment, and they are normally protected *by hydrogen bonding or cations.* (For example, Ca^{2+} and Na^{+} in basalt minerals).

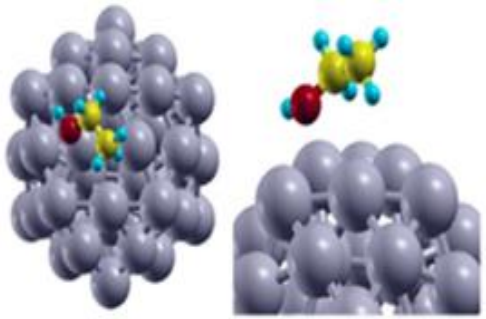
- ✓ Future work should be expanded to basalt minerals.

Nanostructured materials from **Dirty** to Cleaner to **Clean** energy applications

Materials for energy storage and conversion

Wetability in electrochemical devices

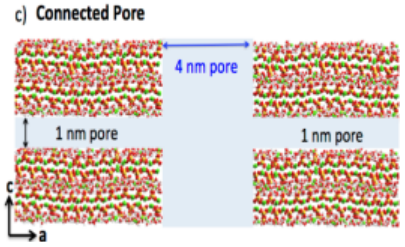


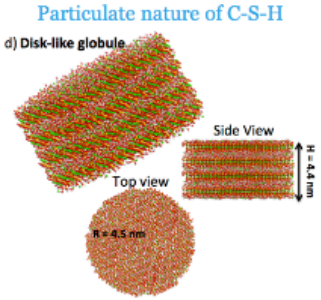


Direct alcohols fuel cells

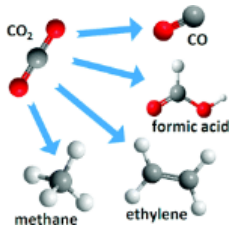
Ethanol catalysis @ NPs

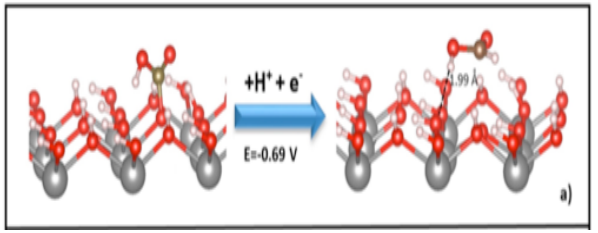
Water and CO_2 in Cement



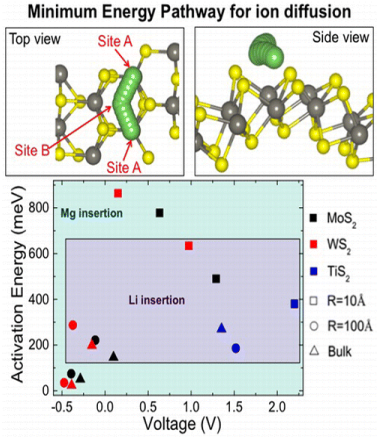


Conversion of CO_2 into feedstock

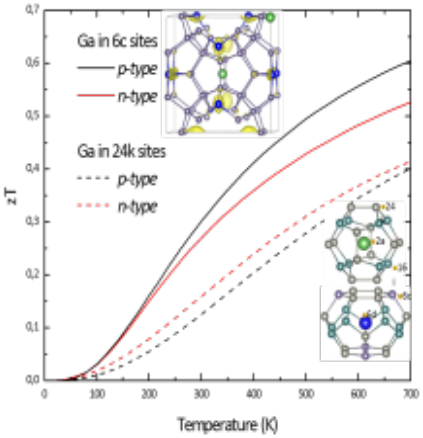




Batteries

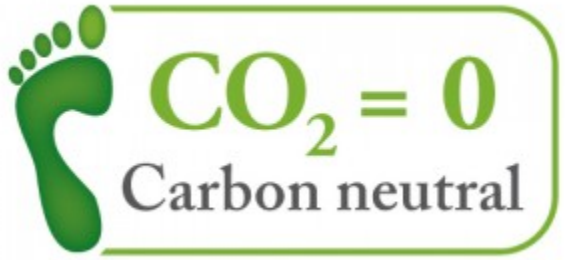


Thermoelectrics



Towards a zero carbon footprint …

Enhanced Oil Recovery
Selective separate CH_4 and CO_2 in Natural Gas
Geochemical trapping of CO_2
Conversion of CO_2 to chemicals



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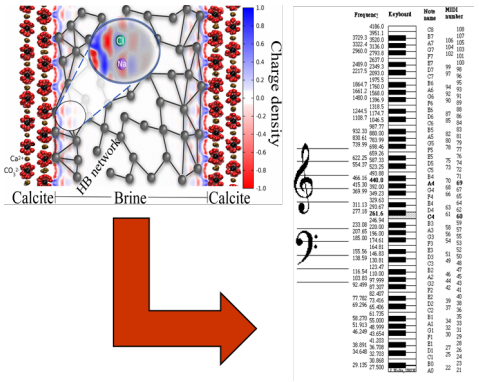
Nanopetro

Materials Physics, Nanotechnology, Immersive Technologies

Contact: Prof. Caetano R. Miranda - *crmiranda@usp.br*



Nanotechnology applied to the Oil & Gas Industry, Renewable Energy, Infrastructure and Food

Multiscale molecular simulations

Materials under extreme conditions and nanofluidics

Perceptual Physics: immersive experiences through Virtual Reality and Sonification