CARMEN
Caractérisation des matériaux pour les énergies nouvelles
Laboratoire Commun de Recherche

CNRS
ENS de Lyon
IFP Energies nouvelles
Sorbonne Université
Université Claude Bernard Lyon 1
Université de Strasbourg

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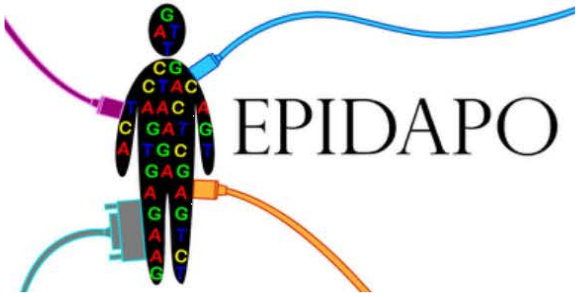
The Scienc'Innov Workshops

CARMEN ■ EVOLUTION

BRIDGING LENGTH and TIME SCALES
in the modeling of complex porous materials

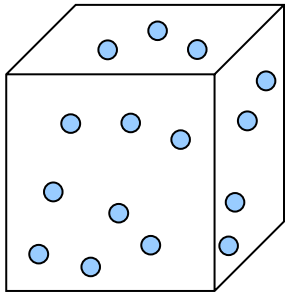
Roland Pellenq and many other colleagues

cnrs
advancing the frontiers



THE GEORGE WASHINGTON UNIVERSITY
1821

Monte-Carlo vs Molecular Dynamics



N ~ 100 – 100,000
Periodic boundaries
Prescribe inter / intra particle potential

Monte Carlo

Specify *ensemble*

↓

Generate random moves

↓

Sample with $P \alpha \exp(- U/kT)$

↓

Take averages

↓

Obtain equilibrium properties

$\mathbf{F} = -\mathbf{grad}\,[\mathbf{U}]$

Molecular Dynamics

Specify *ensemble*

↓

Solve Newton's equations $F_i = m_i a_i$

↓

Calculate $r_i(t)$, $v_i(t)$

↓

Take averages

↓

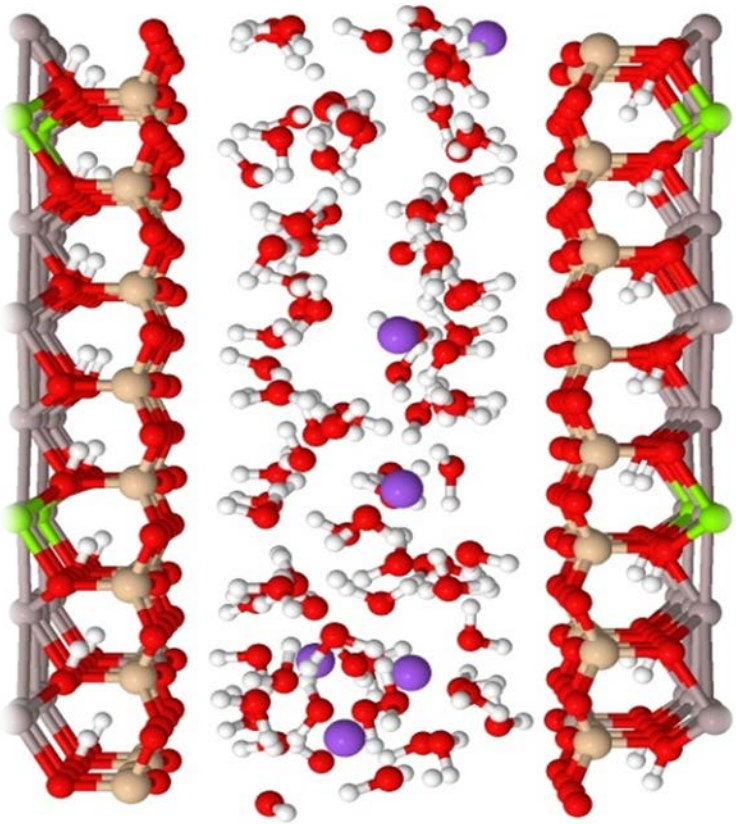
Obtain equilibrium **and** non-equi. props

THE POTENTIAL OF MEAN FORCE: THE TOOL TO BRIDGE LENGTH SCALE…

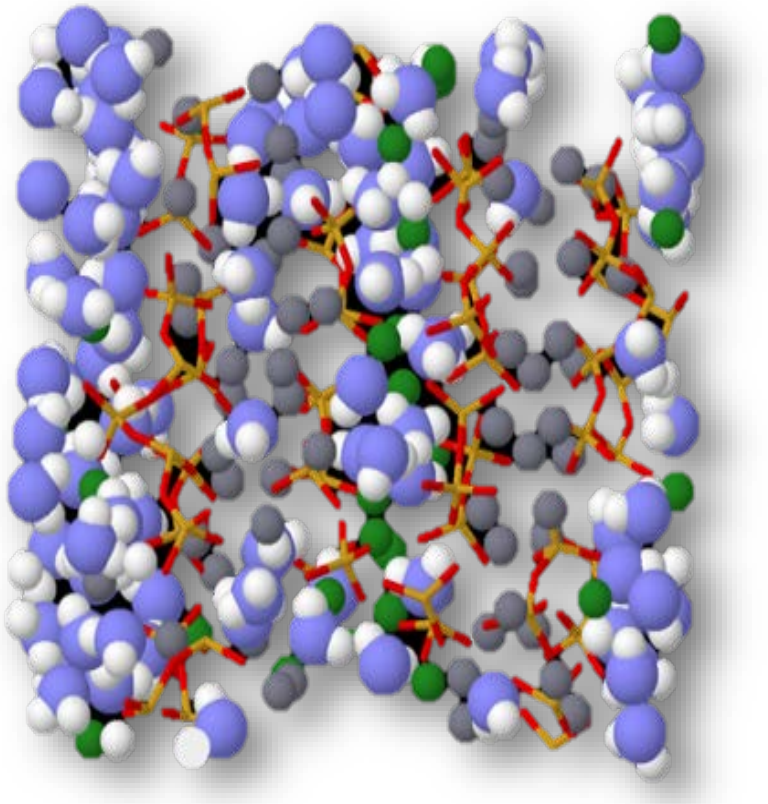
➔ **Application to the modeling of cement and clay…**

Cement, clays … all hydrated layered materials at the nanoscale

with charged layers, ions in between layers and water molecules



Clay



Cement hydrate (C-S-H)

1 – Cohesion: from the DLVO theory to atomistic simulations

➔ get the energy fast and right

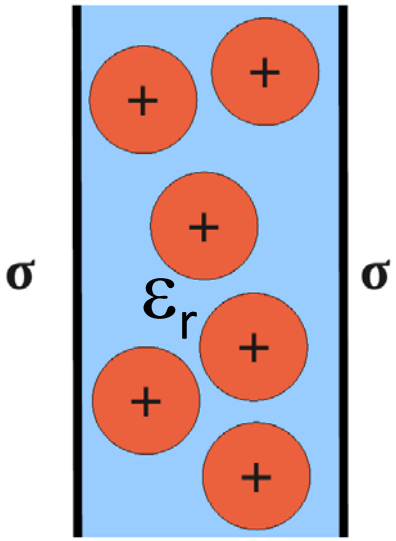
From mean-field ideas (DLVO) to atomistic scale simulations

Electrostatic Interactions between colloids always repulsive (mean-field Poisson-Boltzmann eq.)

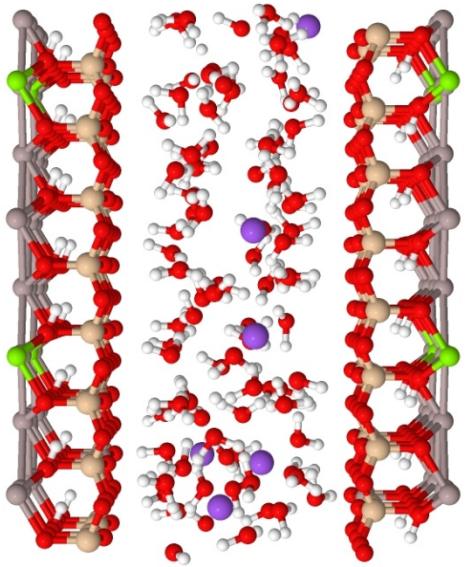
$$P(D) = k_B T\left(\rho_s(D) - \rho_s(\infty)\right)$$

DLVO (point charges, no thermal fluctuations)

(ε_r = dielectric cte of the **bulk** solvent)



Primitive Model

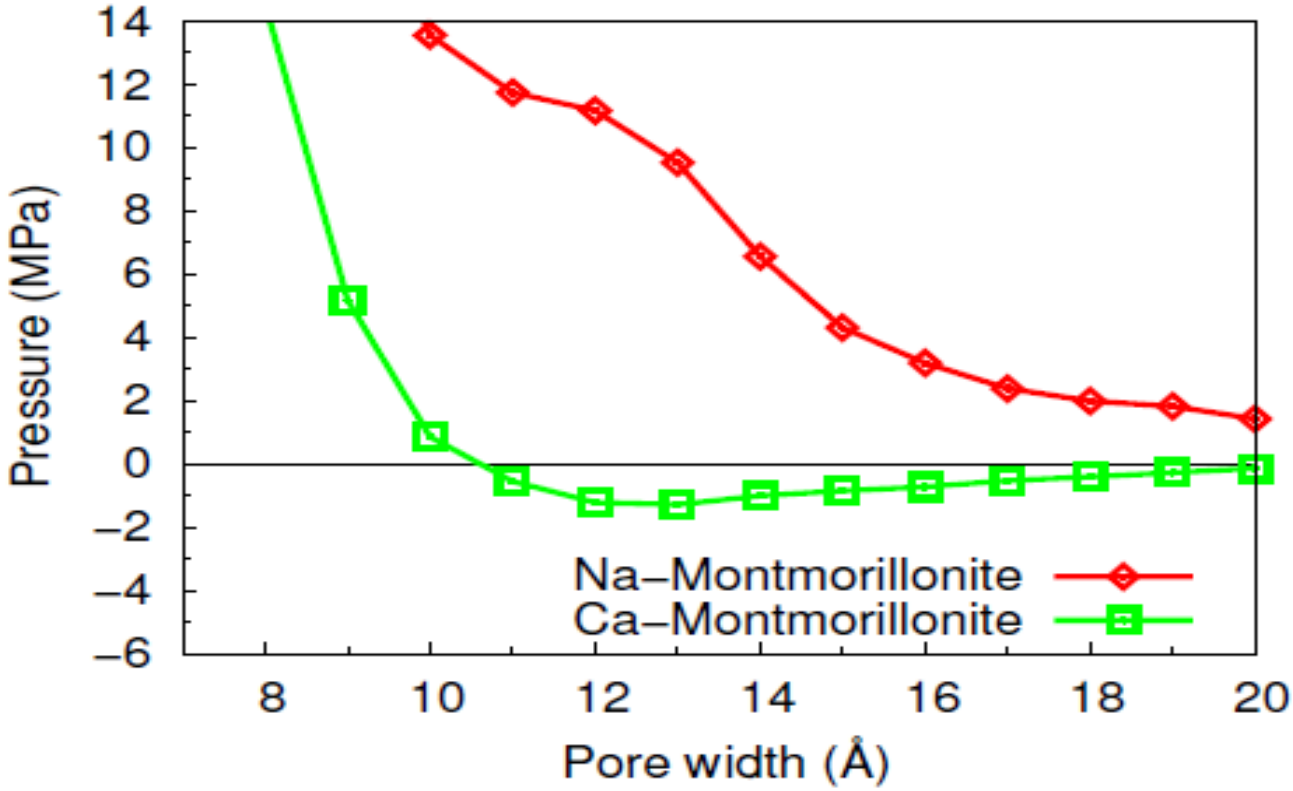


Full atomistic Model

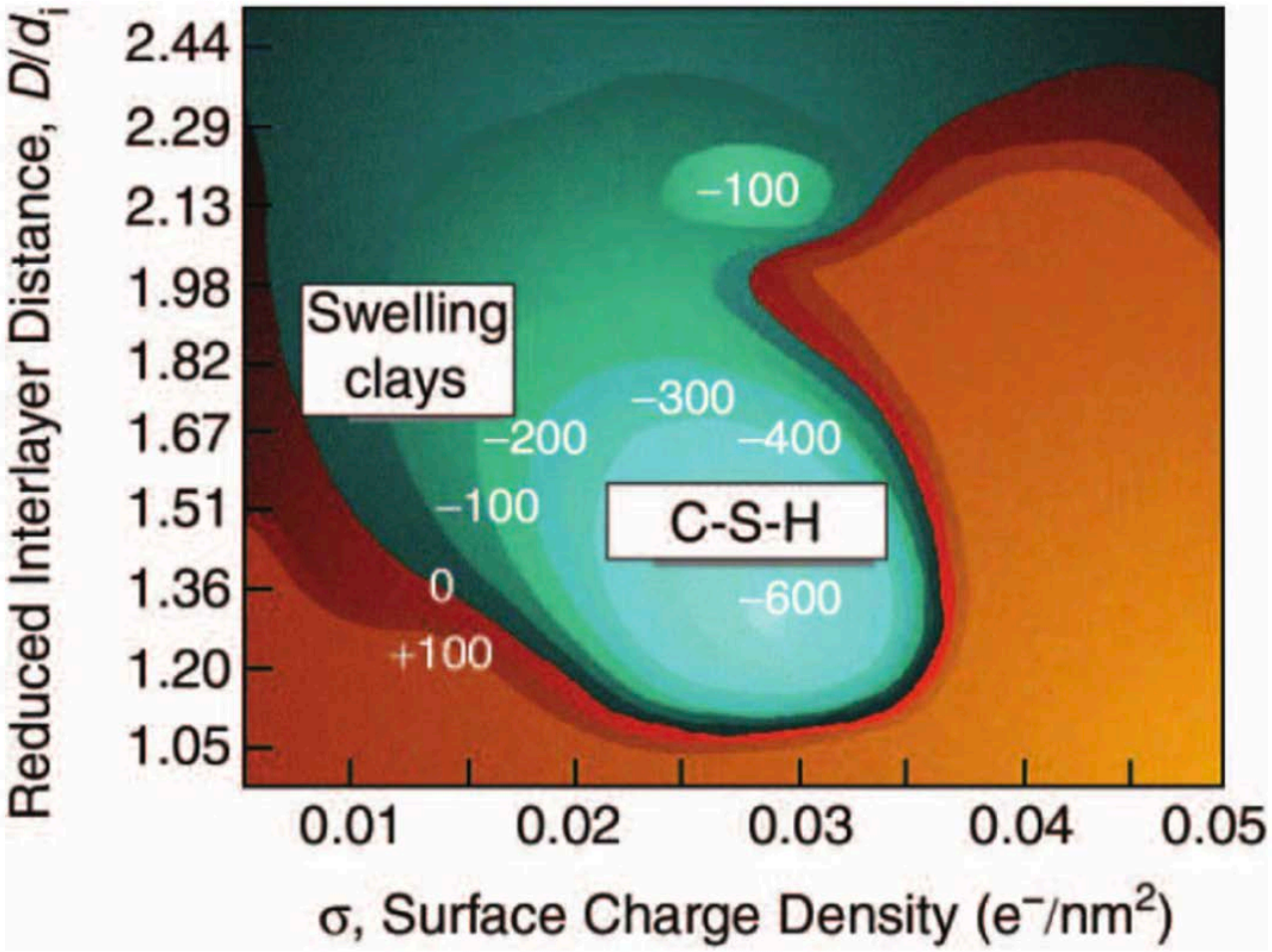
Increasing modeling effort

From DLVO to the Primitive Model

- The primitive model predicts attraction (negative pressure) for divalent ions / clay systems due to so-called ionic correlation forces



Ionic Correlation Forces (ICF)
as described in the Primitive Model with implicit solvent



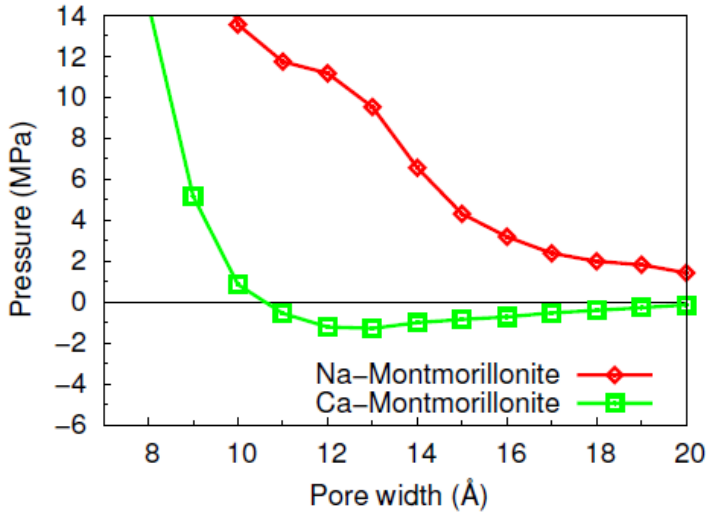
Pellenq et al, J Phys Chem 1997

Limits of the primitive model

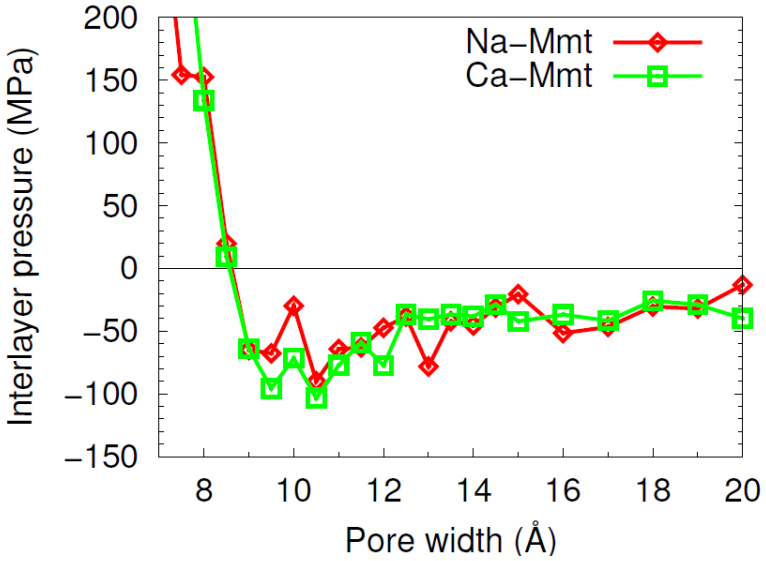
- Solvent : dielectric continuum with dielectric constant equal to that of the bulk (ε=80 for water at 300K).
- Ion size = fully hydrated ion as in the bulk
- Structureless colloids with uniform surface charge density.

There are qualitive and quantitatite differences between the PM and the atomistic approaches

Primitive model



Atomistic Model

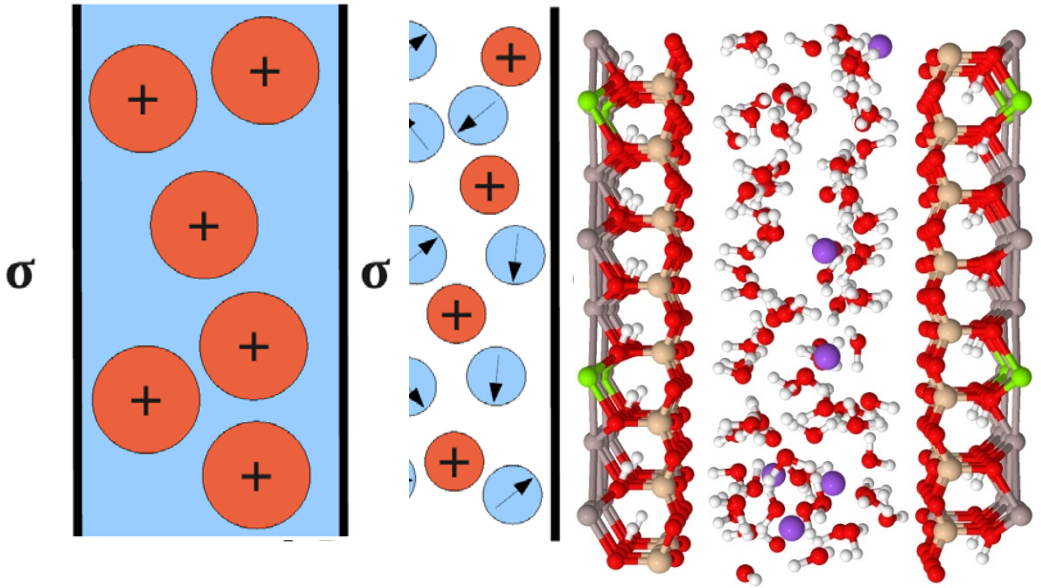


Introducing the solvent in the primitive model

Electrostatic Interactions between colloids always repulsive (Poisson-Boltzmann eq.)

$$P(D) = k_B T\left(\rho_s(D) - \rho_s(\infty)\right)$$

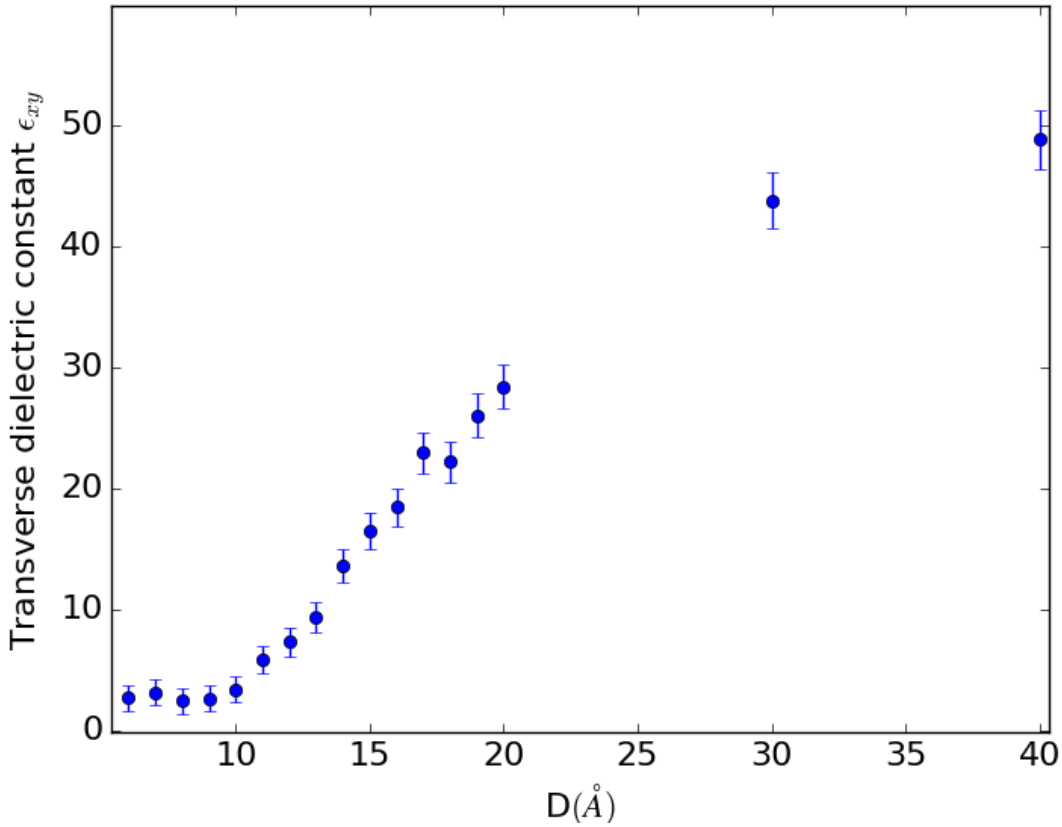
DLVO

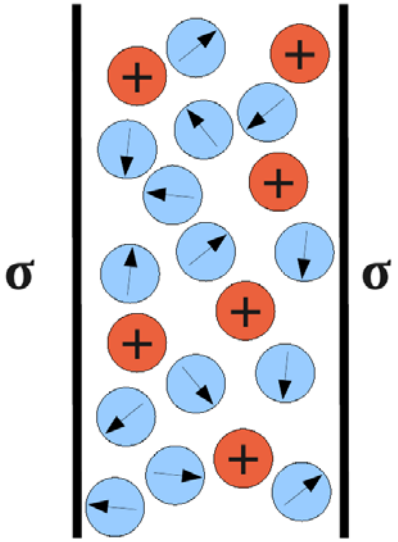


Primitive Model **Explicit Solvent Model** **Atomistic Model**

Introducing the solvent in the primitive model

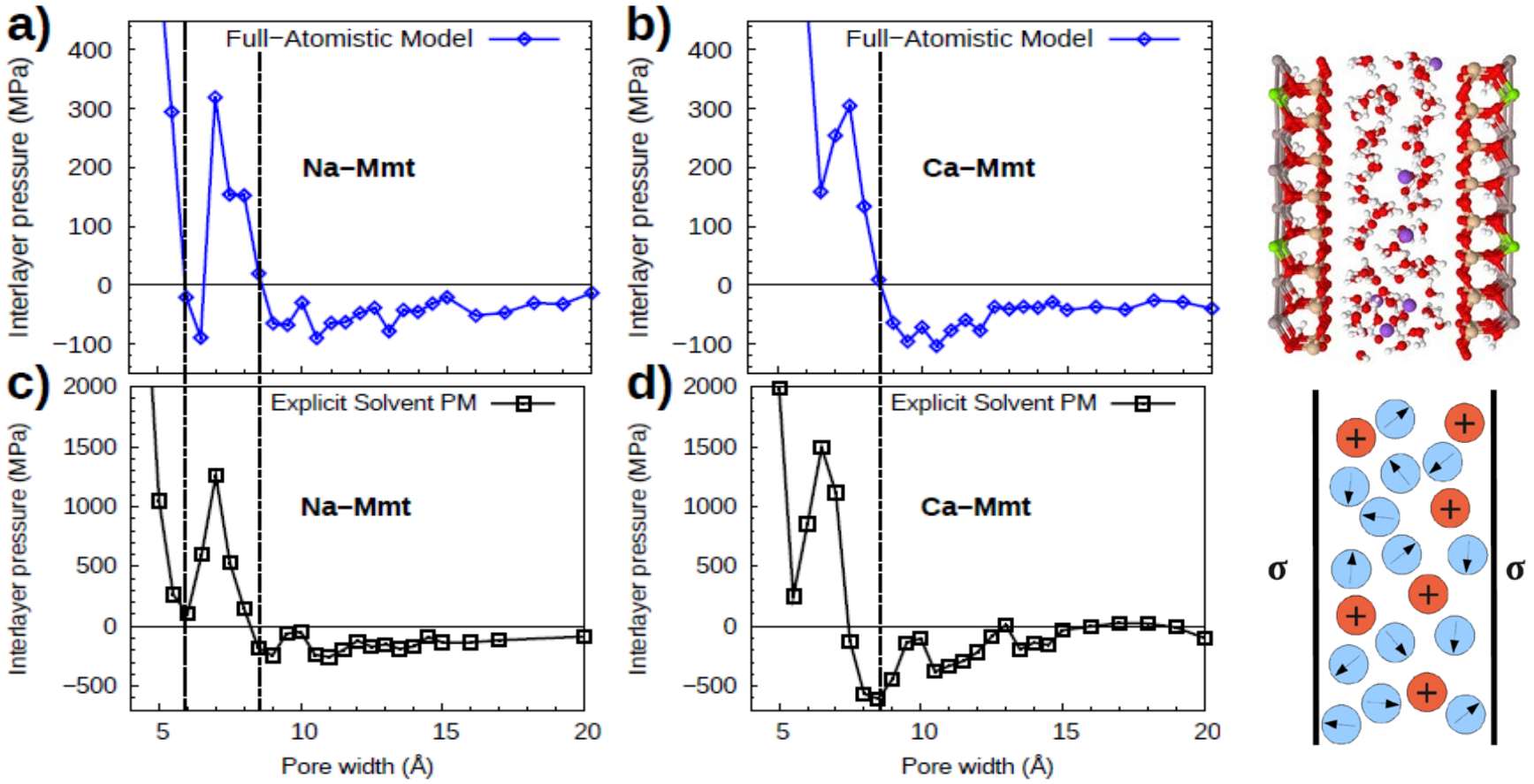
$$\varepsilon_{xy} = 1 + \frac{1}{\varepsilon_0 V k_B T} \frac{< M_x^2 + M_y^2 >}{2}$$





Introducing the solvent in the primitive model

- Na - Montmorillonite
- Ca - Montmorillonite



(B. Carrier et al, Europ. J. Phys, 2017, Goyal, Science Adv., 2021)

2 - « Bridging the GAP »

- Going from nano (atomistic) to meso
  using the PMF trick (free energy function)

PMF from the Free energy perturbation method:

$$\Delta G(r_i \rightarrow r_{i\pm1}) = -\frac{1}{\beta} ln \left[\frac{\langle exp(-0.5\beta \Delta U_{i,i+1}) \rangle_i}{\langle exp(-0.5\beta \Delta U_{i+1,i}) \rangle_{i+1}} \right] \quad \beta = (k_B\, T)^{-1}$$

$$\Delta U = U(r_{i\pm1}) - U(r_i)$$

Note: Changes must be small.

Two parallel charged clay (or cement) infinite plates were put into an electroneutral simulation box containing ions and water molecules. The unperturbed distances between the particles were set to a preselected series of values di.

The free energy difference between the adjacent states with separation di and di+1 were calculated as ensemble averages of potential energy difference brought about by the small perturbation of δ = di±1 − di.

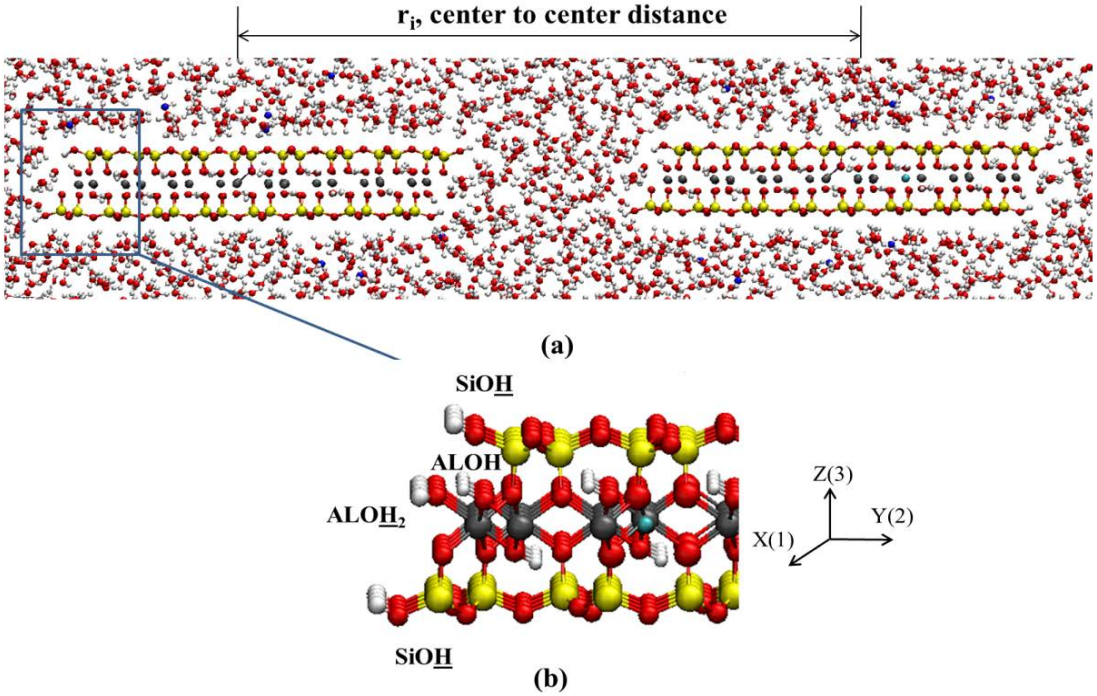
One can get the free energy from the integration of the pressure vs distance curve

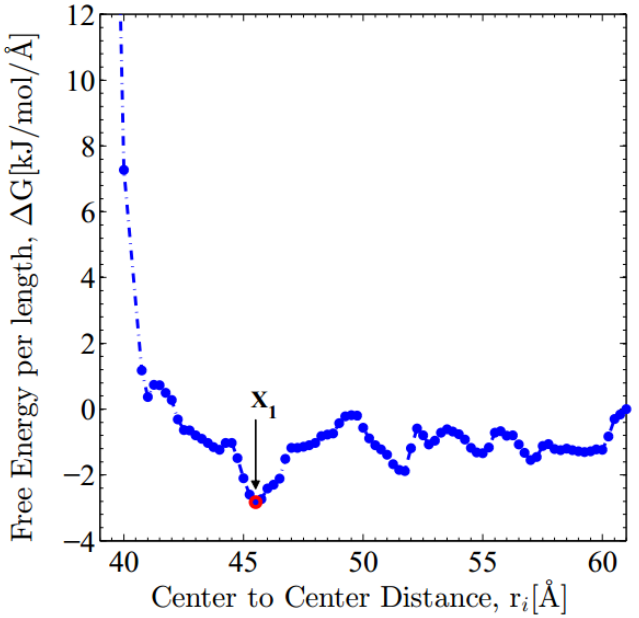
$$P_z = -\frac{1}{A}\frac{\partial G}{\partial z} \text{ or } G = -\int A P_z \mathrm{d}z$$

(D. Ebrahimi et al, J. chem. Phys, 2014)

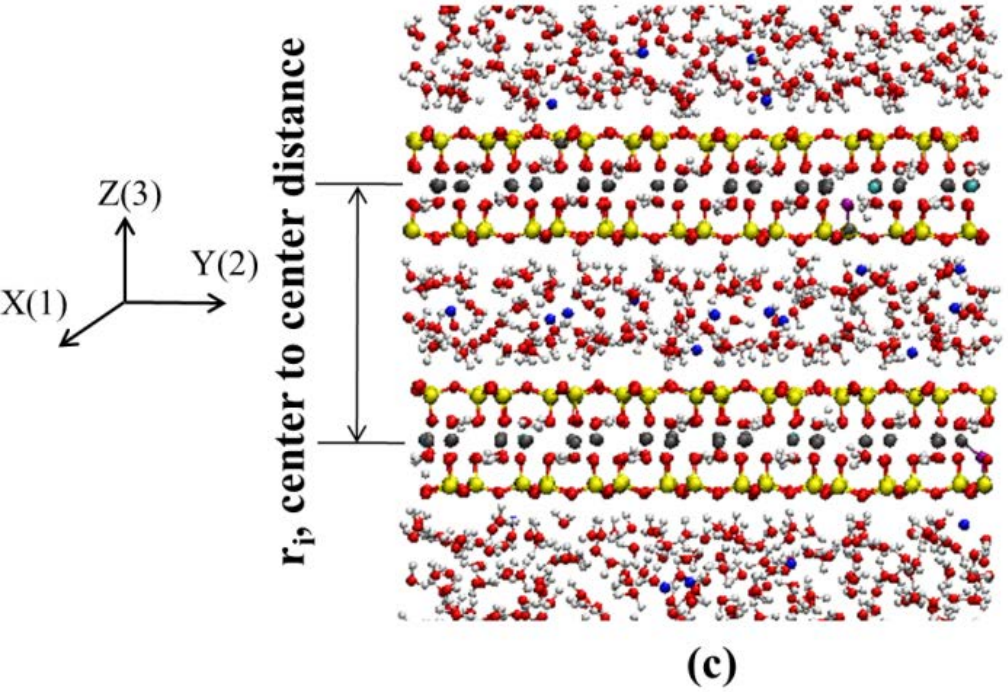
R. W. Zwanzig (1954) J. Chem. Phys. 22: 1420-1426.
Choudhury, Niharendu, and B. Montgomery Pettitt. "On the mechanism of hydrophobic association of nanoscopic solutes." Journal of the American Chemical Society 127.10 (2005): 3556-3567.
Chipot, C., & Pohorille, A. (Eds.). (2007). Free energy calculations:theory and applications in chemistry and biology (Vol. 86). Springer.

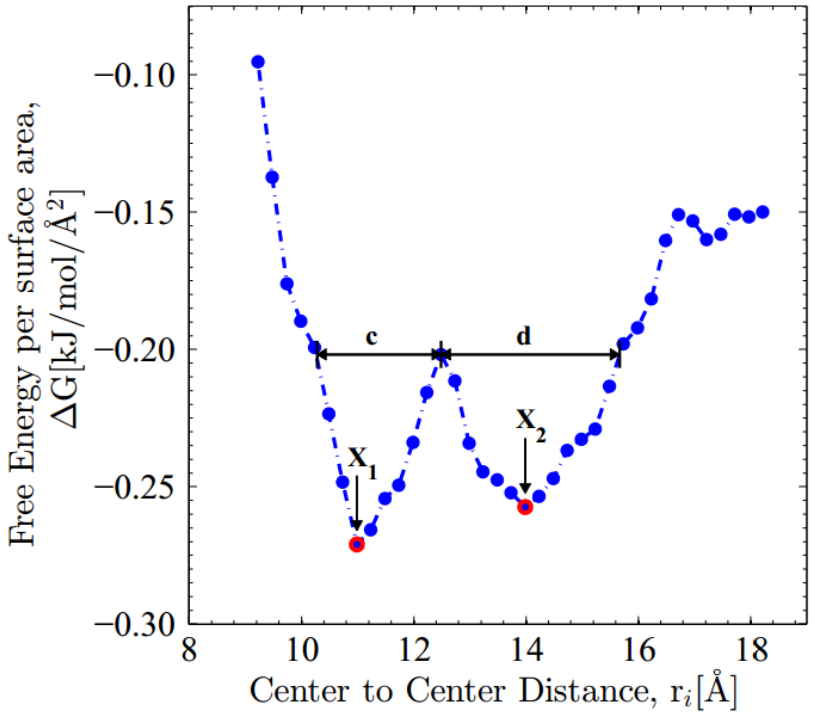
Free energy perturbation method: Typical set up for edge-to-edge interaction





Free energy perturbation method: Typical set up for face-to-face interaction





Gay-Berne: A coarse-grained inter-particle potential

$$U = 4\epsilon \left[\left(\frac{\sigma}{h_{12} + \sigma} \right)^{12} - \left(\frac{\sigma}{h_{12} + \sigma} \right)^{6} \right] \cdot \eta_{12} \cdot \chi_{12}$$

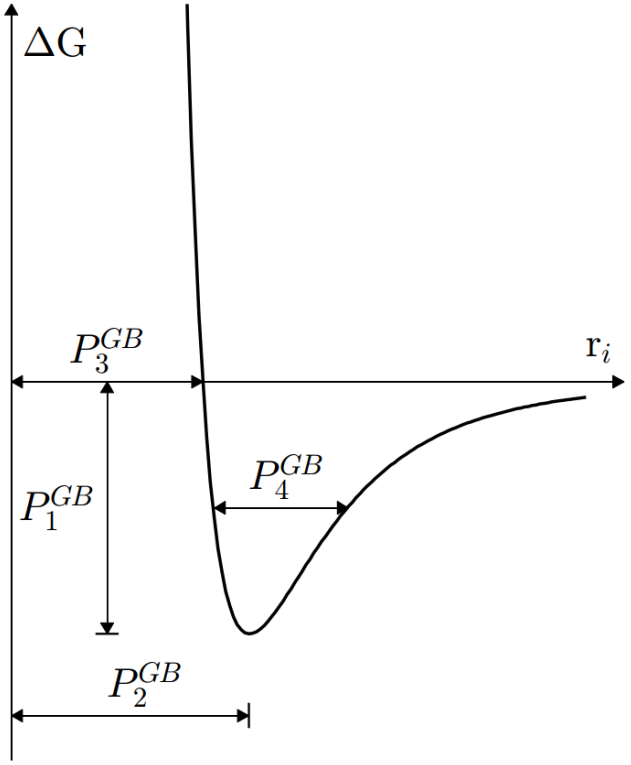
Five parameters $\{a(b), c, \sigma, \epsilon_a(\epsilon_b), \epsilon_c\}$

$$(1) \quad P_1^{GB} = -\epsilon \cdot \eta_{12} \cdot \chi_{12}$$

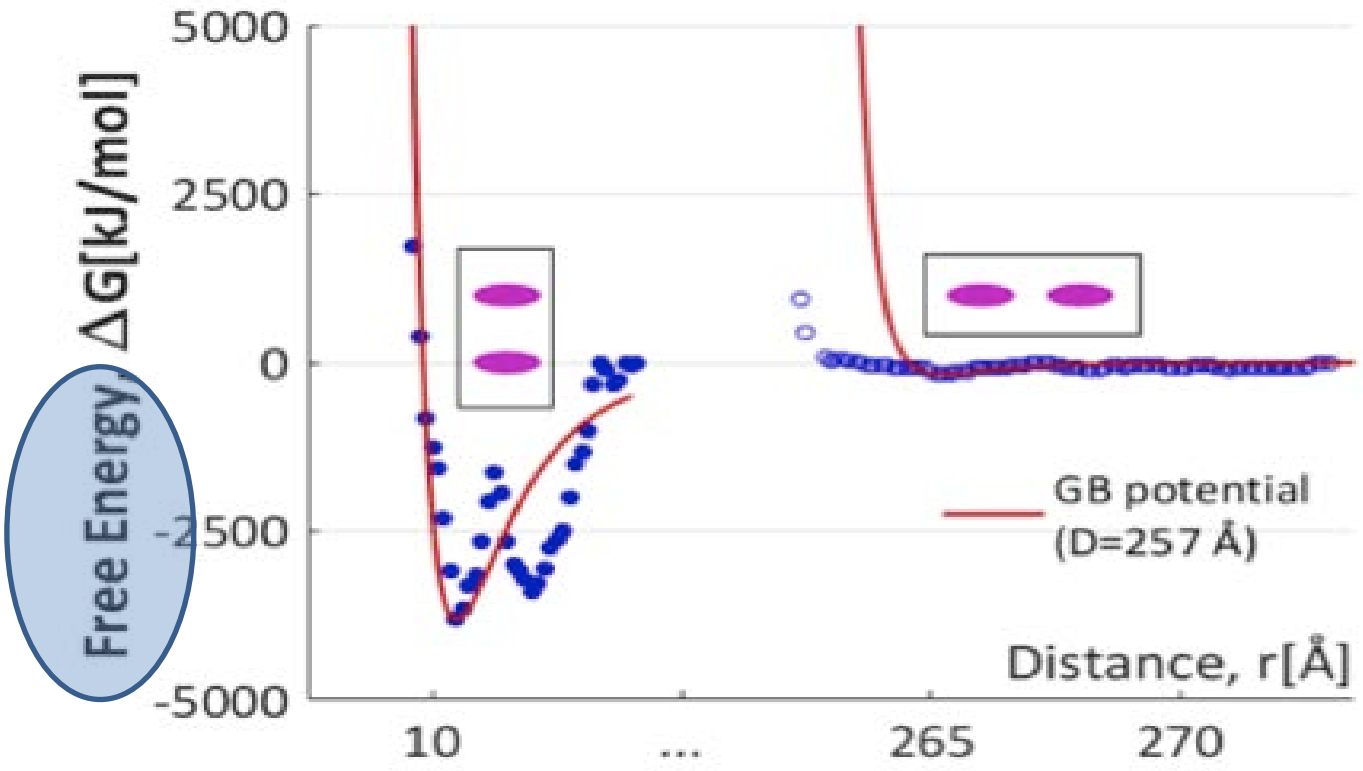
$$(2) \quad P_2^{GB} = \sigma_{12} + \sigma(2^{1/6} - 1)$$

$$(3) \quad P_3^{GB} = \sigma_{12}$$

$$(4) \quad P_4^{GB} = \sigma \left[(4 + 2\sqrt{2})^{1/6} - (4 - 2\sqrt{2})^{1/6} \right]$$

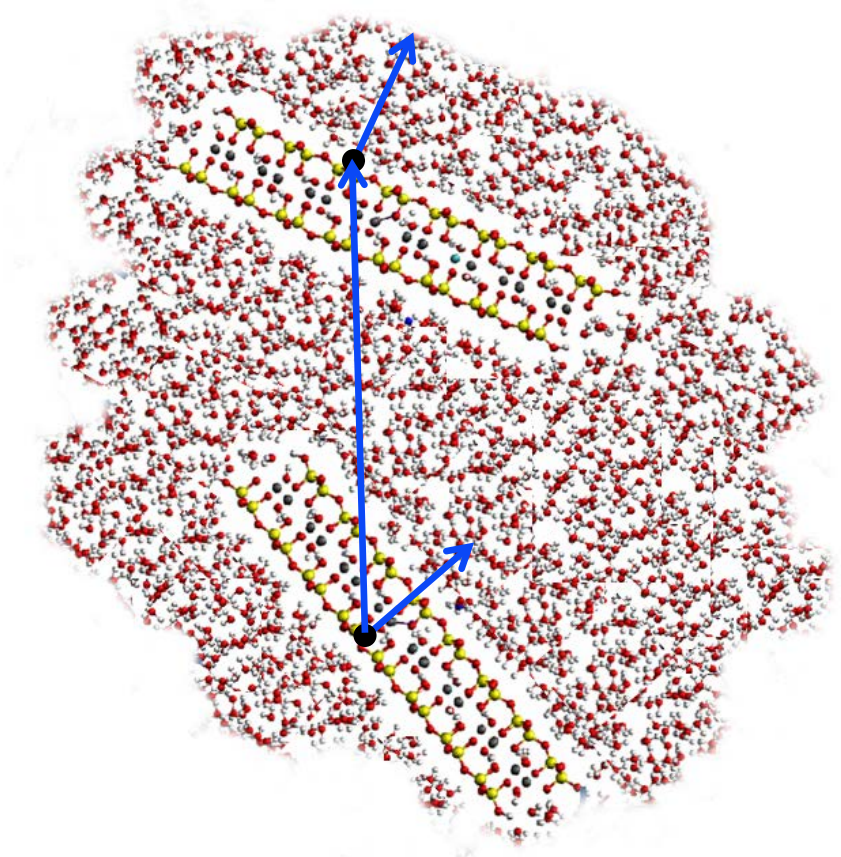


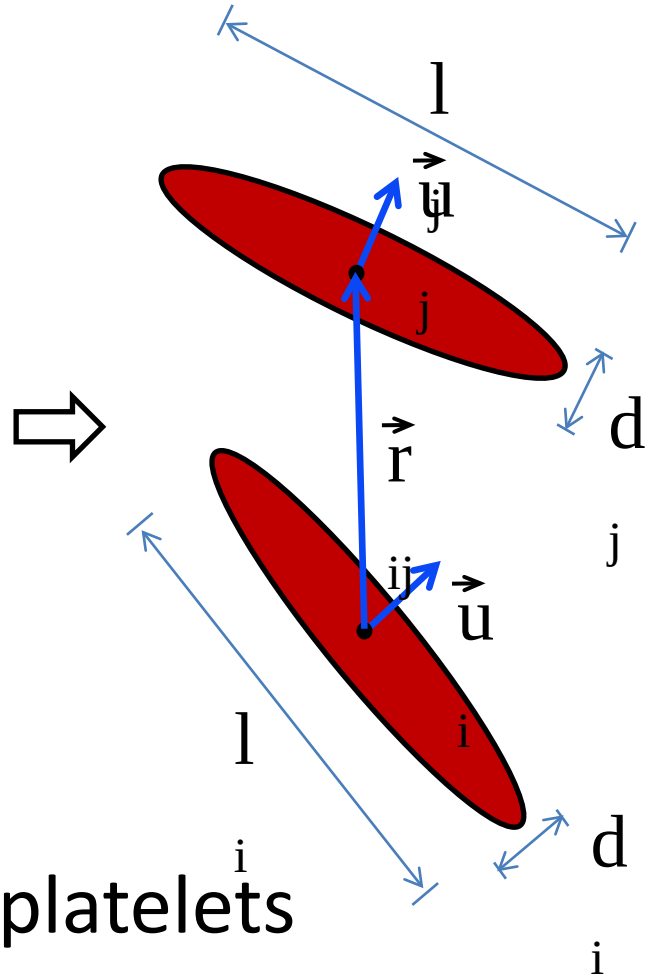
Gay-Berne: A coarse graining inter-particle potential



Gay-Berne: A coasne Graining inter-particle potential

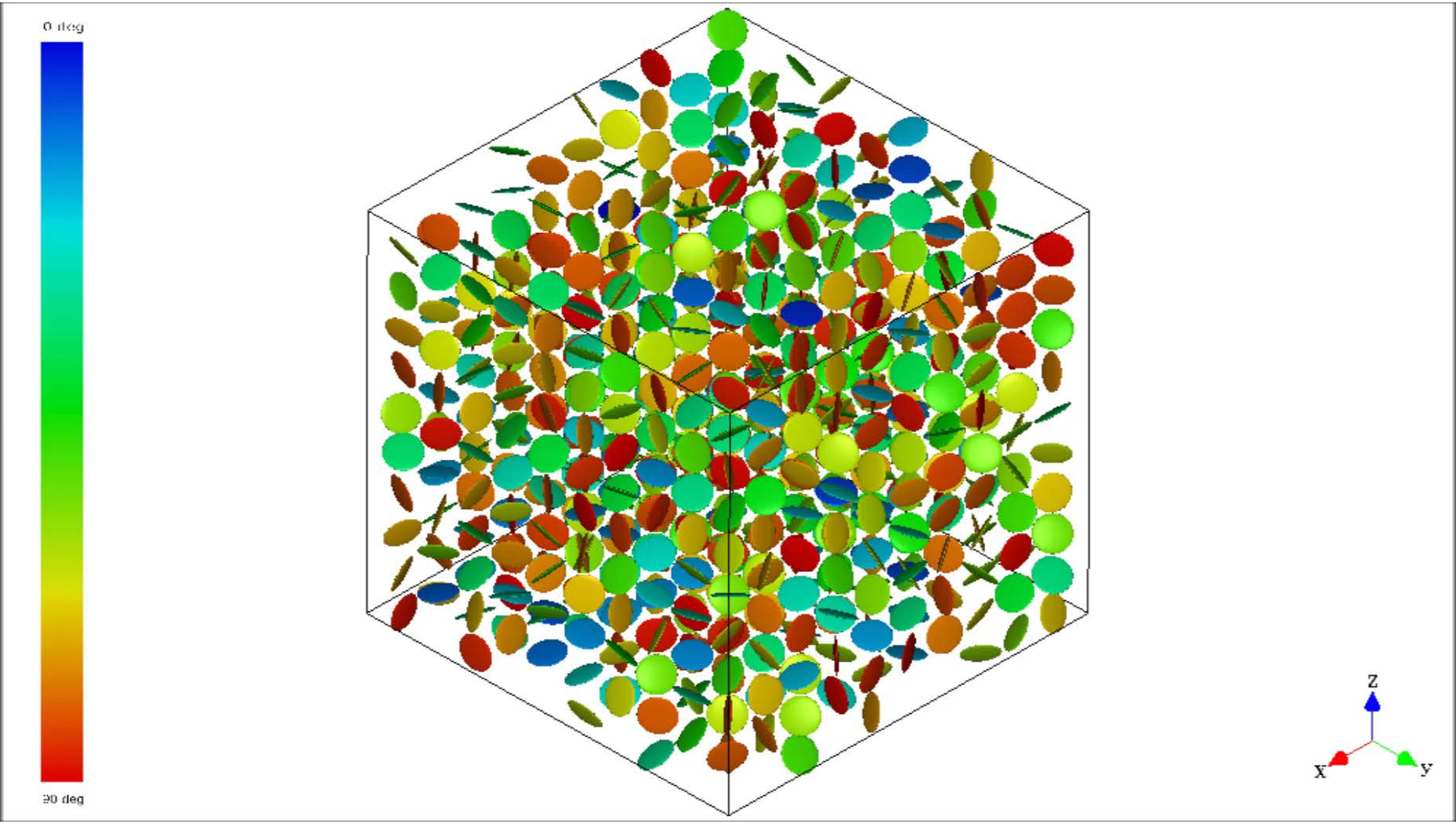
GB : Approximating each platelet of clay with an effective ellipsoidal (oblate) particle



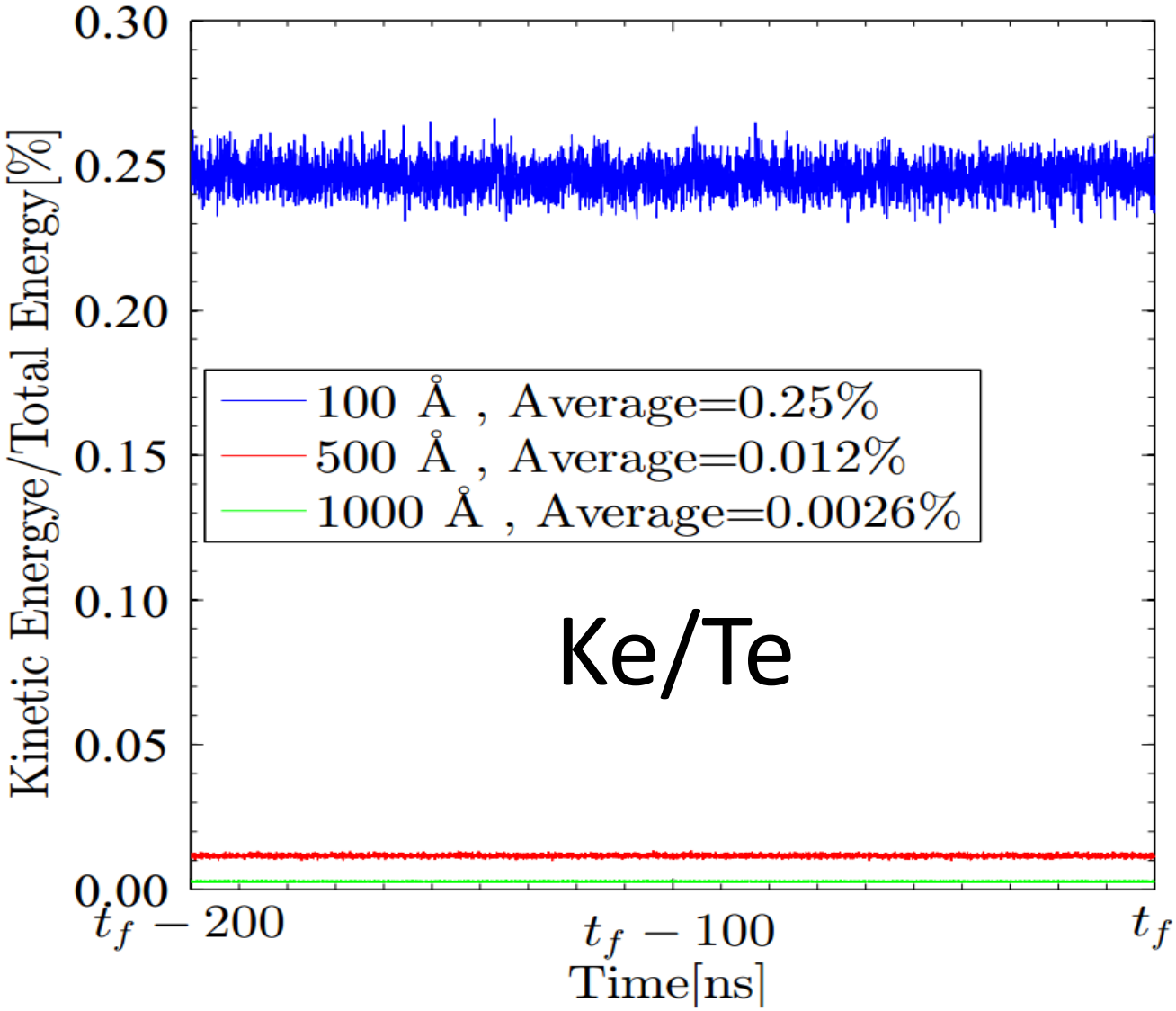


➔ Grains = platelets

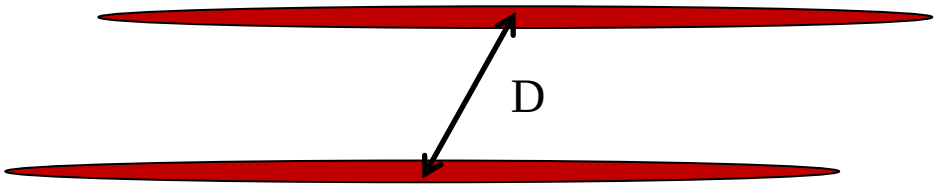
How it works? MD (NPT) + PMF + platelets (100A, laponite clay)



Out-of-equilibrium jammed configurations

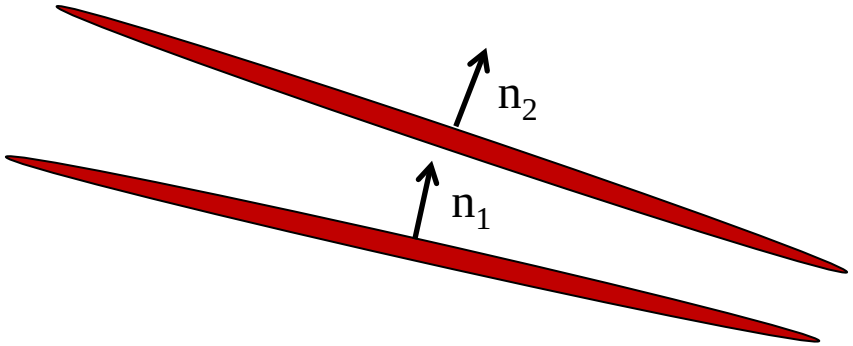


Analysis of aggregate structure using distance and angle pair correlation function



Criterion 1:

$D < 14$ Angstrom

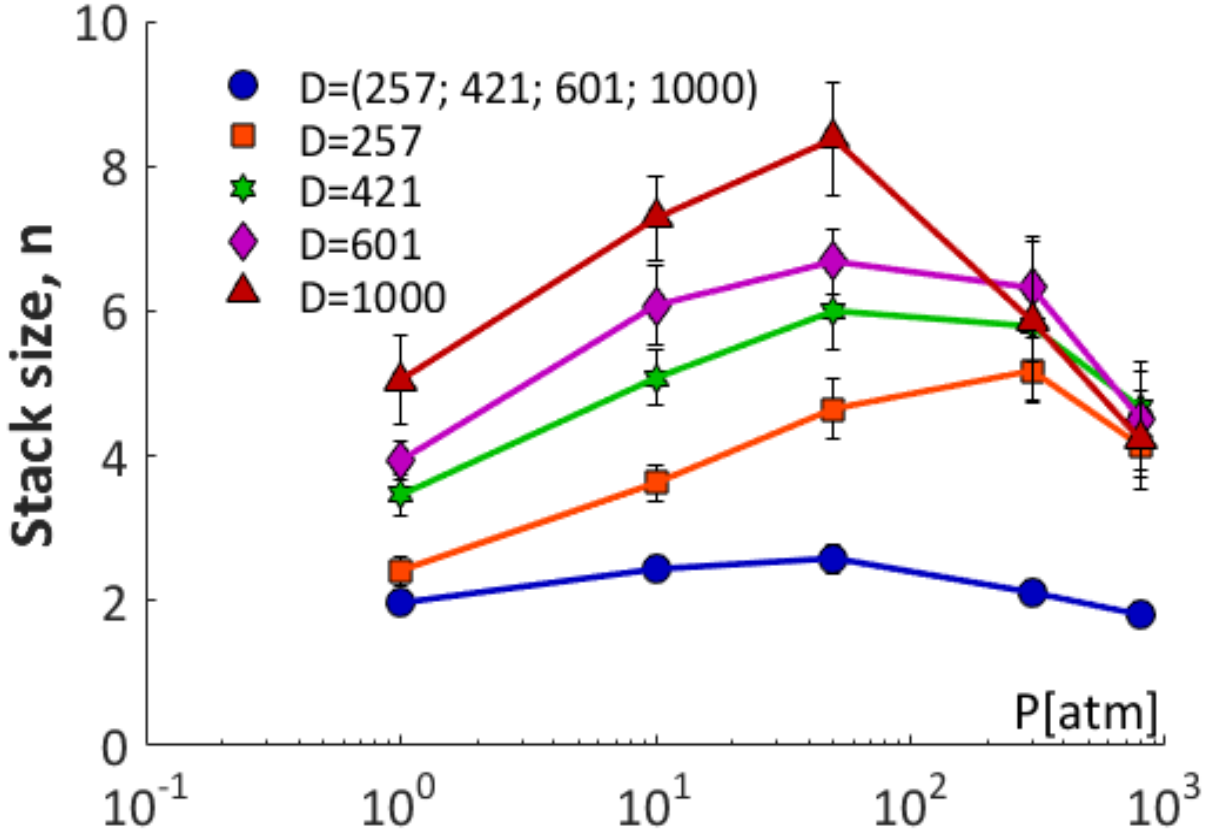


Criterion 2:

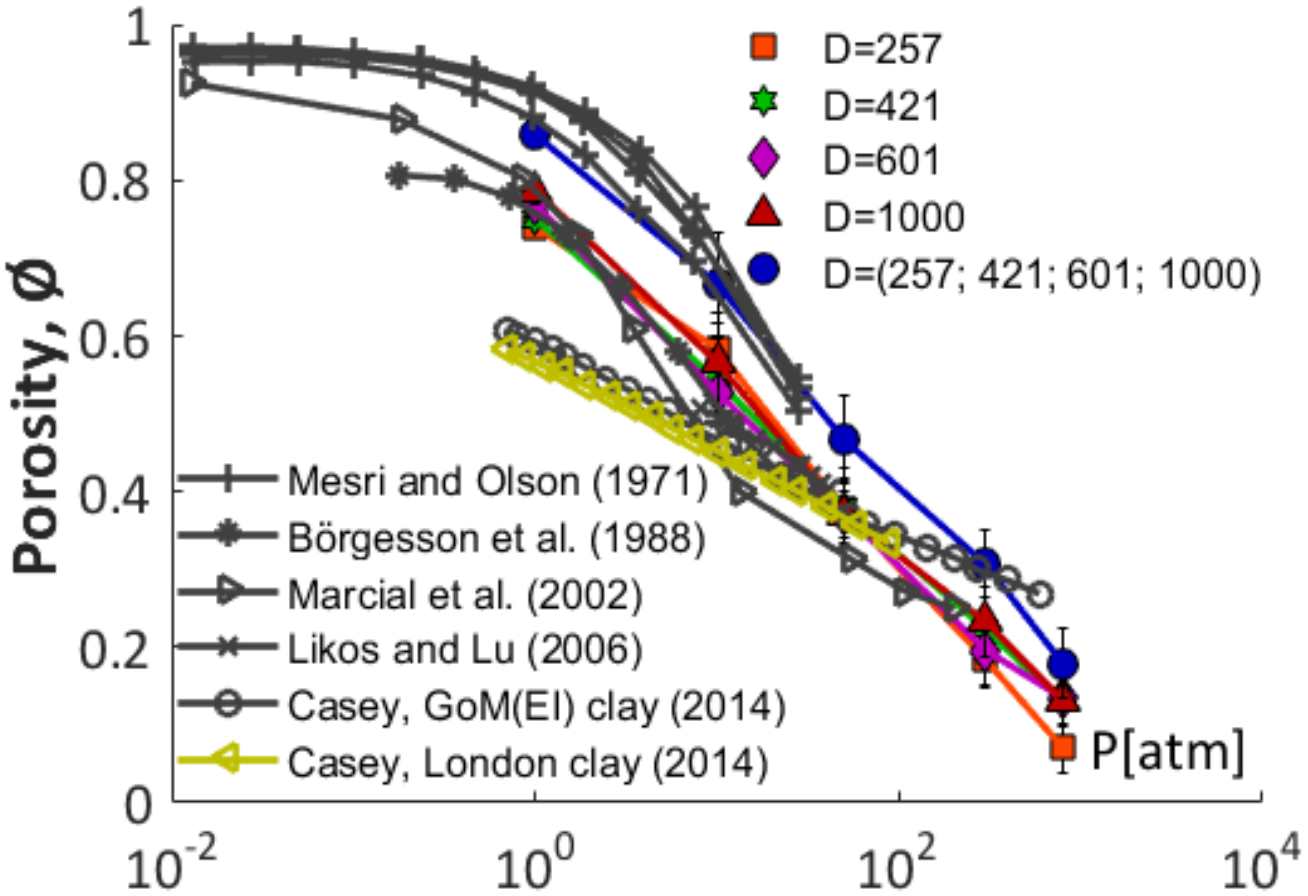
$\vec{n}_1.\vec{n}_2 < 0.95$

Ref: Chen, Chun-teh, et al. "Self-Assembly Of Tetramers Of 5, 6 Dihydroxyindole Explains The Primary Physical Properties Of Eumelanin: Experiment, Simulation And Design." ACS nano (2013).

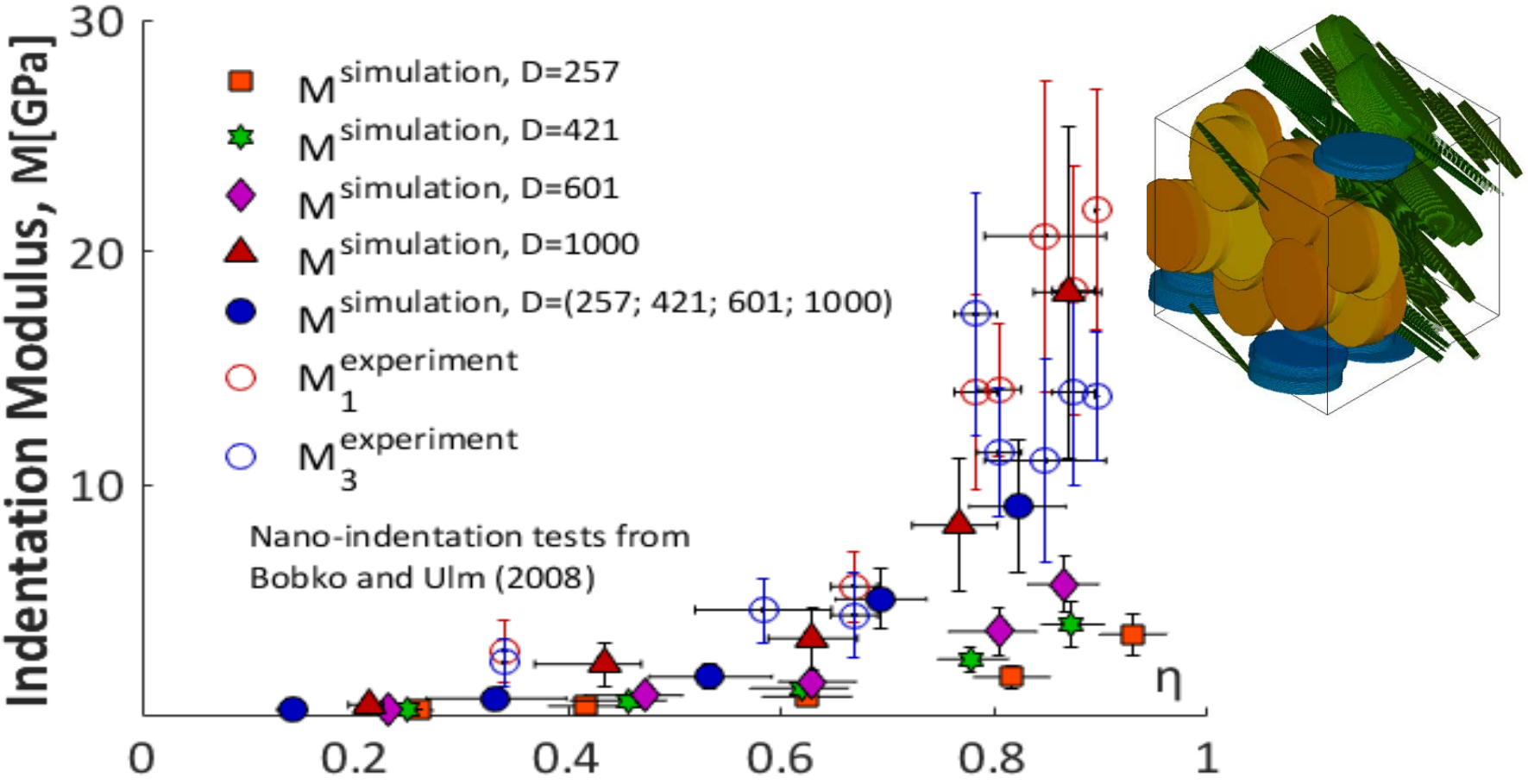
Analysis of aggregate structure using distance and angle pair correlation function



Porosity
(at the scale of the assembly of aggregates)

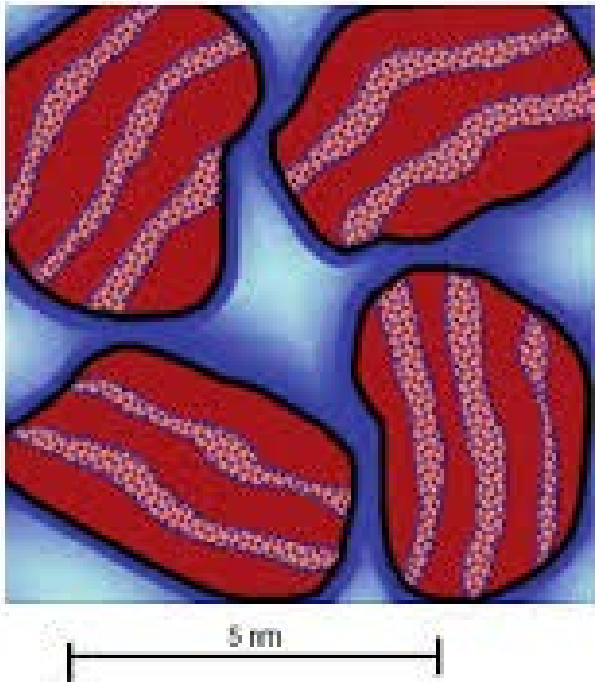


Elasticity at the scale of the assembly of aggregates (at the mesoscale)

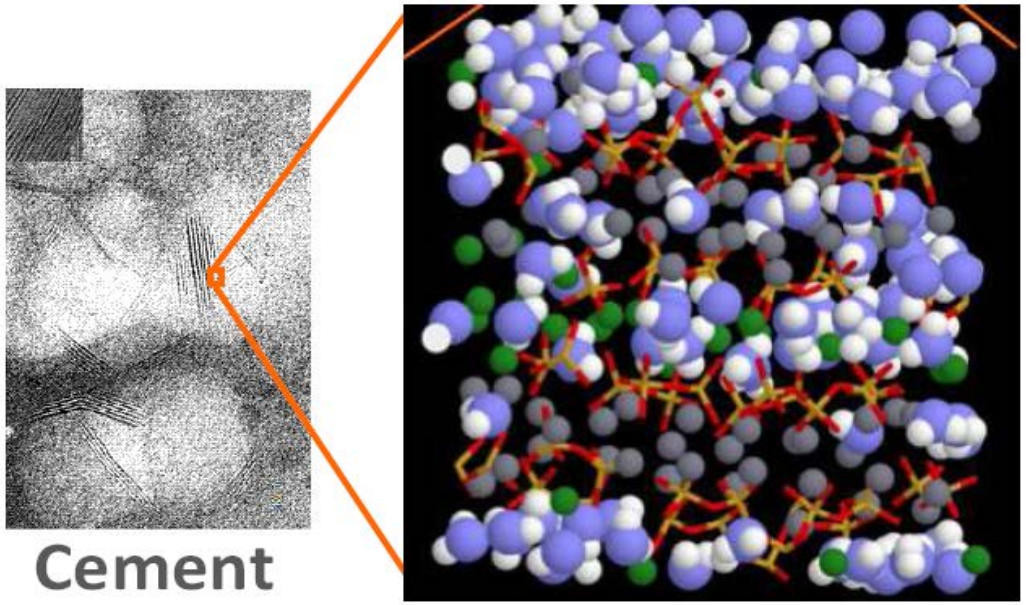


(D. Ebrahimi et al, J. chem. Phys, 2014)

(Jennings et al , Nat. Mat. 2007)



(Pellenq et al , PNAS 2009)



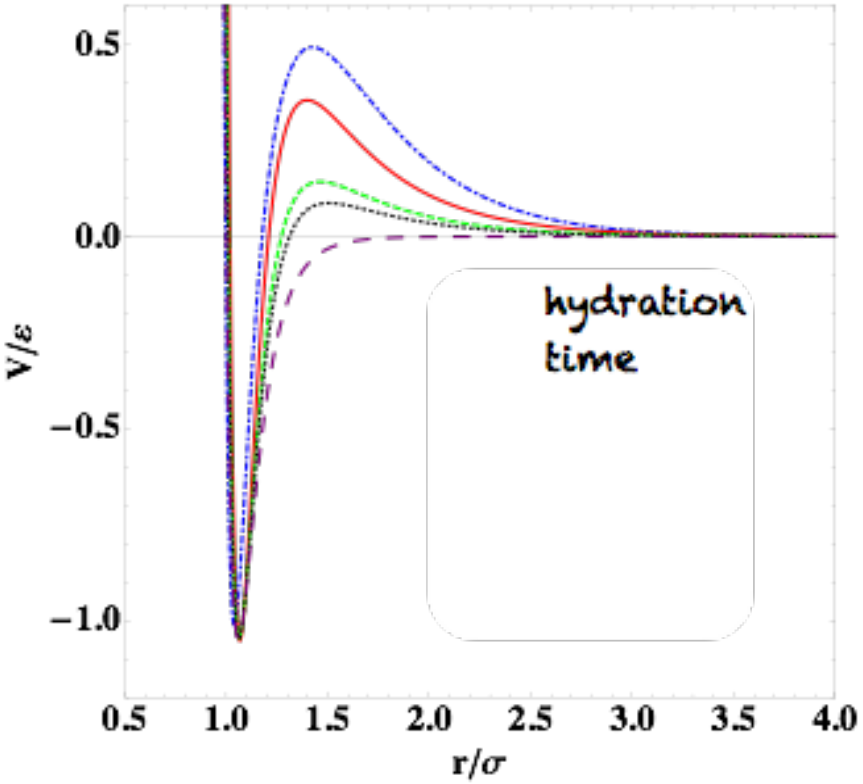
- Going from nano (atomistic) to meso with CSH

3 - « The case of cement hydrates, CSH »

➔ Grains = spheres

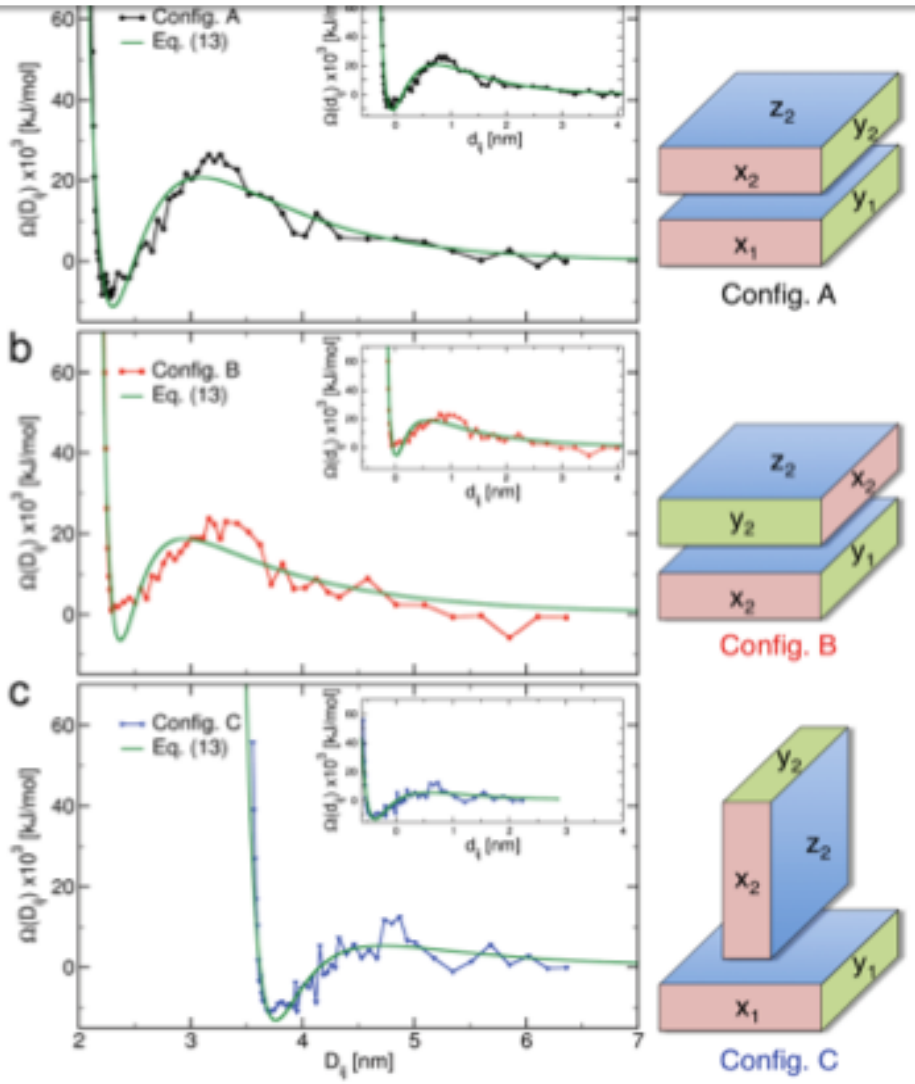
The case of CSH: interactions between two grains

attracto-repulsive potential



$$V(r) = A\frac{e^{-\kappa r}}{r} + \epsilon\left\{\left(\frac{\sigma}{r}\right)^{24} - \left(\frac{\sigma}{r}\right)^{12}\right\}$$

K. Ioannidou, R. J.-M. Pellenq and E. Del Gado, Soft Matter, 10, 1121-1133 (2014)

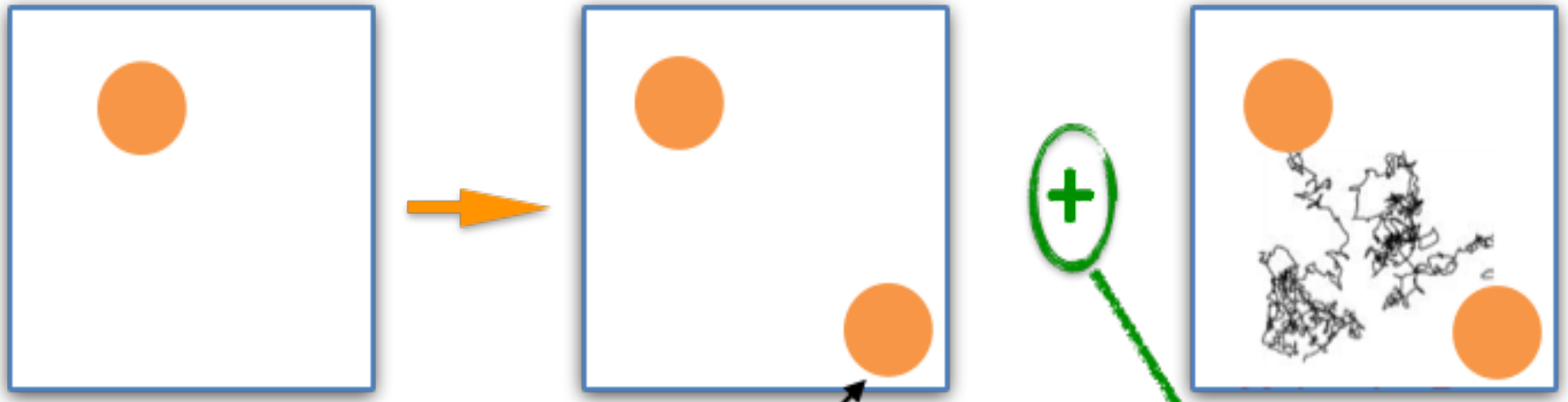


Bonnaud P. et al, Nanoscale, 2016, 8, 4160

A statistical physics approach for upscaling C-S-H modeling

Grand Canonical Monte Carlo

Molecular Dynamics



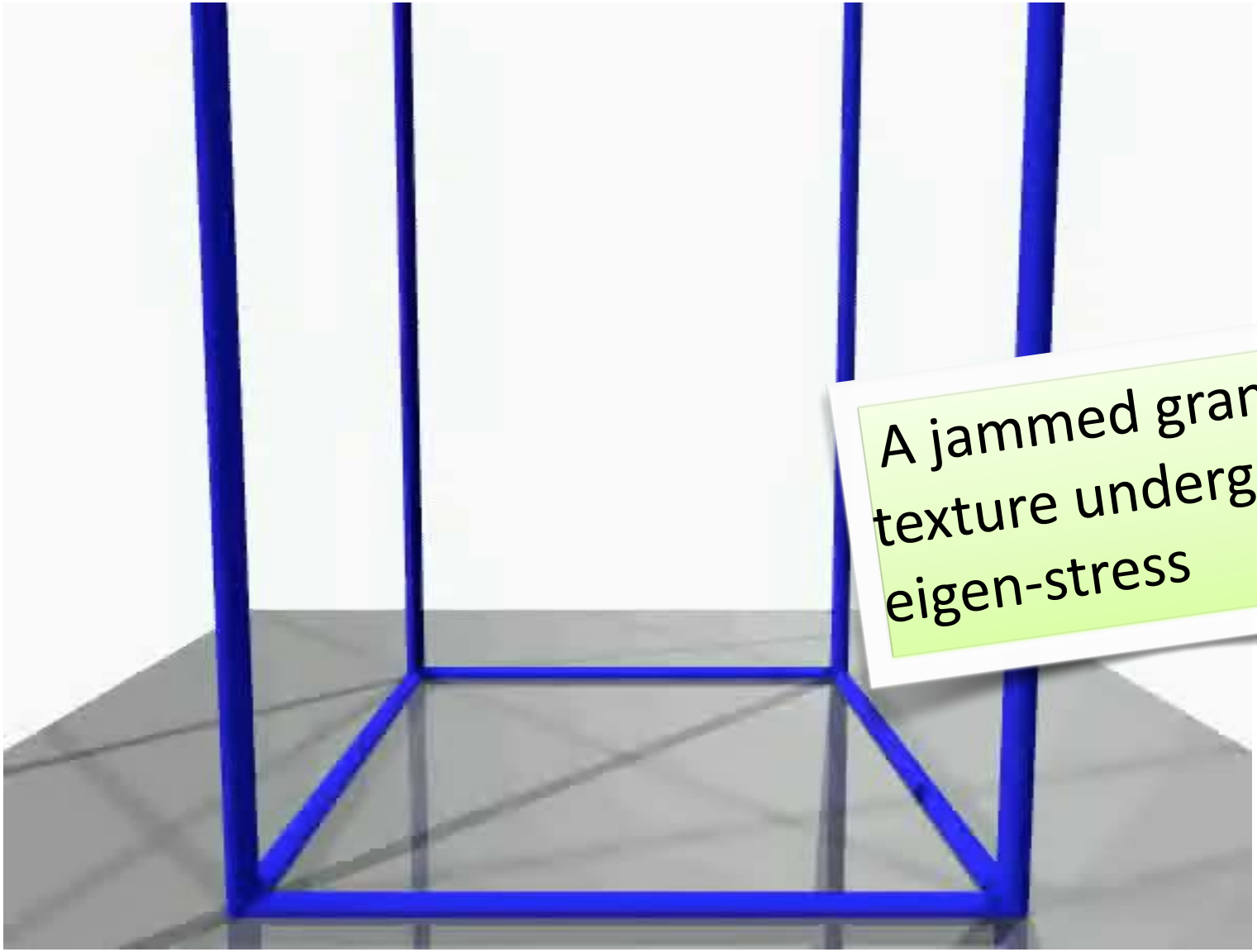
$$P_{ins} = min[1, e^{(\mu - \Delta U)/K_B T}]$$

chemical potential:
free energy gain for
hydrate production

R kinetic rate:
MC events/MD steps

monodisperse $\sigma = 5nm \quad T = 0.15$

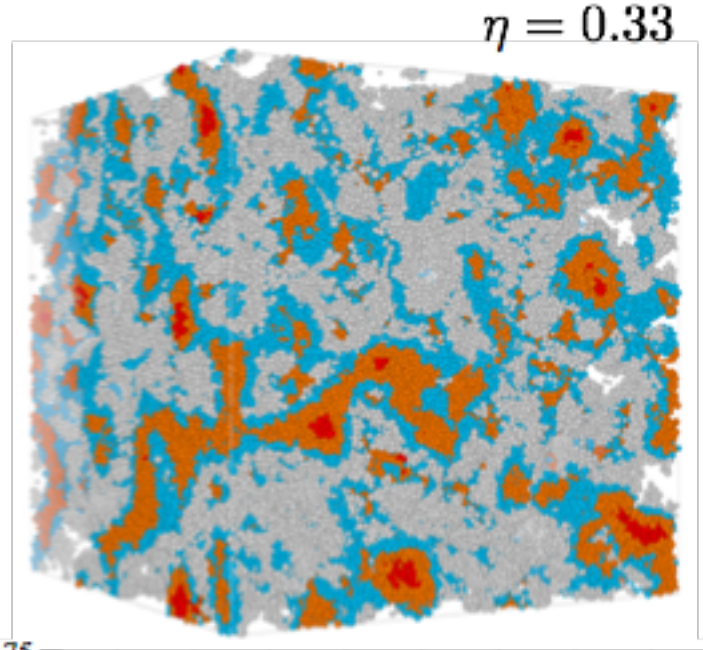
Hardened cement paste

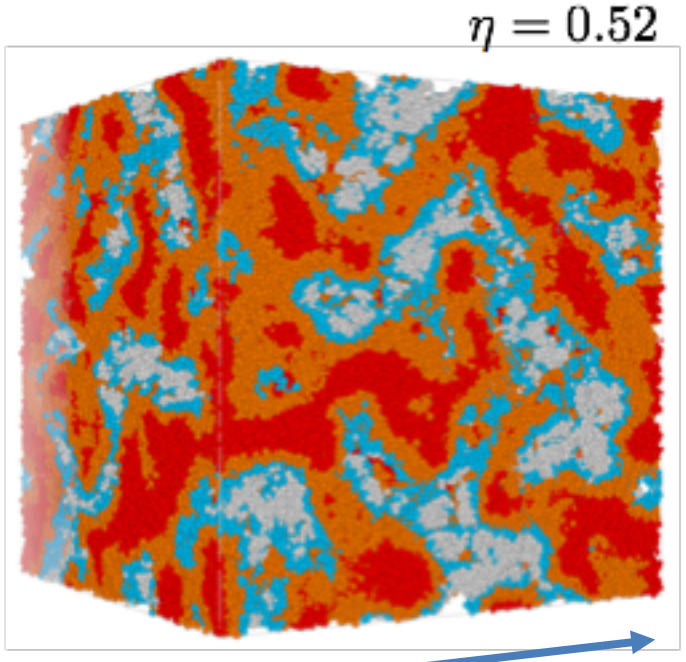


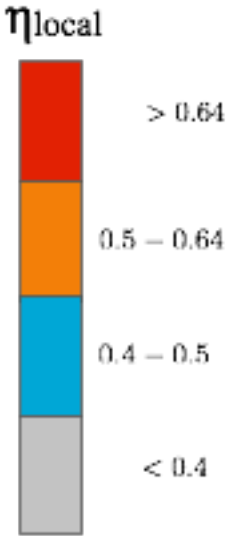
Masoero et al Phys. Rev. Lett., 2012

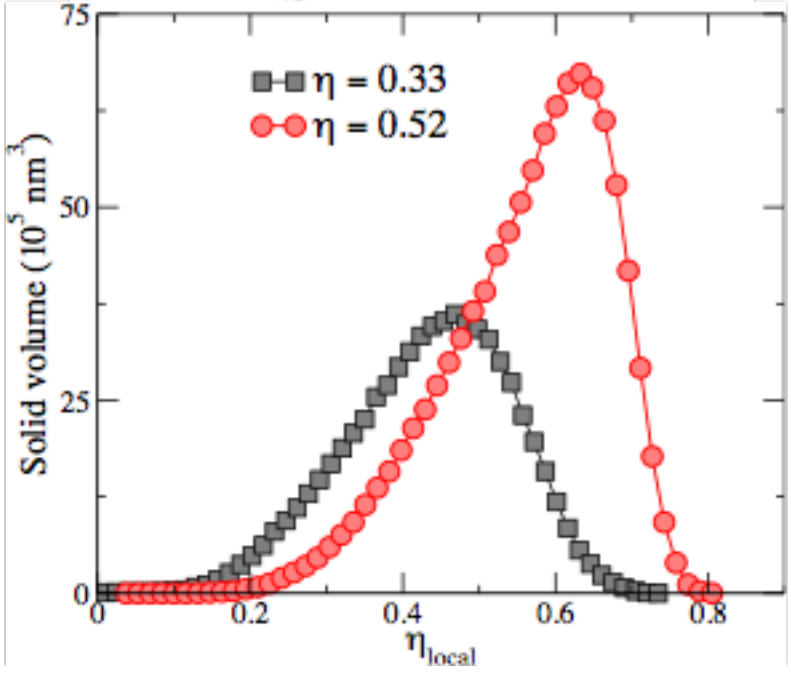
29

Meso-scale texture of C-S-H: local volume fractions







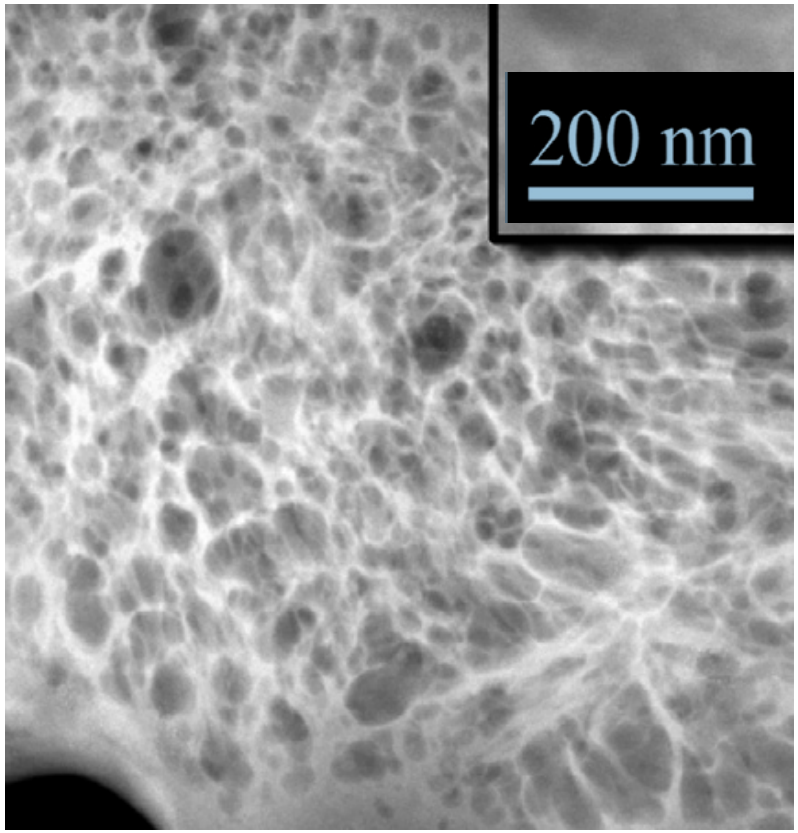


0.6 million particles

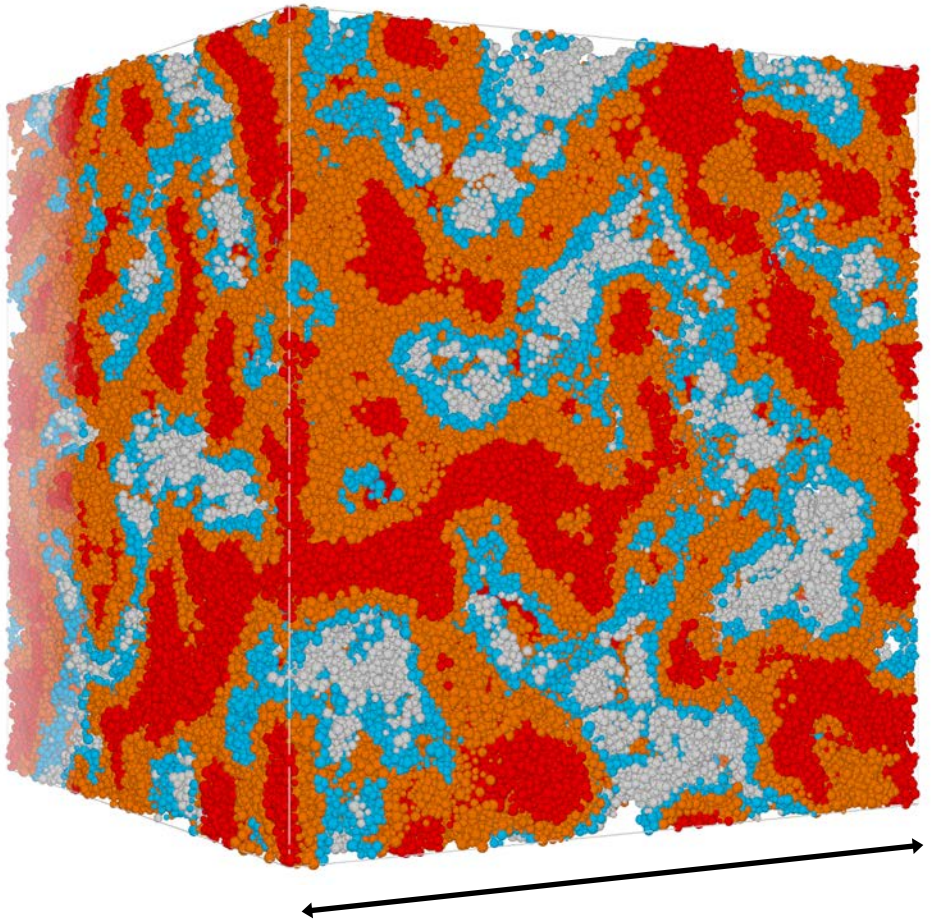
- local volume fraction is defined in sphere of R=35nm
- continuous distribution of C-S-H densities

K. Ioannidou et. al, *Mesoscale texture of cement hydrates*, PNAS USA 113, 8,2029-2034 (2016)

COMPARING with Tomography exp.



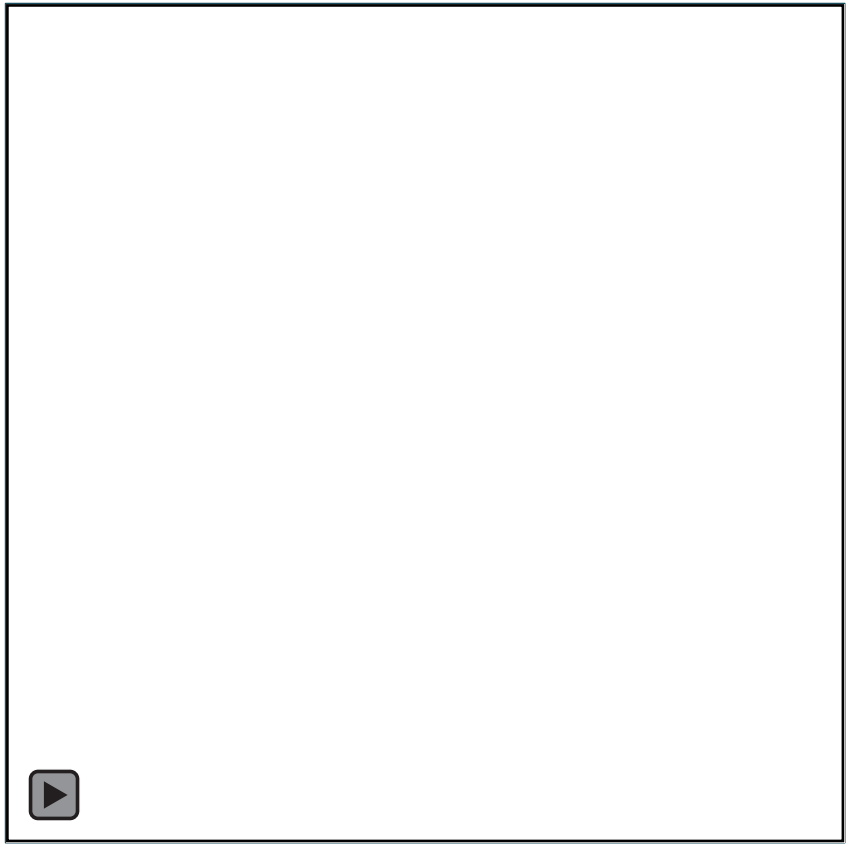
O. Wenzel, Material Characterization, 2018



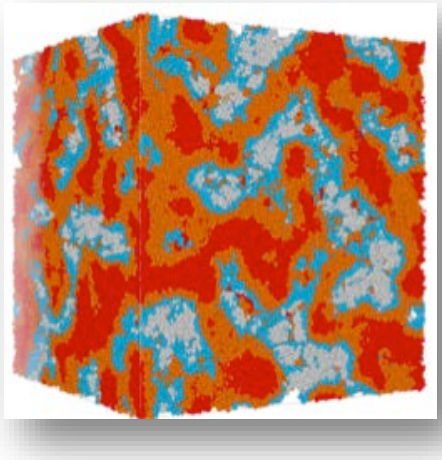
$0.6\mu m$

0.6 million particles

Electron imaging the capillary porosity of cement paste

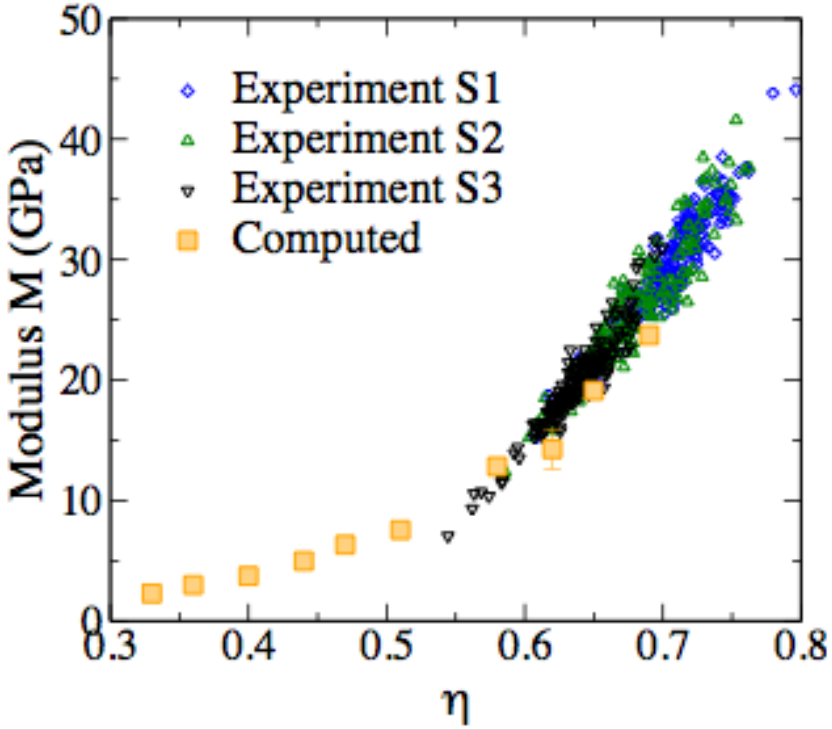


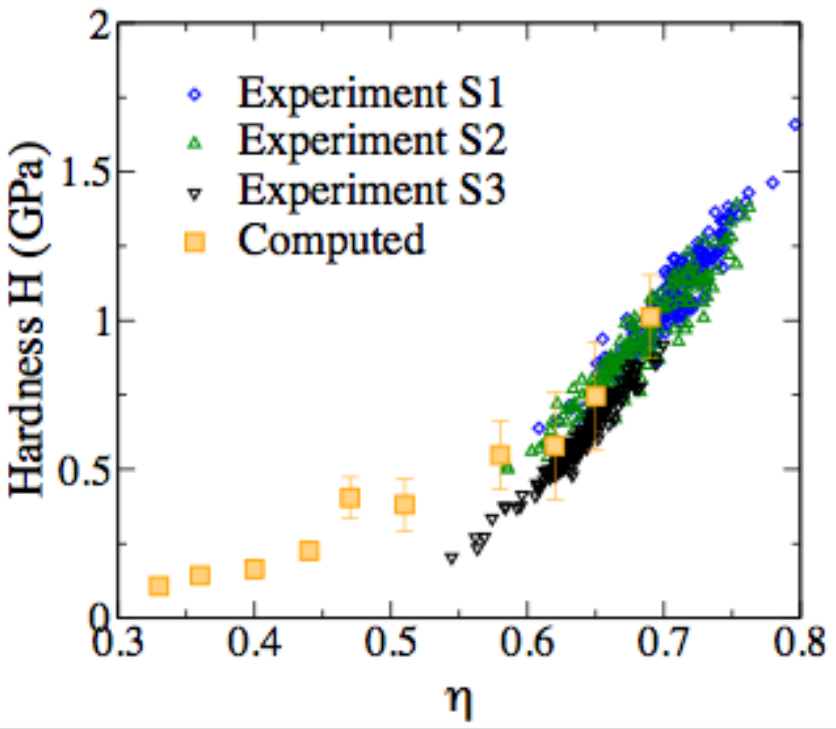
J. Berthonneau, D. Ferry. O. Grauby,
CINaM, CNRS-AMU



0.6 μm

Nano-scale mechanics of C-S-H



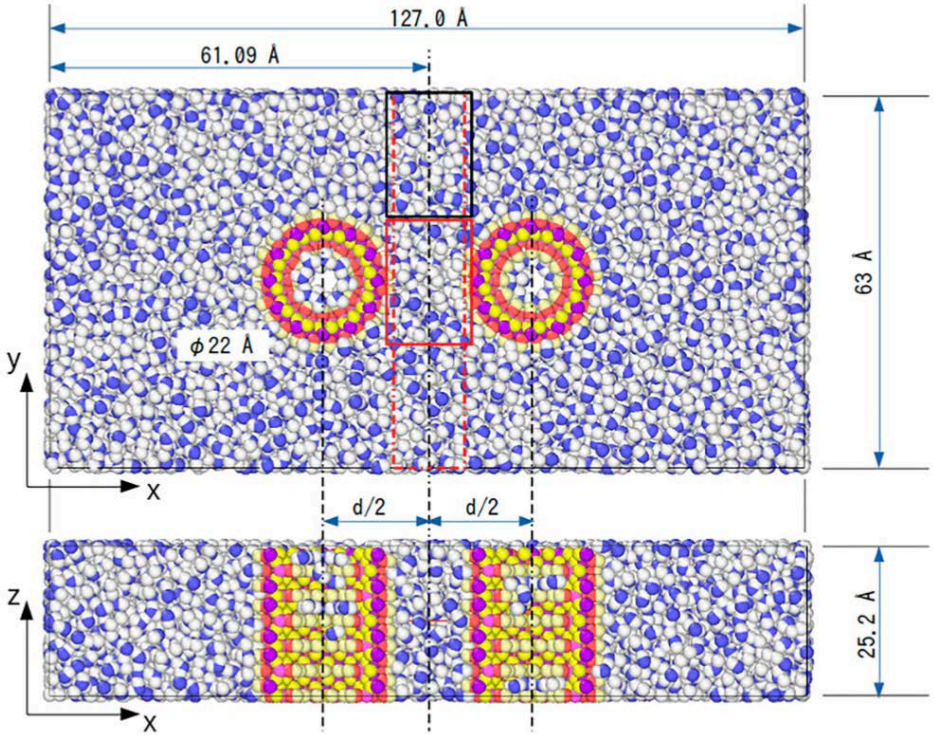


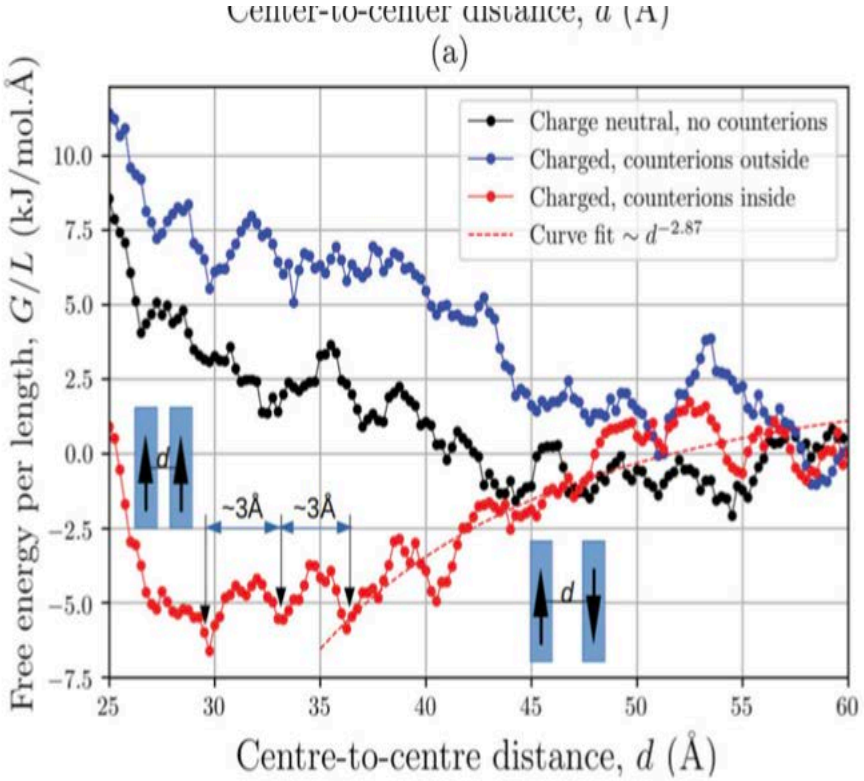
Nano-indentation experiments:

S1: cement class G &quartz, w/c=0.43, 5y curing

S2: OPC, w/c=0.45, 24h curing

S3: OPC & C-S-H seed, w/c=0.45, 17h curing





- Going from nano (atomistic) to meso with nanotubes

4 - « The case of imogolite tubes »

➔ Grains = cylinders (L, R)

imogolite tubes

$$U_{AB} = \sum_{\alpha \in A} \sum_{\beta \in B} u_{\alpha\beta}$$

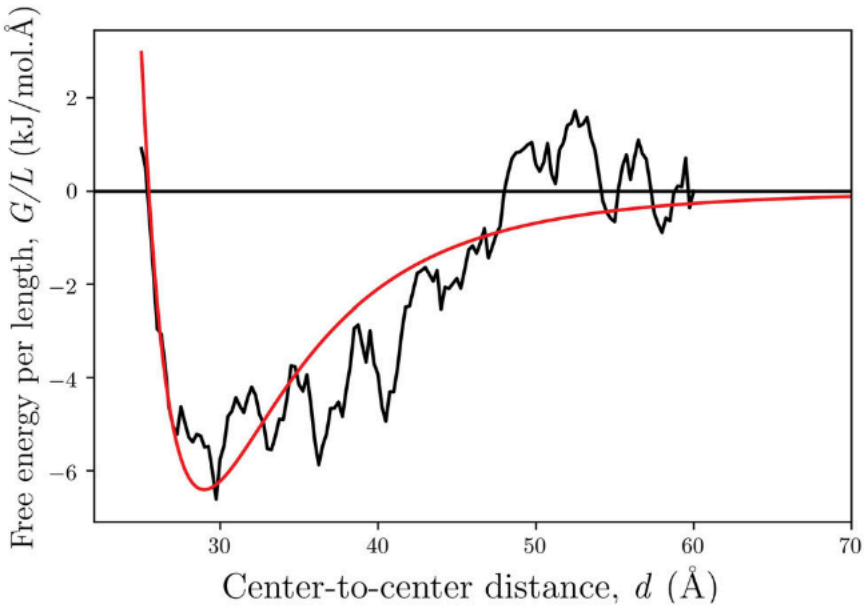
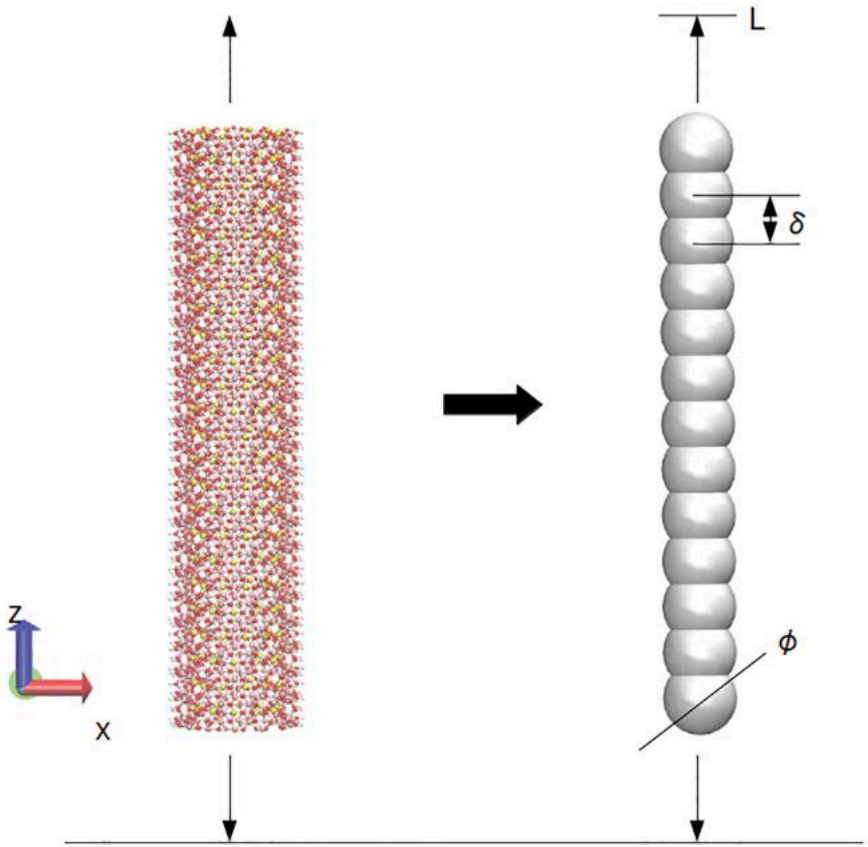
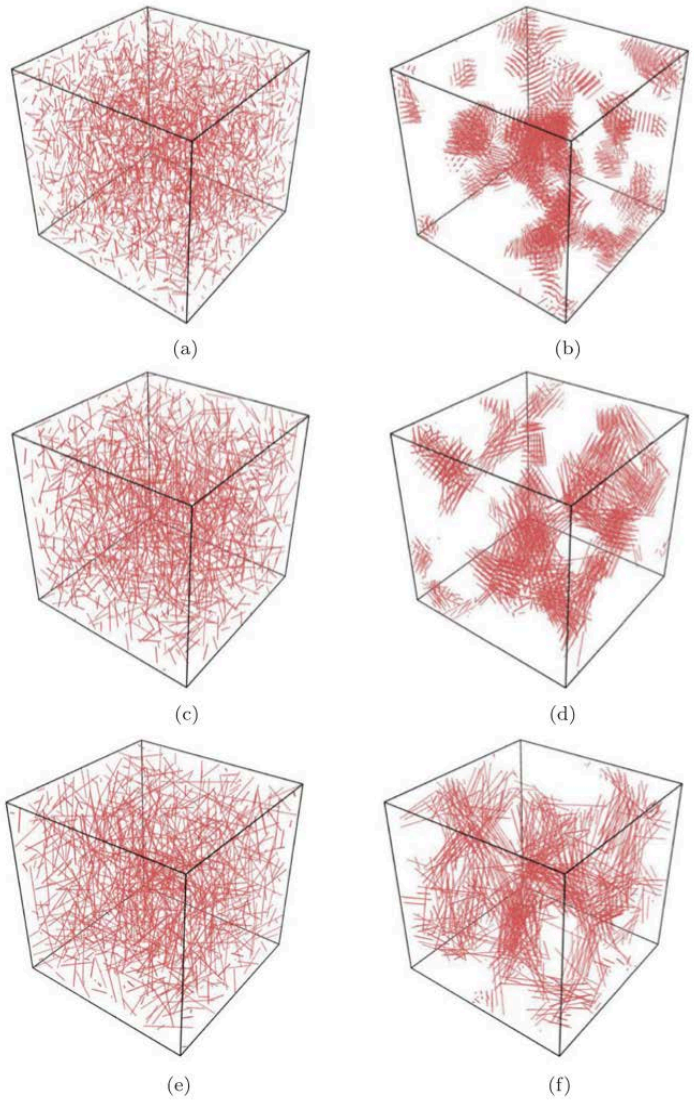


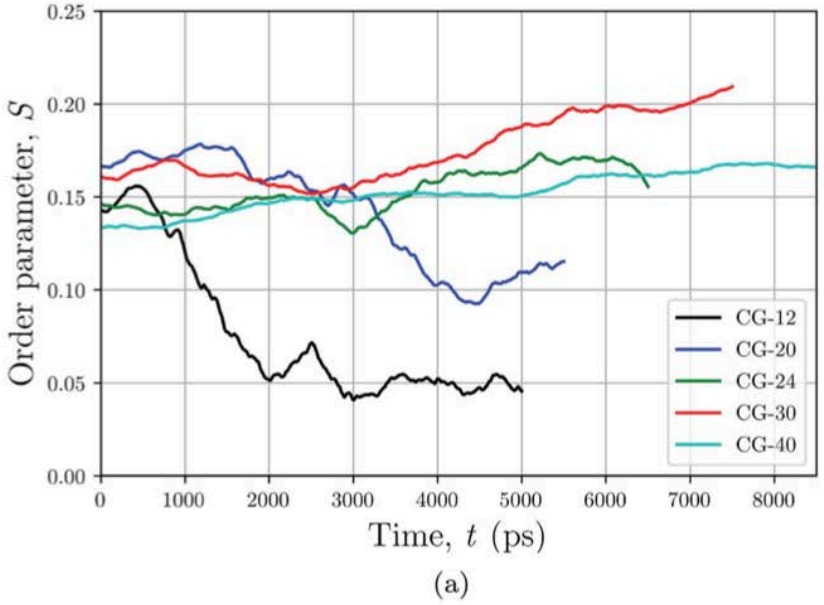
Figure 6. Curve-fitting with LJ and LJ/Coulomb potential forms according to free energy per length data.



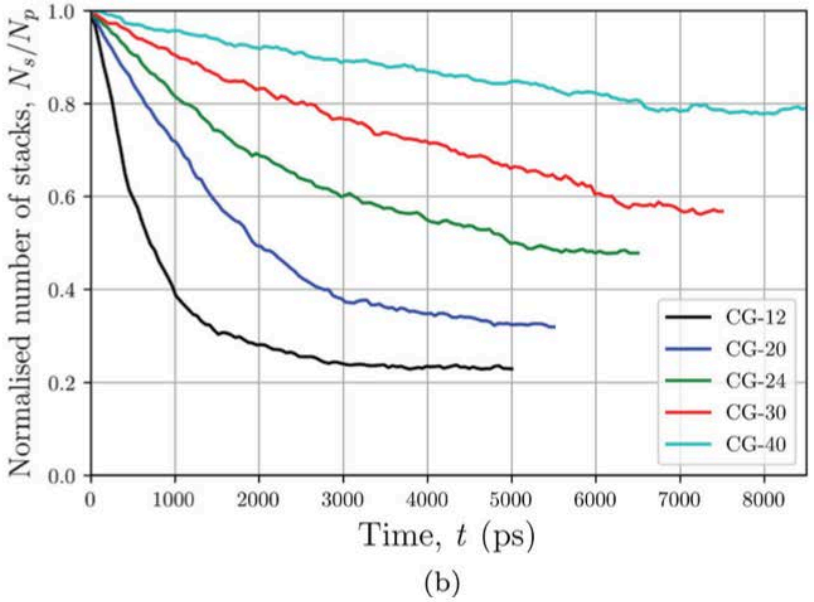
(H. Zhu, Mol. Phys, 2019)

imogolite tubes





(a)

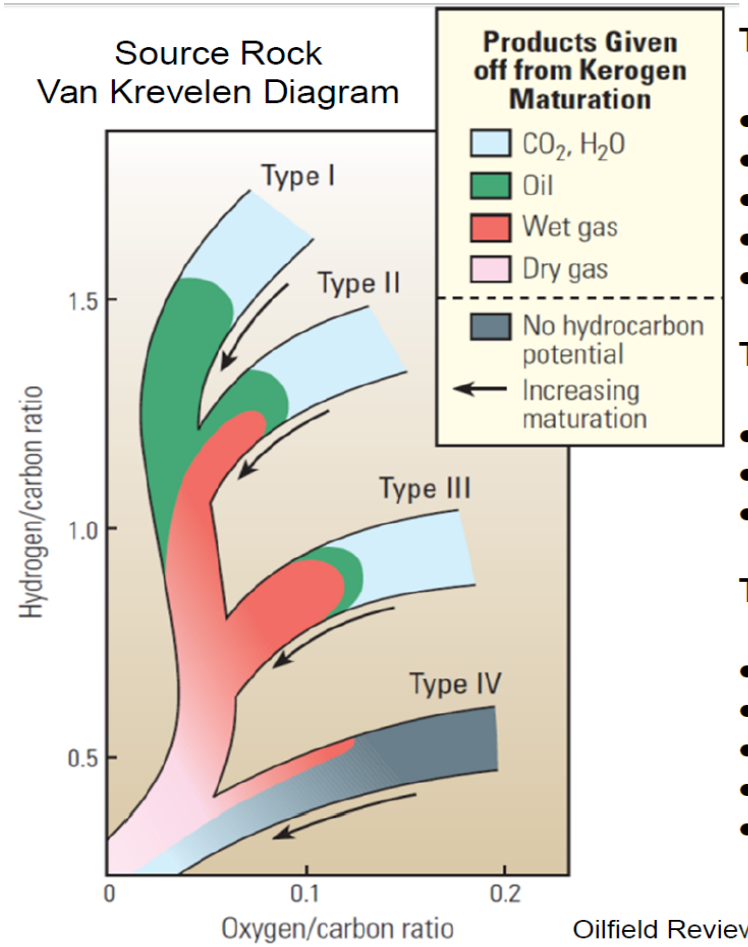


(b)

THE REPLICA-EXCHANGE MD: THE TOOL TO BRIDGE TIME SCALE

➔ Application to the degradation of wood: the molecular simulation of geological process…

Gas/oil shale reservoirs



Oilfield Review, Winter 2010/2011

Type I (Green River Oil Shale)

- Freshwater cyanobacteria & algae
- Hydrogen/carbon ratio > 1.25
- Oxygen/carbon ratio < 0.15
- Few cyclic or aromatic structures
- Produces mostly oil

Type II (Typical Petroleum Source Rock)

- Terrestrial & marine plant matter
- Accumulated in shallow inland seas
- Produces oil and gas

Type III (Typical Coal)

- Terrestrial plant matter
- Hydrogen/carbon ratio < 1
- Oxygen/carbon ratio 0.03 to 0.3
- Extensive ring and aromatic systems
- Produces coal and gas

MIMICKING the geological degradation of organic matter (type III kerogen: cellulose, lignin)

- Cellulose/lignin decomposition

10^6 years (10^{13} seconds)

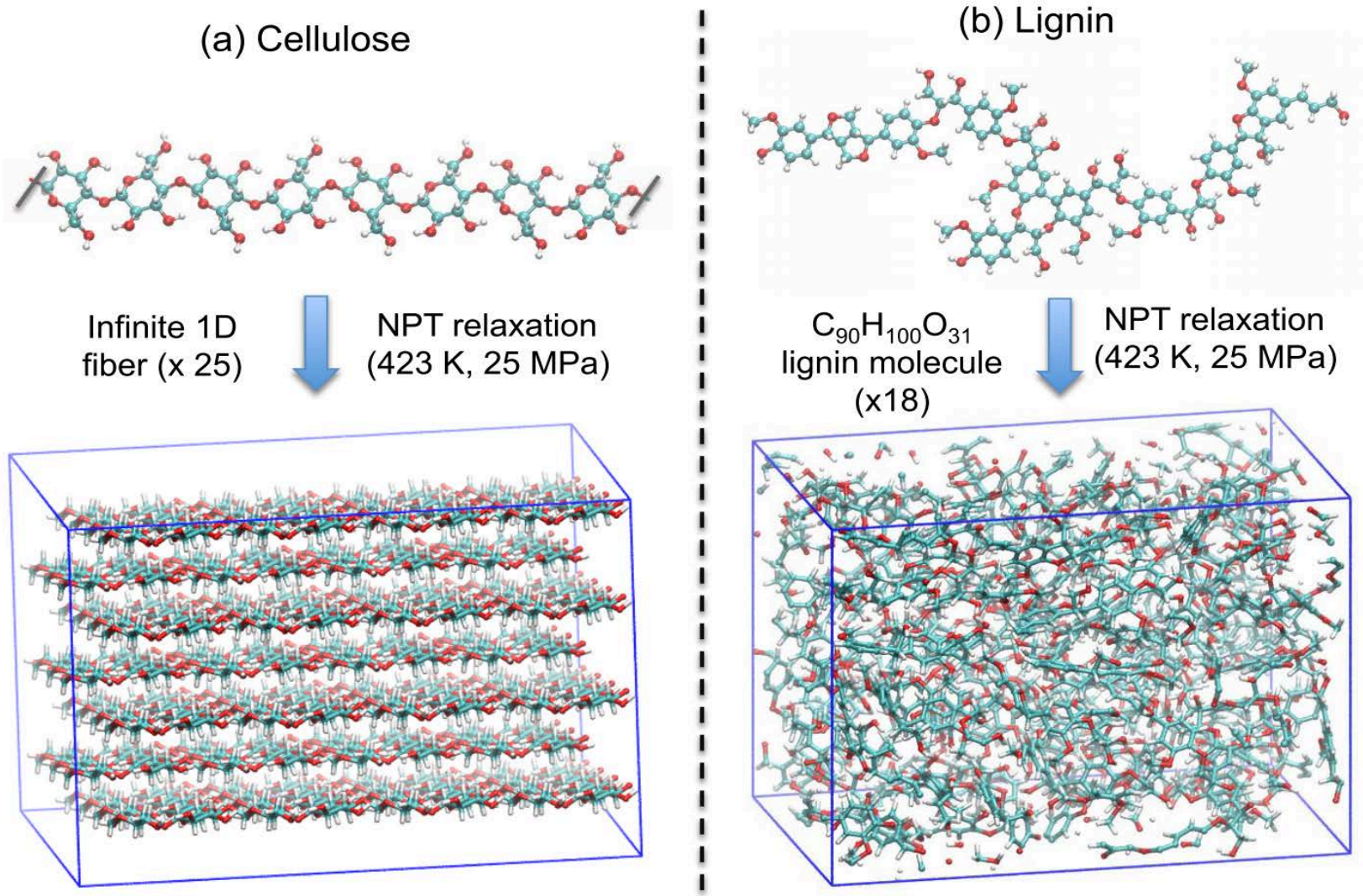
- Molecular dynamics: **10^{-9}** secondes

→ Replica Exchange Molecular Dynamics (REMD) / Parallel Tempering with a reactive potential (Reaxff)

(Based on statistical Physics at thermodynamic equilibrium : a reasonable way to speeding aging process with MD)

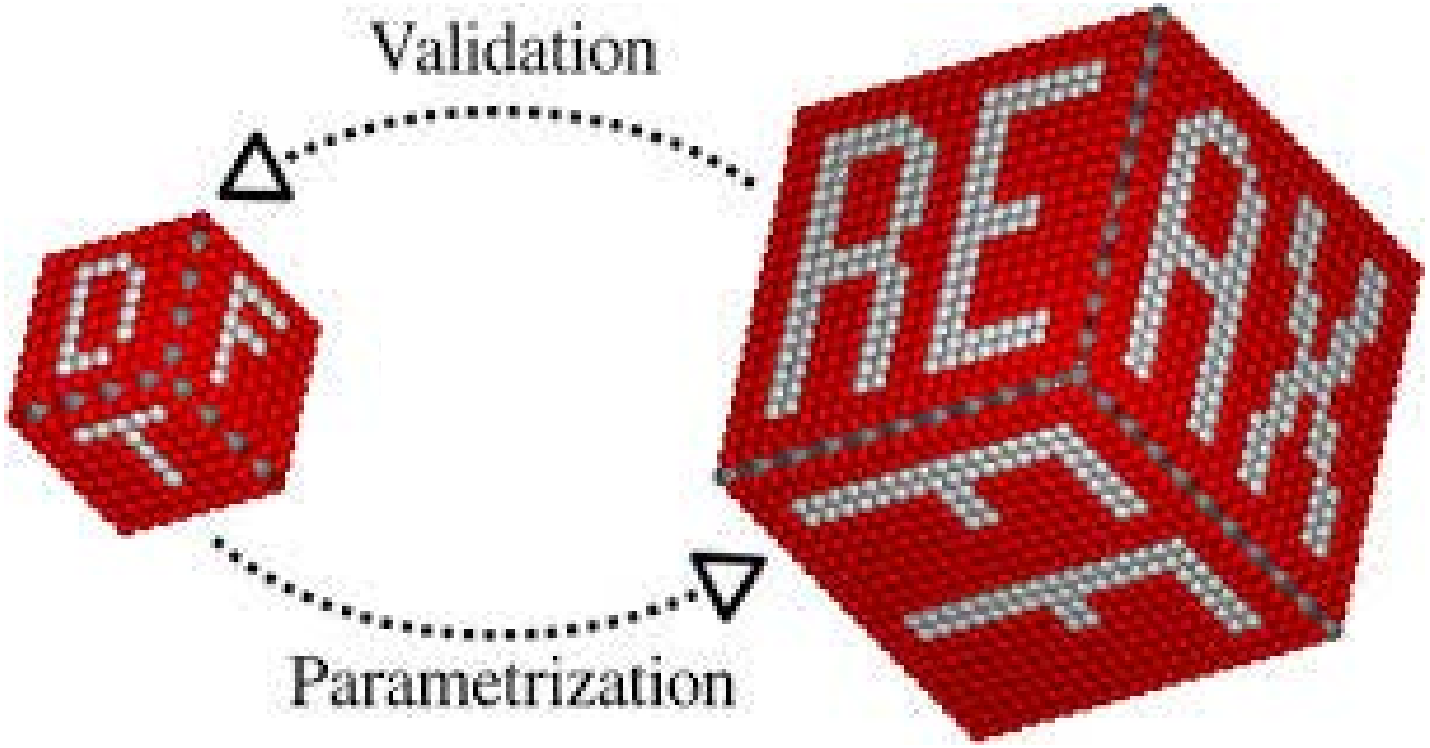
(L Atmani et al, Energy & Fuels, 2020)

MIMICKING the geological degradation of organic matter (type III



MIMICKING the geological degradation of organic matter (type III kerogen, cellulose, lignin)

➔ Reactive potential : REAXFF / AIREBO

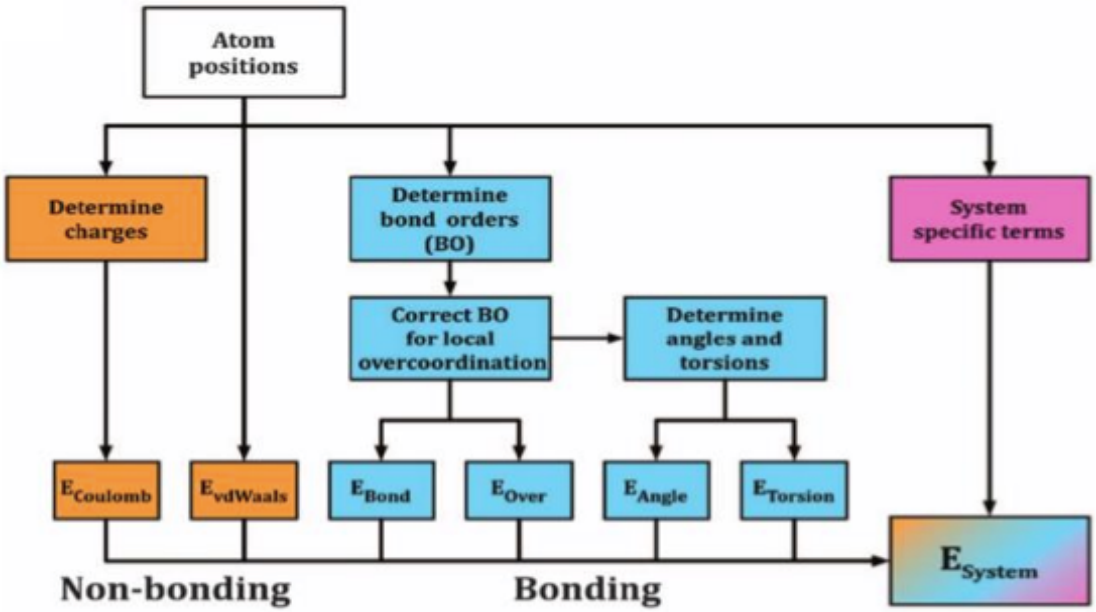


MIMICKING the geological degradation of organic matter (type III kerogen, cellulose, lignin)

➔ Reactive potential : REAXFF / AIREBO

- First version: Van Duin et al. (2001)
- Bond-order based reactive force field

$$E_{system} = E_{bond} + E_{over} + E_{under} + E_{val} + E_{pen} + E_{tors} + E_{conj} + E_{vdWaals} + E_{Coulomb}$$



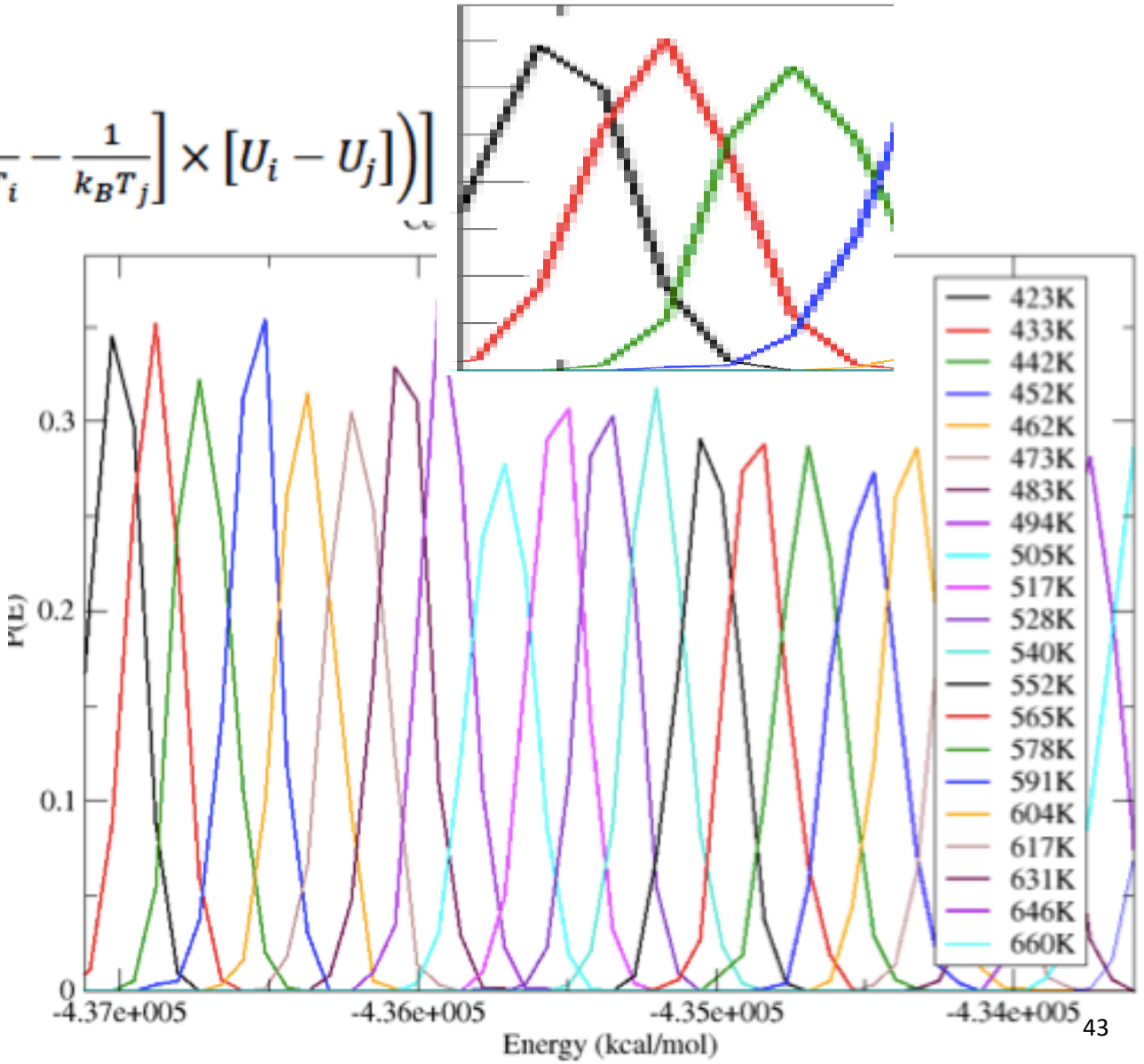
MIMICKING the geological degradation of organic matter (type III kerogen, cellulose, lignin)

$$P_{ij}^{acc} = min\left[1, exp\left(\left[\frac{1}{k_B T_i} - \frac{1}{k_B T_j}\right] \times [U_i - U_j]\right)\right]$$

Replica Exchange Molecular Dynamics (Parallel Tempering)

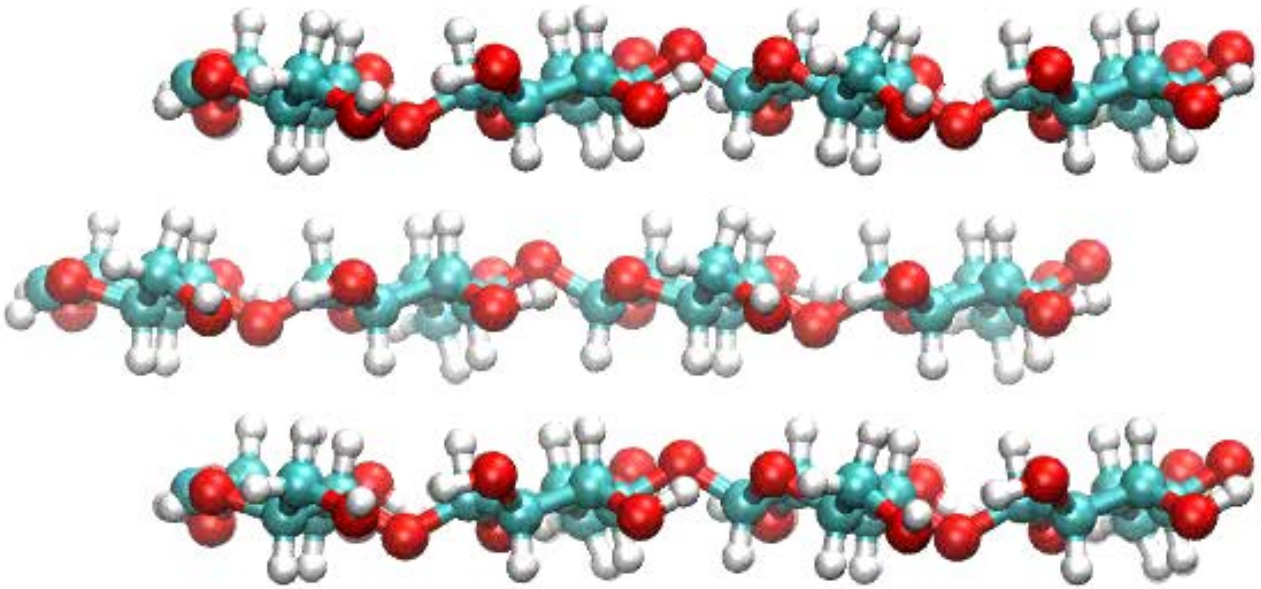
+

Reactive potential



MIMICKING the geological degradation of organic matter (type III kerogen, cellulose, lignin)

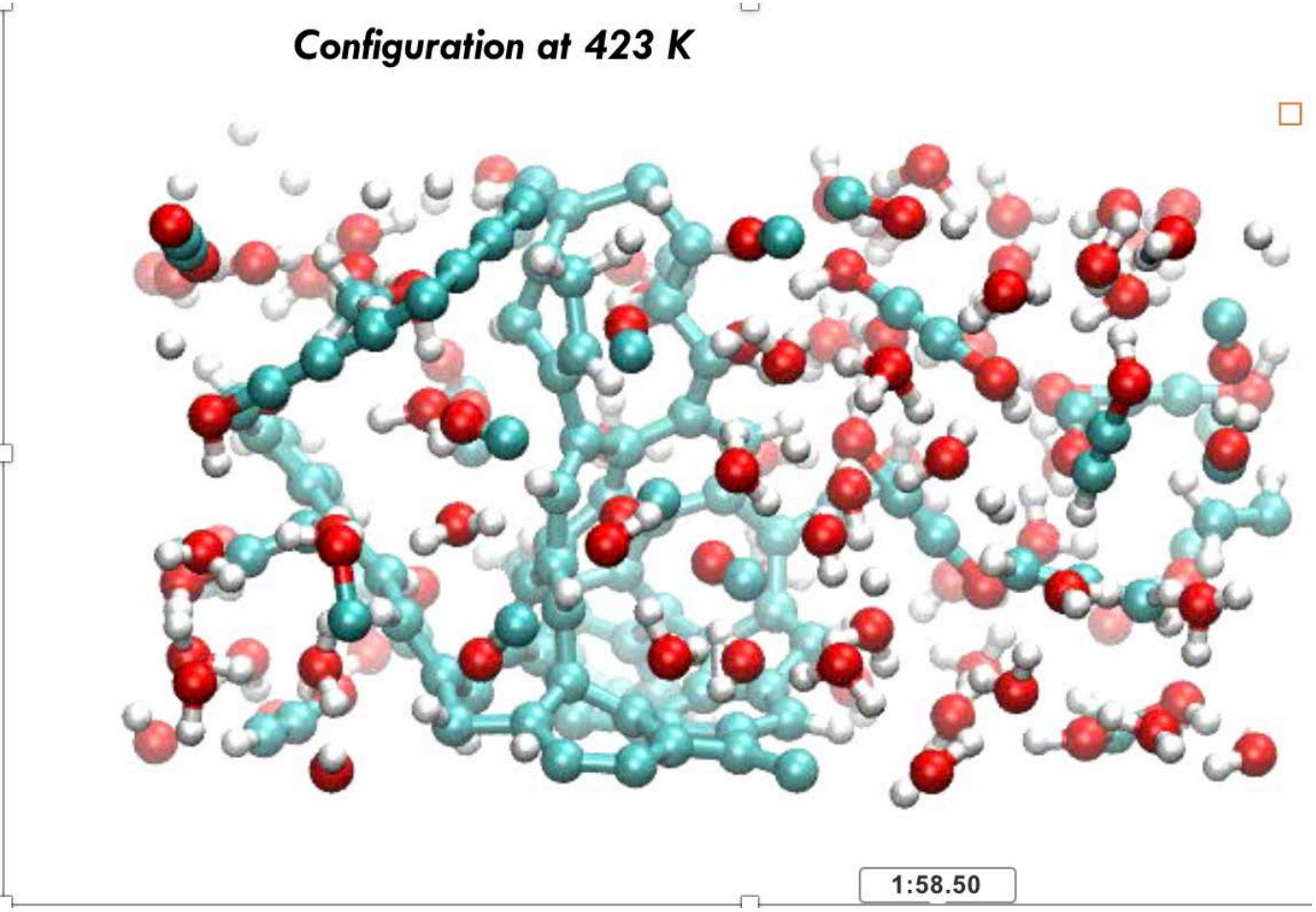
Configuration at 423 K



- Conditions:
  - Initial configuration: molecular crystal of cellulose
  - 32 replica between T=423 K and T = 3500 K
  - Potential ReaxFF 2013

L. Atmani et al, RS Chem. Science, 2017

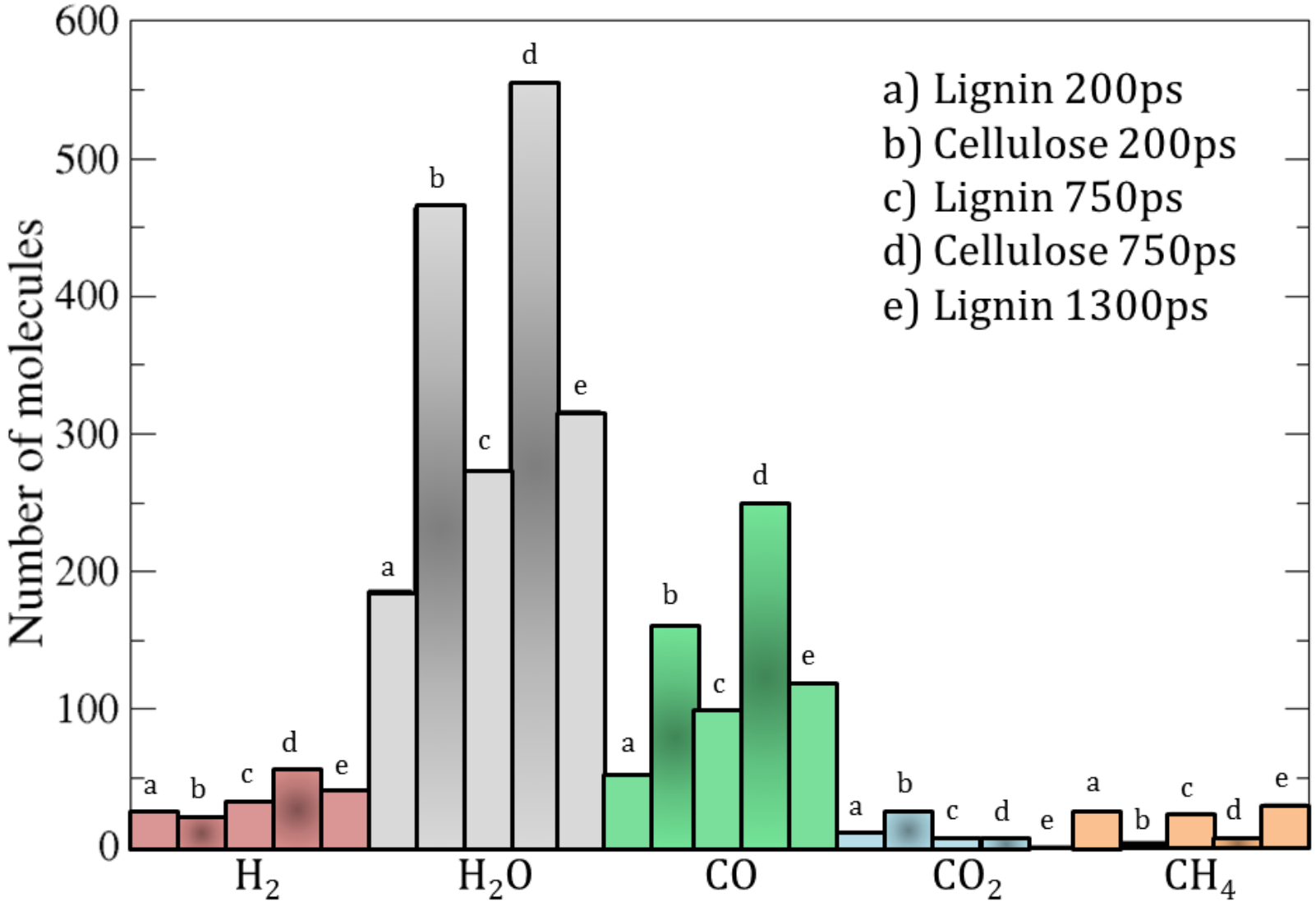
MIMICKING the geological degradation of organic matter (type III kerogen, cellulose, lignin)



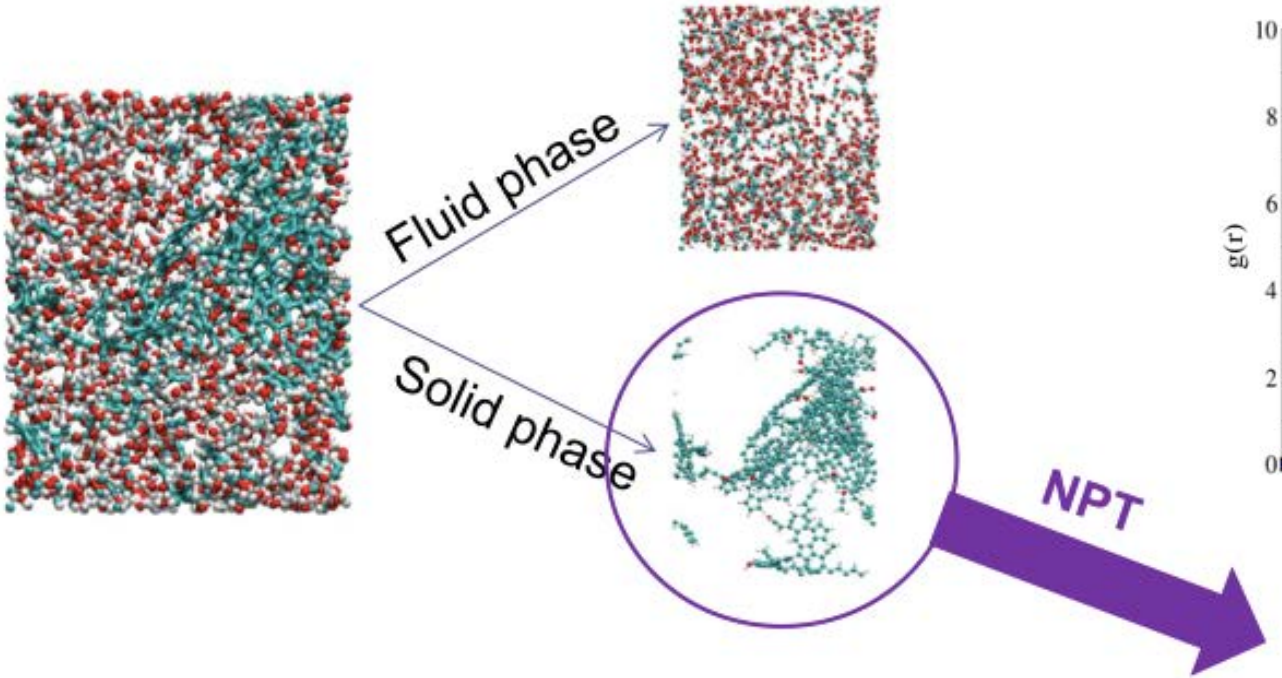
- Conditions:
  - Initial configuration: molecular crystal of cellulose
  - 32 replica between T=423 K and T = 3500 K
  - Potential ReaxFF 2013

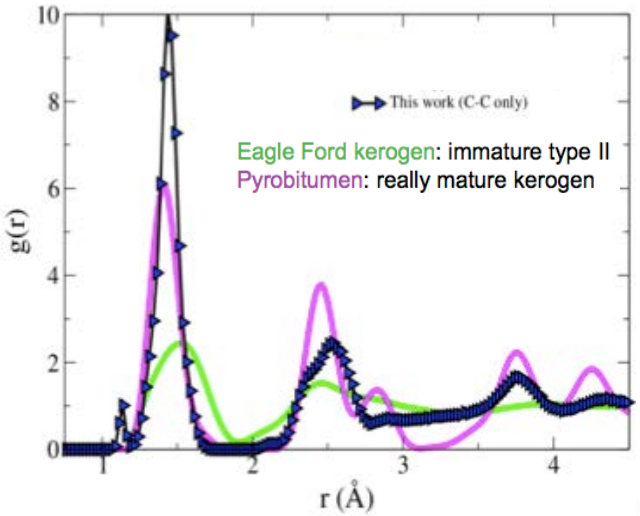
L. Atmani et al, RS Chem. Science, 2017

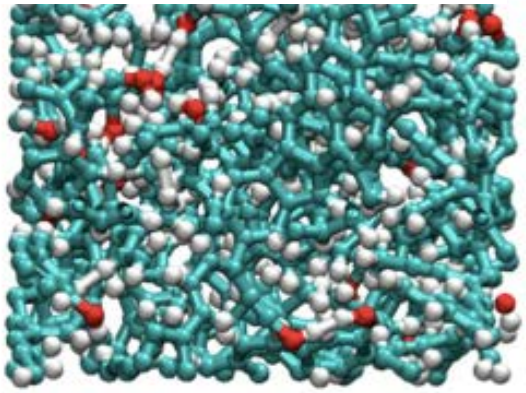
Small molecules formation



MIMICKING the geological degradation of organic matter (type III kerogen, cellulose, lignin)





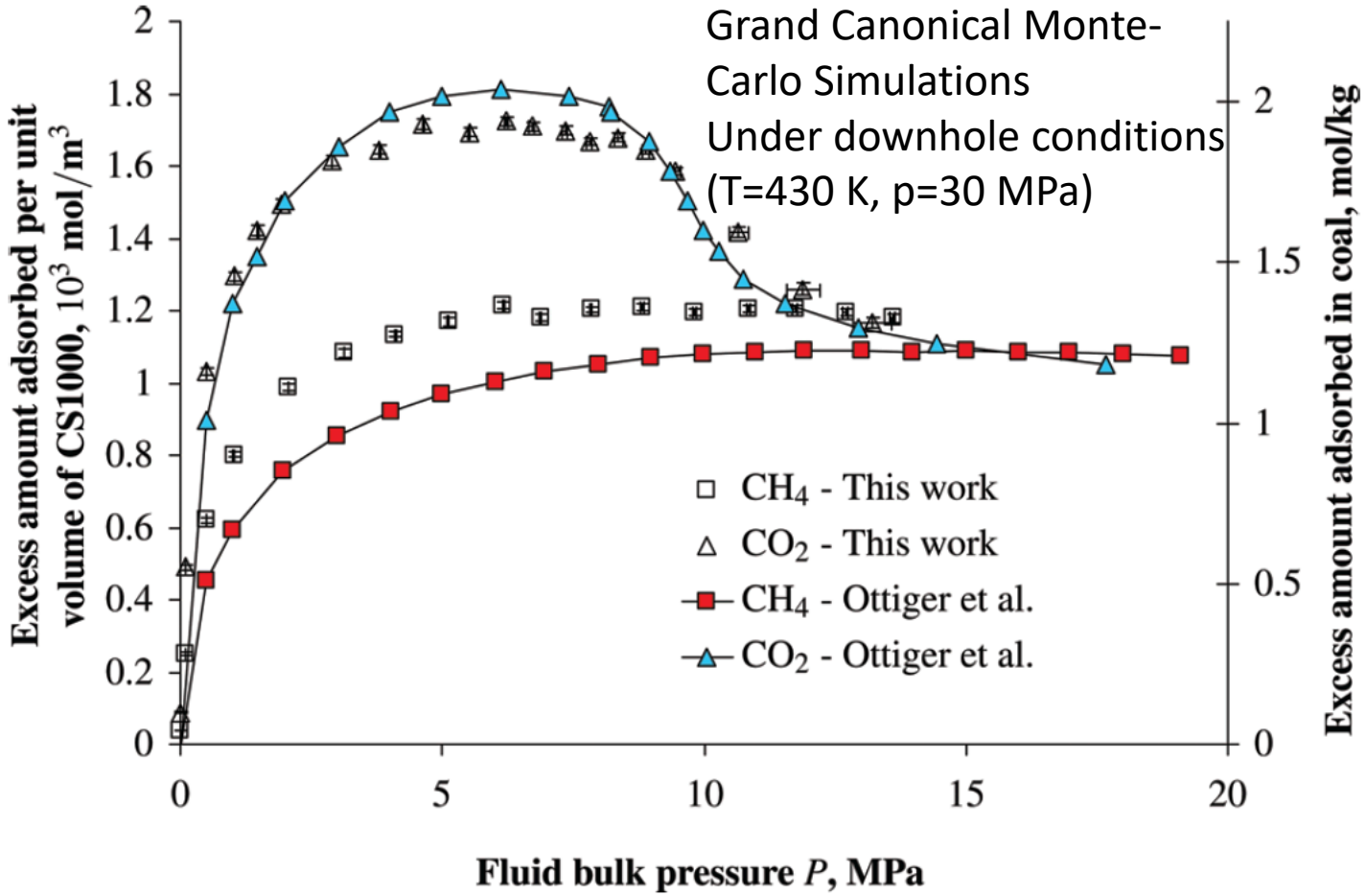


Isothermal compressibility

Kerogen*	2.7 10^{-10} Pa^{-1}
Bulk fluid*	2.9 10^{-8} Pa^{-1}
Our solid	2.4 10^{-9} Pa^{-1}

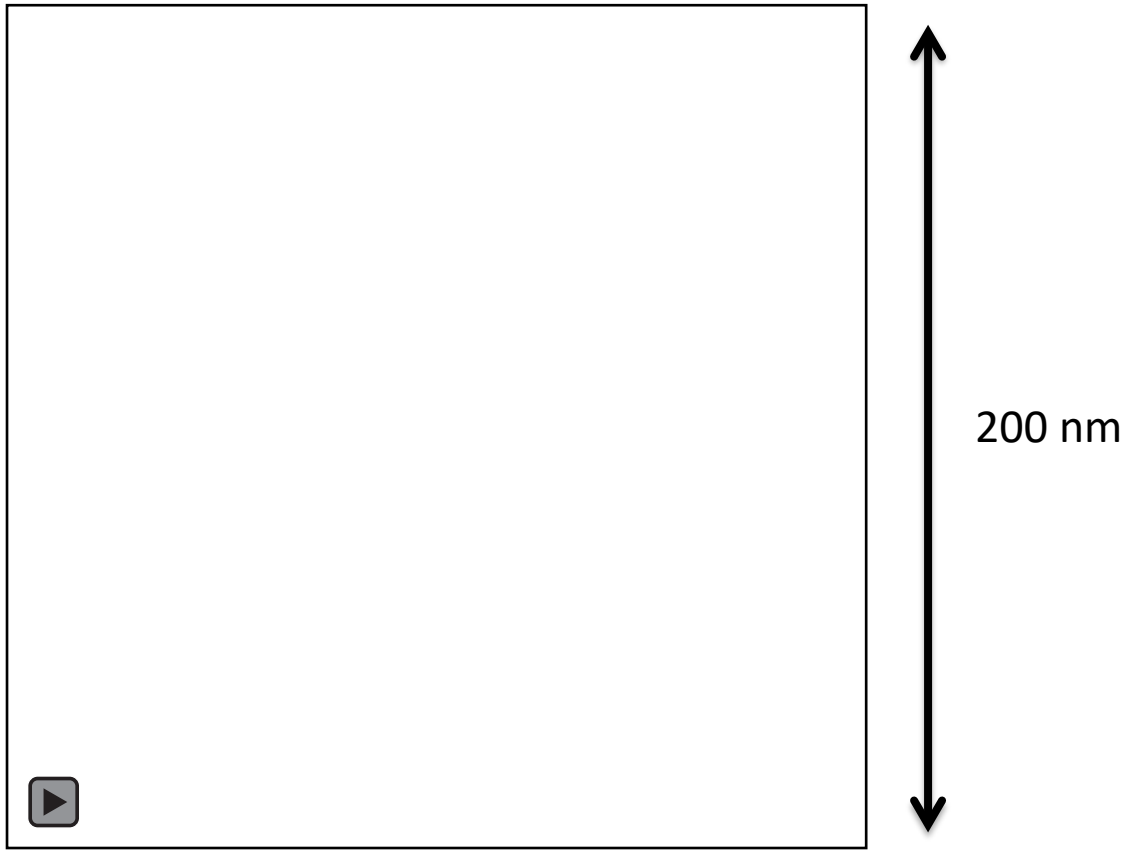
* J. Collell et al., *Molecular simulation of bulk organic matter in type II shales in the middle of the oil formation window*, (2014)

Sim. vs exp. Validation through adsorption



L. Brochard et al, Langmuir 2012

IMAGING the nanopore network of kerogen using e-tomography (TEM)

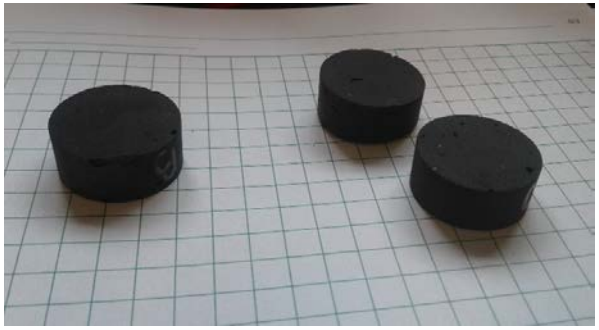


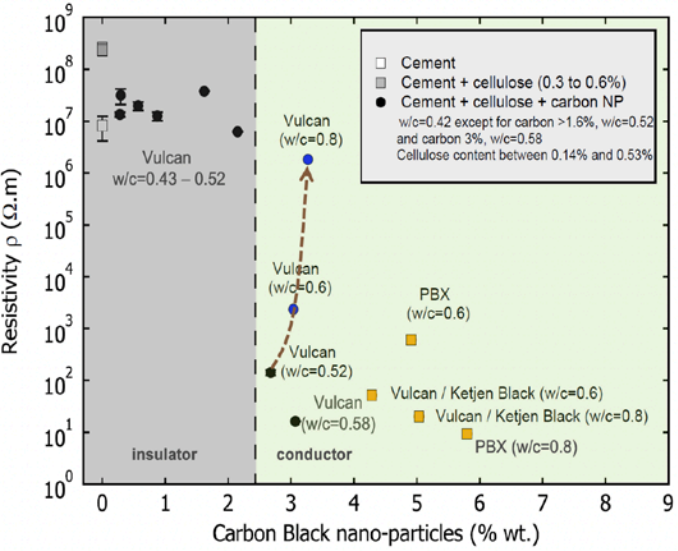
➔ We finally “see” the nanopore 3D-network (with a resolution ~ 1 nm)
FIB/SEM sample cutting / Denoising the images / Correct for missing wedge

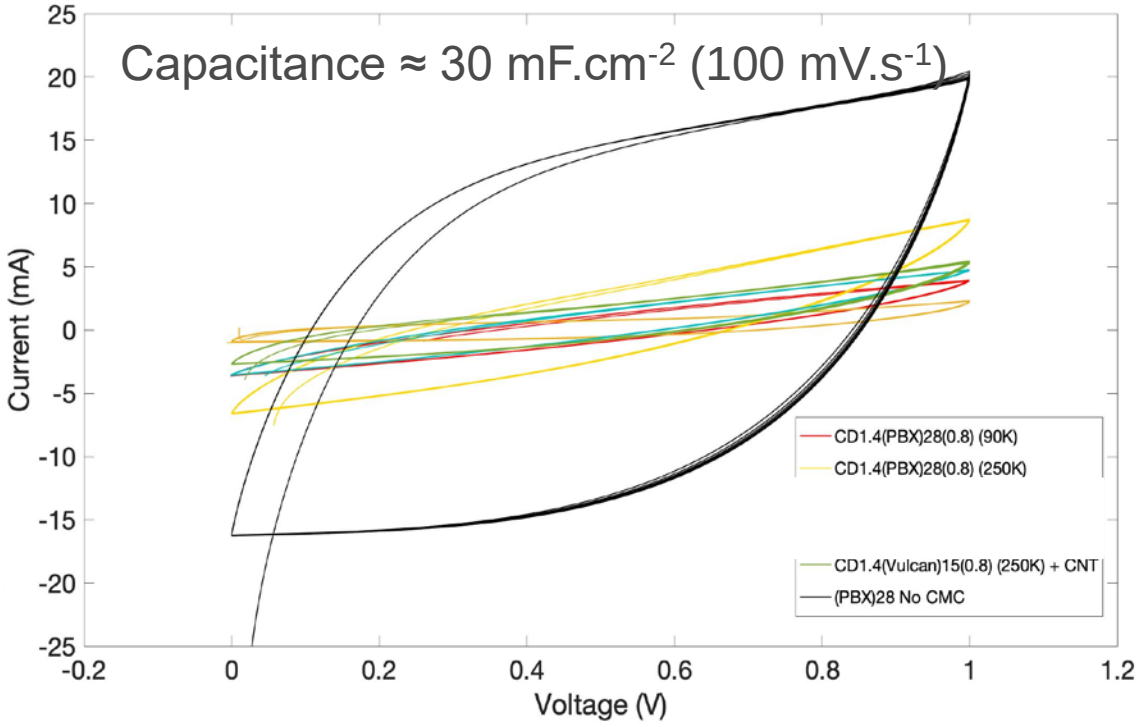
(Daniel Ferry, Olivier Grauby, – CINaM, Aix Marseille Univ./CNRS, Marseille, France**)**

From simulations to new materials:

…mixing cement and porous carbons:







… and more goodies: FT resistant / large Joule effect / accelerated carbonation (CCUS strategy)

MIT-CNRS International Patent, Jan-12-2019

Thanks for your attention