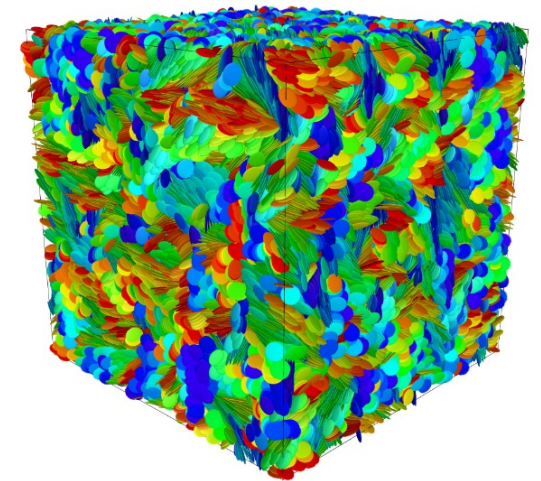
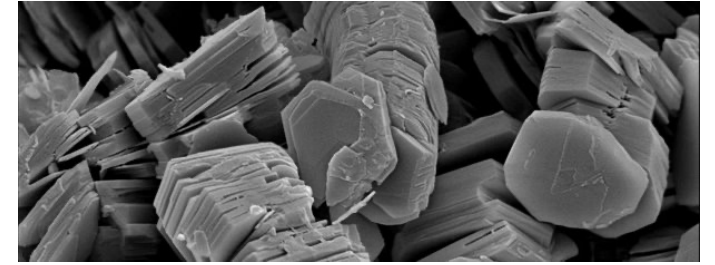
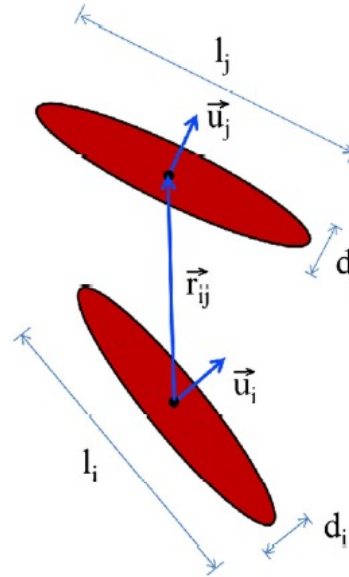
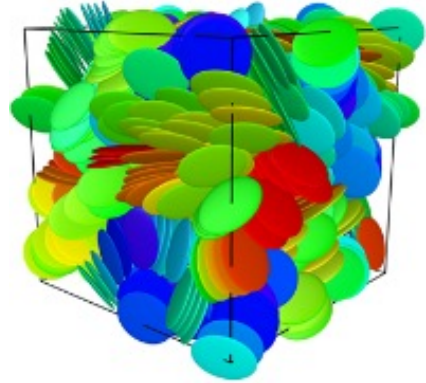
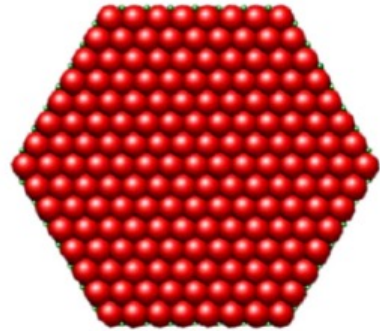


Particle-Scale Modelling of clays

Catherine O'Sullivan

Sara Bandera, Yohei Nakamichi, Stefano Angioletti Uberti, Paul Tangney

Particle scale modelling of clay



Part 1: Motivation

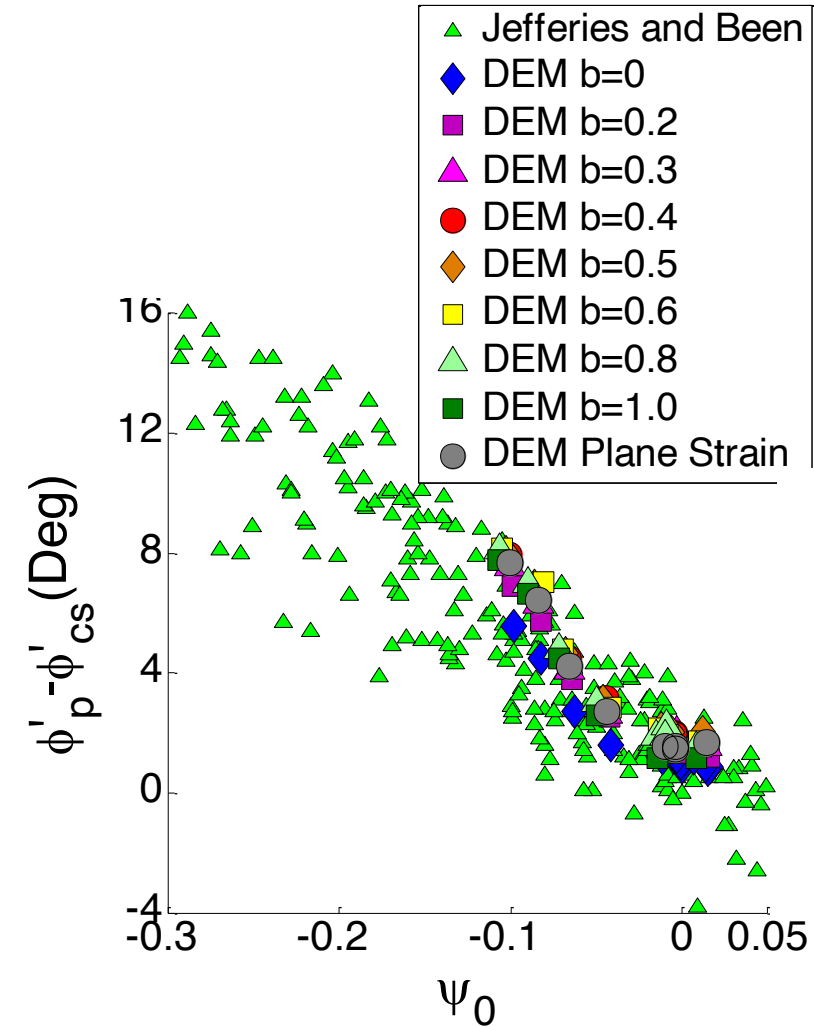
Part 2: Modelling
Options

Part 3: Particle
Interactions

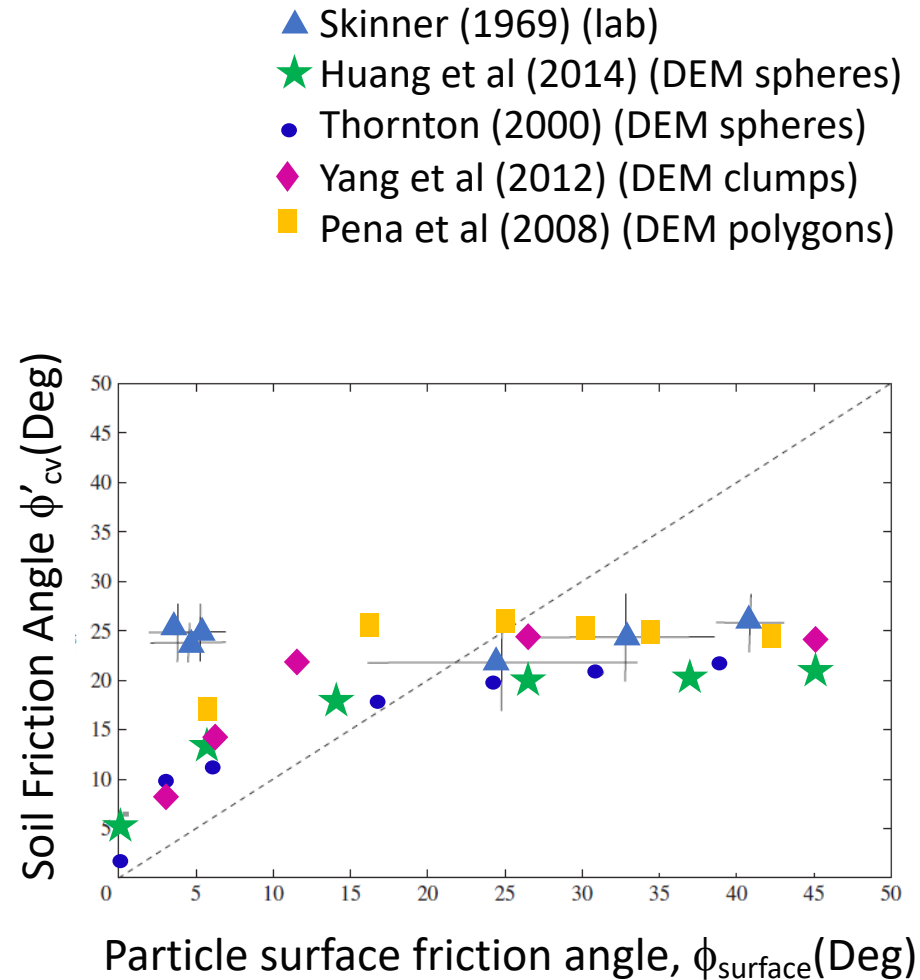
Part 4: System
Response

Part 1: Why model clay at the particle scale?

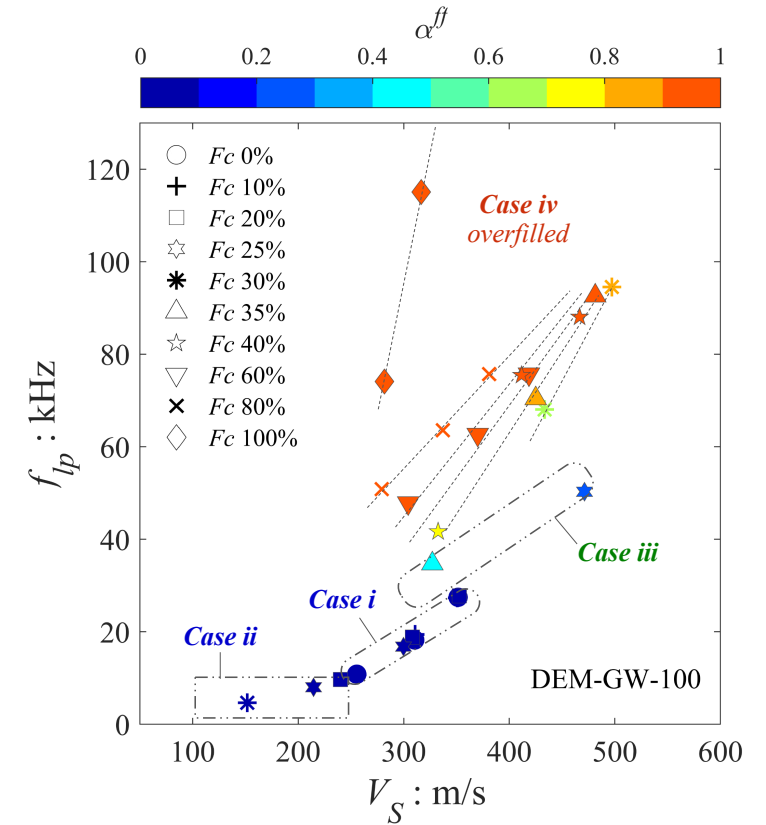
Sand Behaviour Contributions from DEM



Verification of frameworks

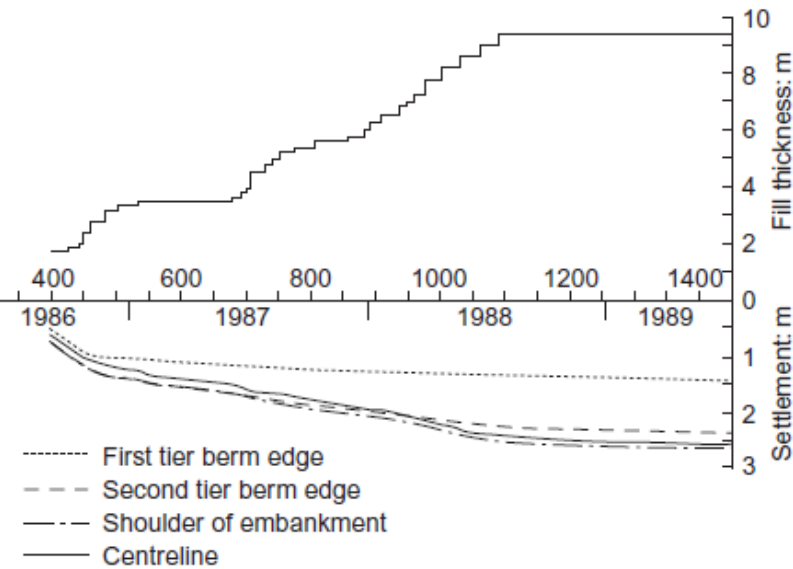


Thought experiments



New experimental methods

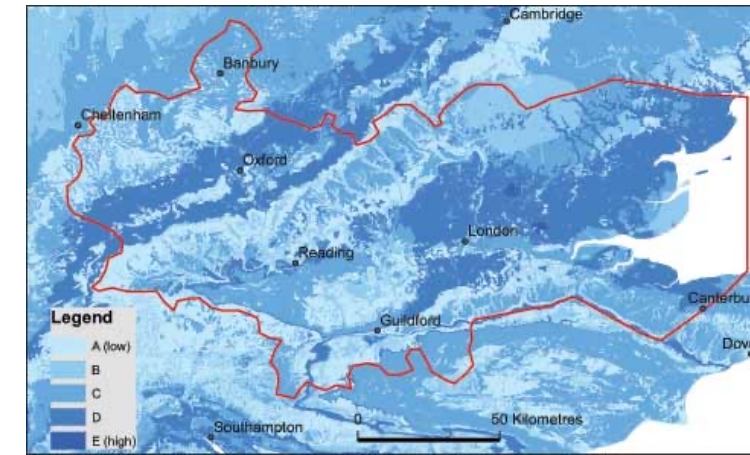
Clay – challenges posed



Large, time dependant settlement observed at Athlone road embankment in Ireland (Long and O’Riordan, 2001)

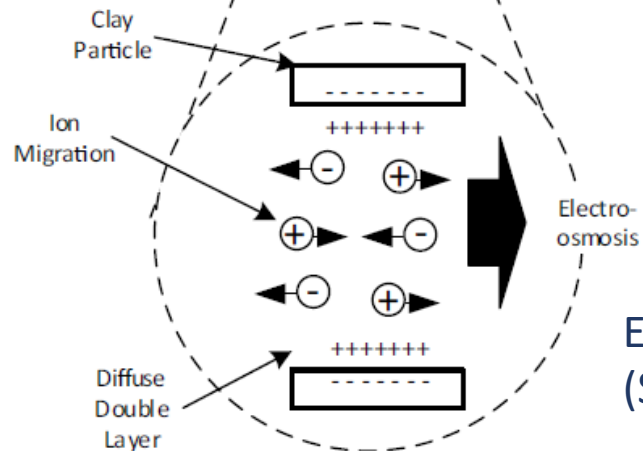
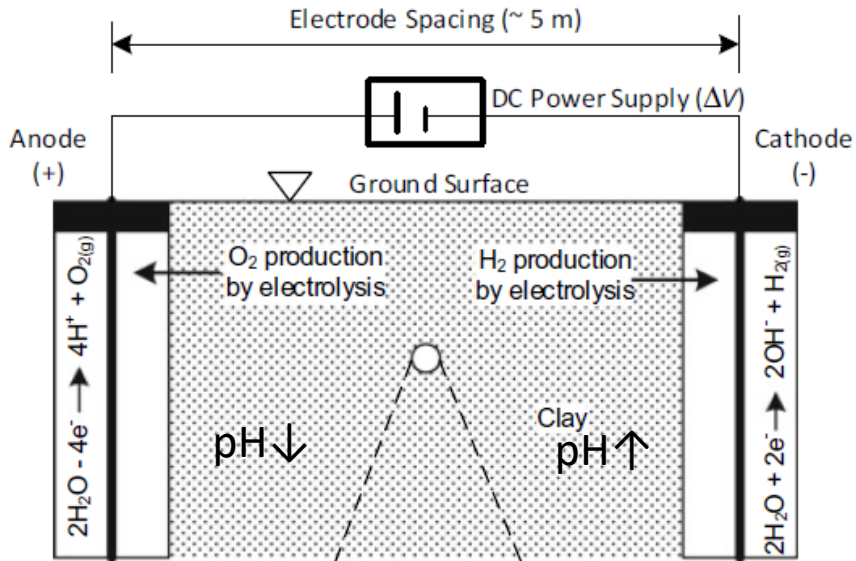


Quick clay landslide at Lyngseidet, Norway
September 3, 2010 (220,000 m³)
(Geological survey of Norway, 2015)



Hazard potential for shrink–swell clay in the Thames basin (British Geological Survey, 2019)

Clay – challenges posed

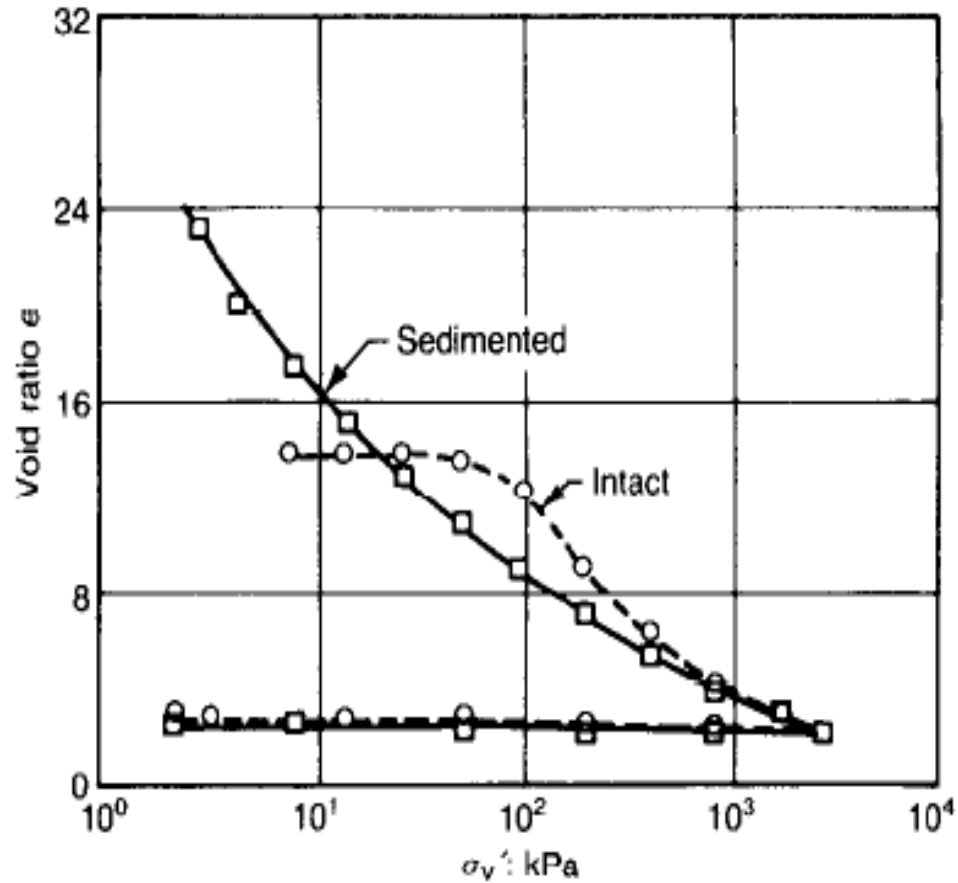


Electro-osmosis
(Shackleford et al., 2019)

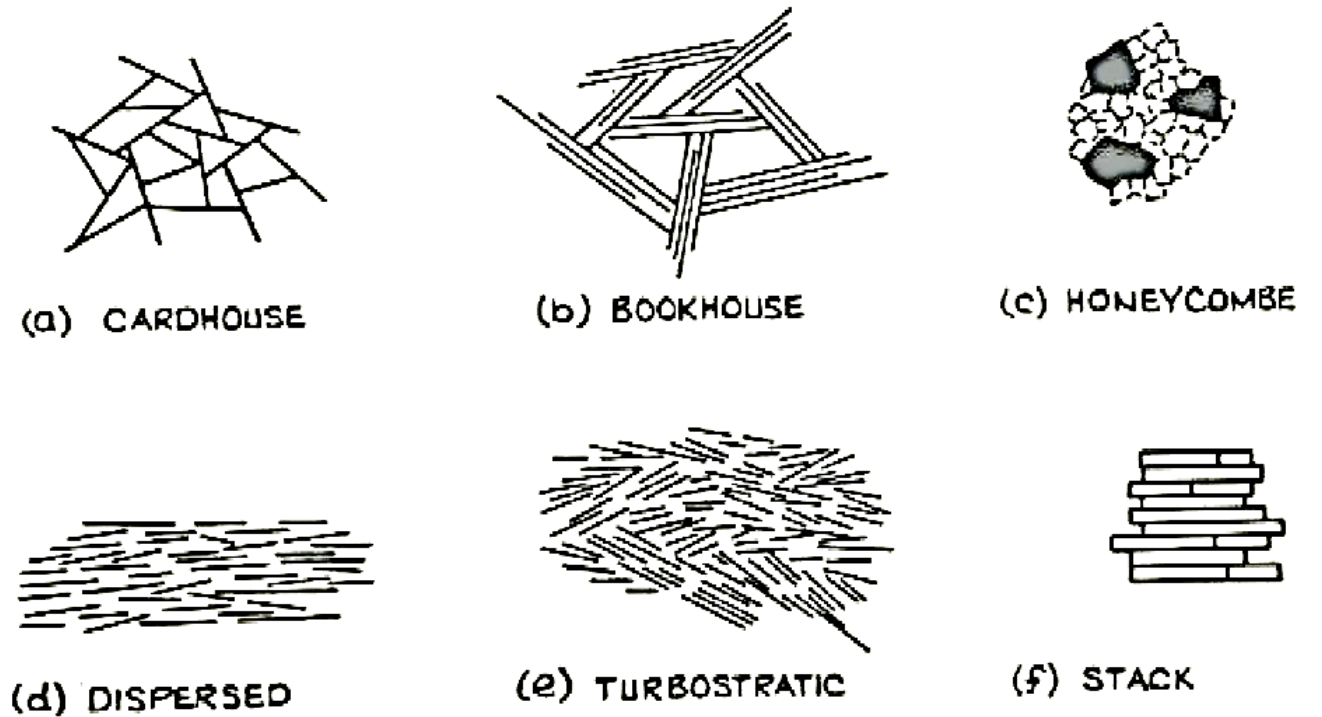


RemediaClay - Keller
injection of a potassium and
ammonium ion solution
Ground Engineering - 2022

Clay behaviour

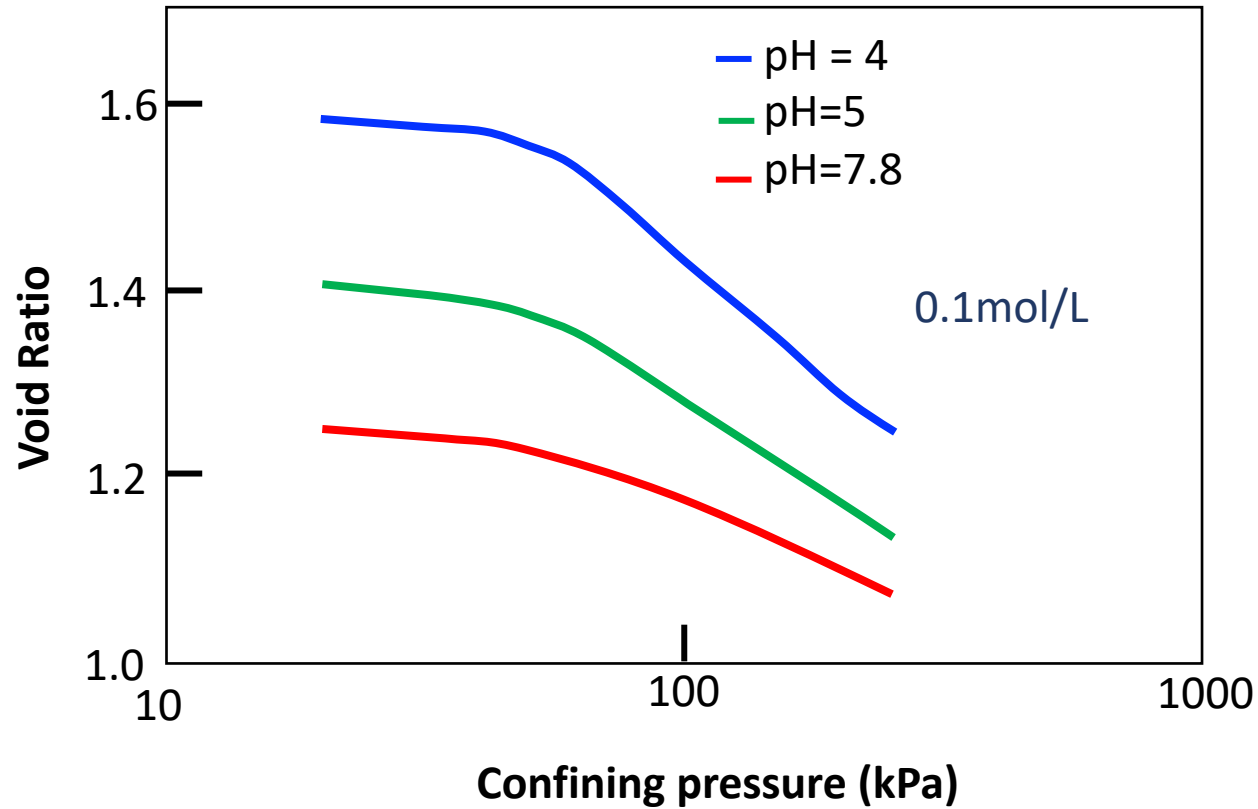


Comparison between natural and reconstituted clays for Mexico City clay (Leroueil and Vaughan, 1990)

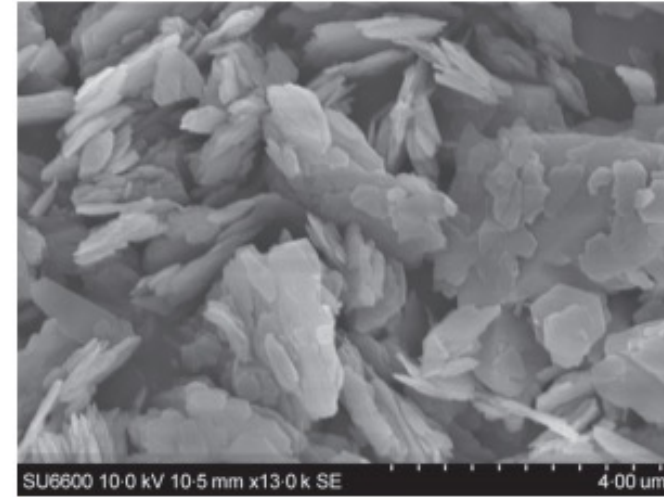


Idealised clay fabrics (Sides and Barden, 1971)

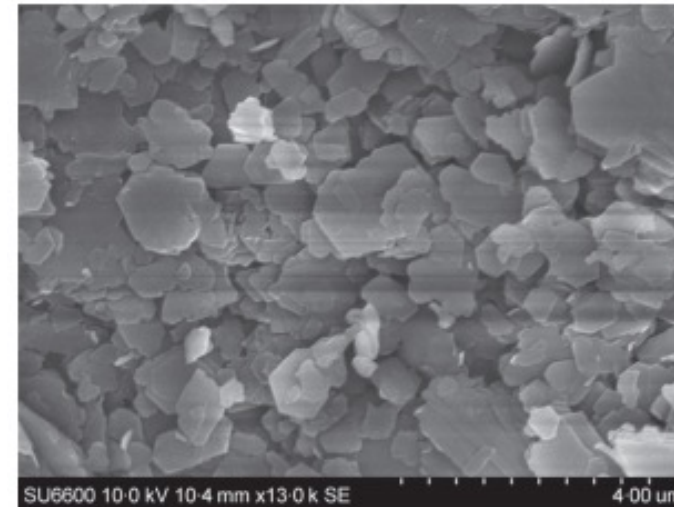
Clay behaviour



(Kaolinite: Wang and Siu, 2006)



SEM image of kaolinite prepared with acidic water (pH < 5.5)

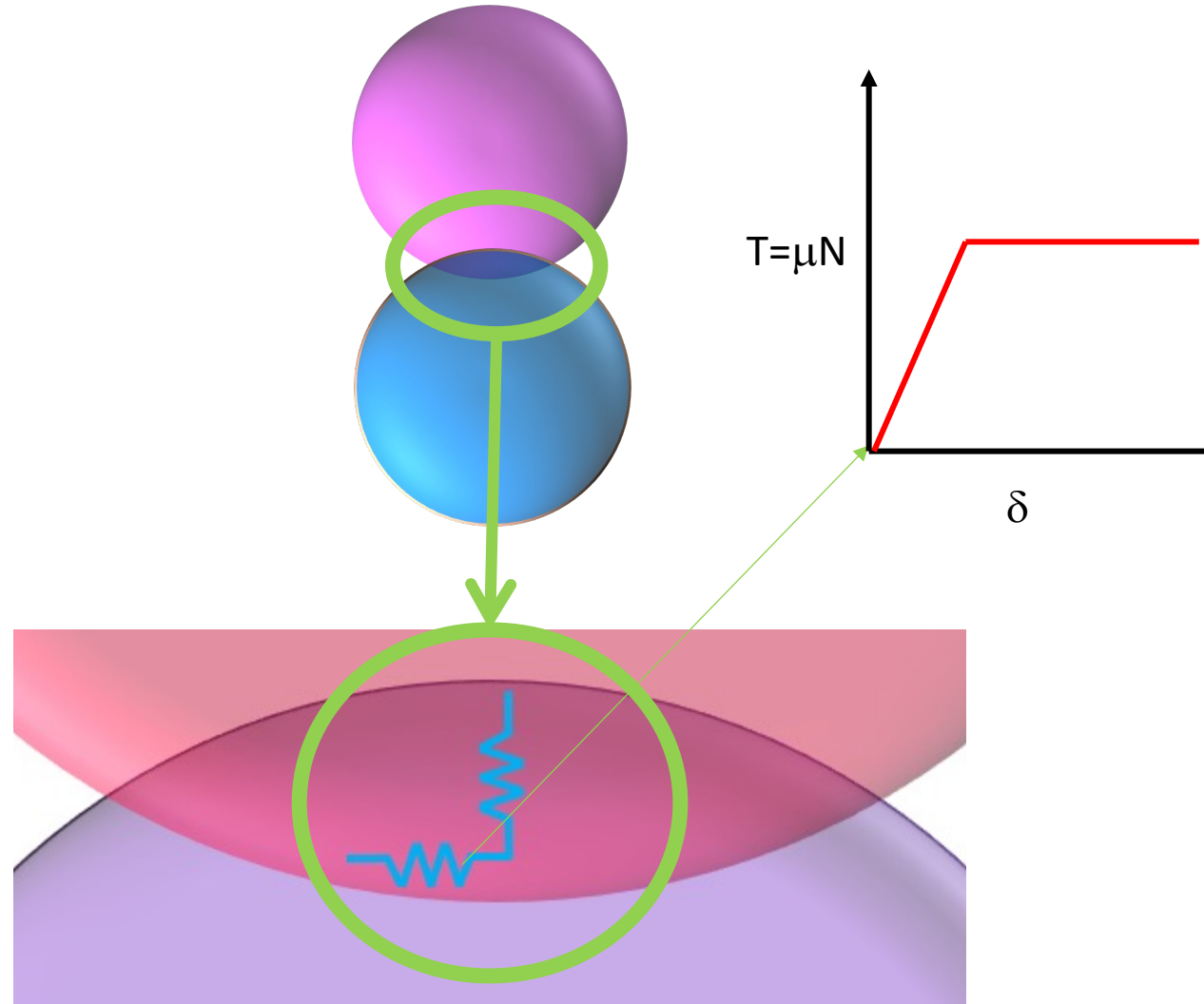
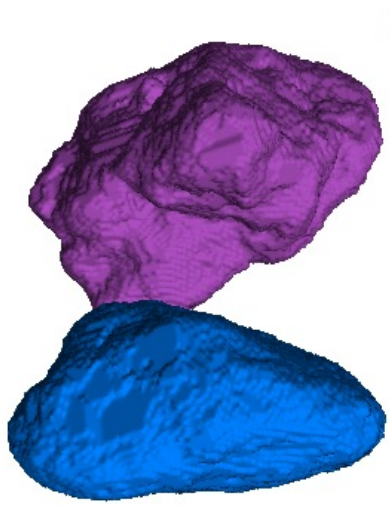


SEM image of kaolinite prepared with alkaline water (pH > 5.5)

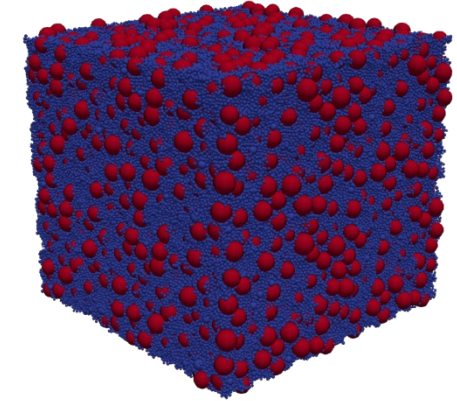
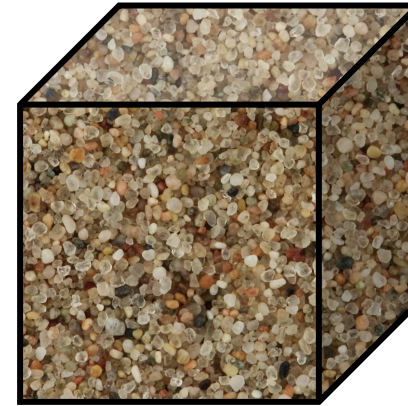
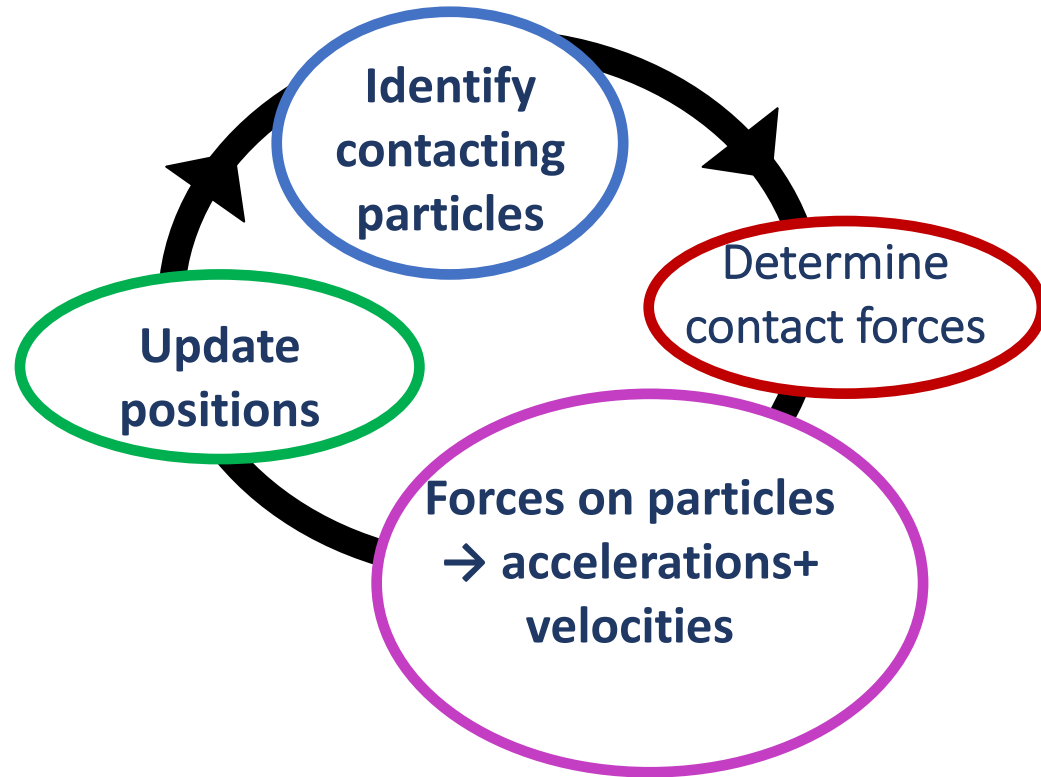
Electrolyte concentration negligible

(Pedrotti and Tarantino, 2017)

Modelling Tool: Discrete element method



Modelling Tool: Discrete element method



HPC at Imperial College



HPC Computer Room

Molecular Dynamics

Simulates interaction between atoms and molecules

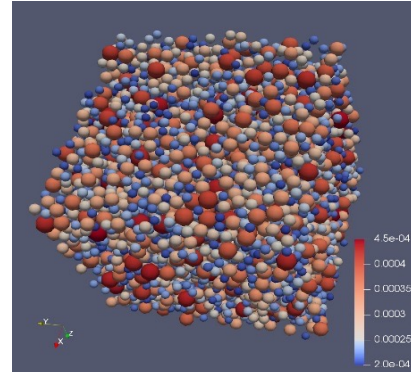
Algorithmically similar to DEM

Can use MD codes to run DEM simulations

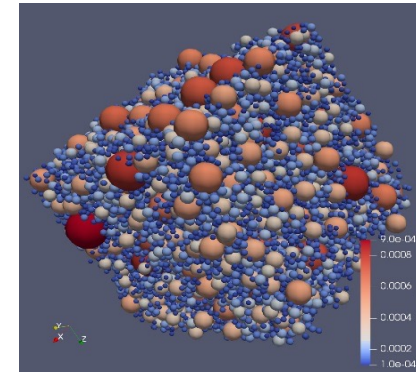
Considers energy between particles (atoms) “potentials”

Gradient of potential energy – separation distance plot gives force

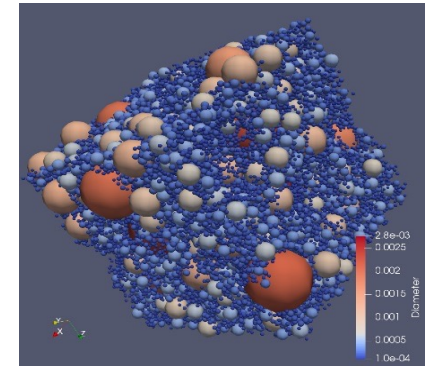
Consider dynamic equilibrium of particles



Spheres
 $C_u=1.2$

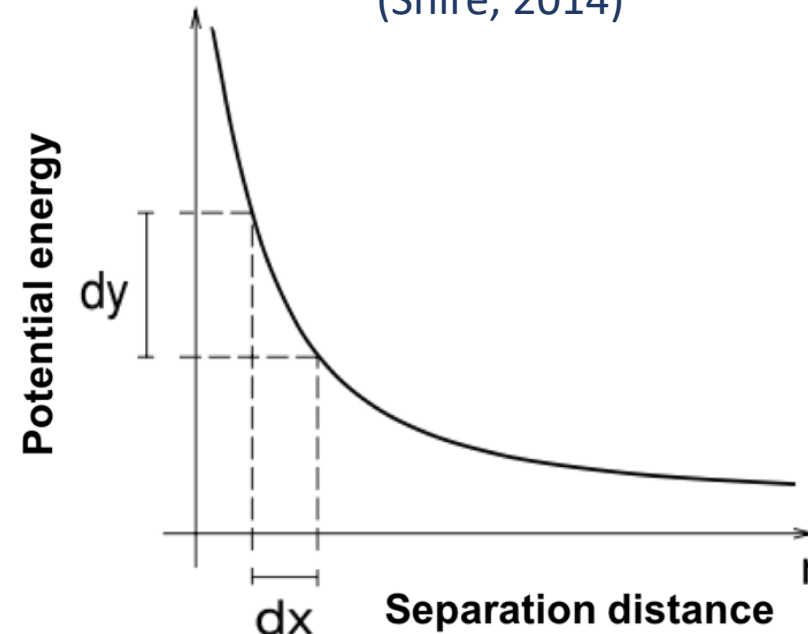


Spheres
 $C_u=3.0$

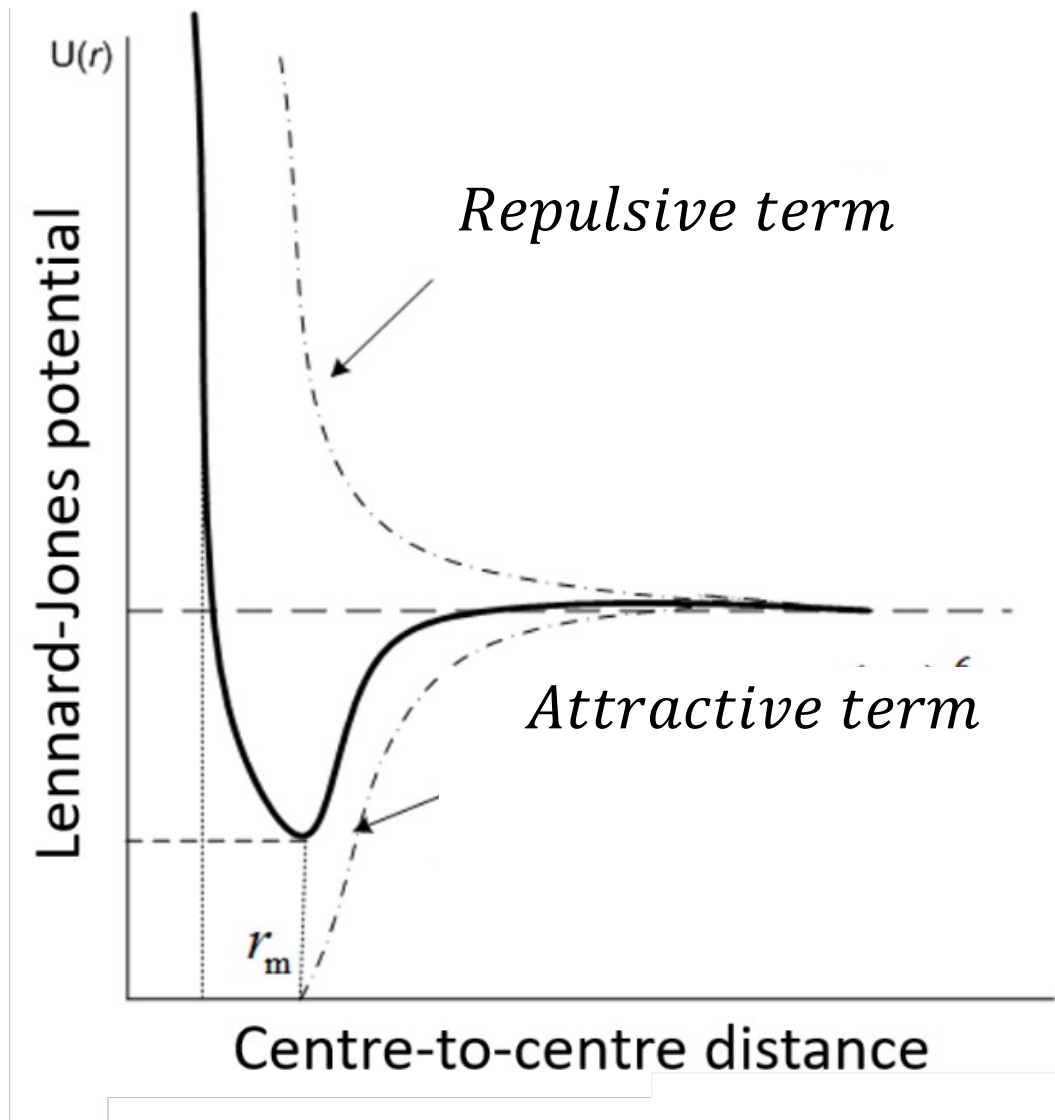


Spheres
 $C_u=6.0$

DEM models of sand generated using Molecular Dynamics code LAMMPS (Shire, 2014)

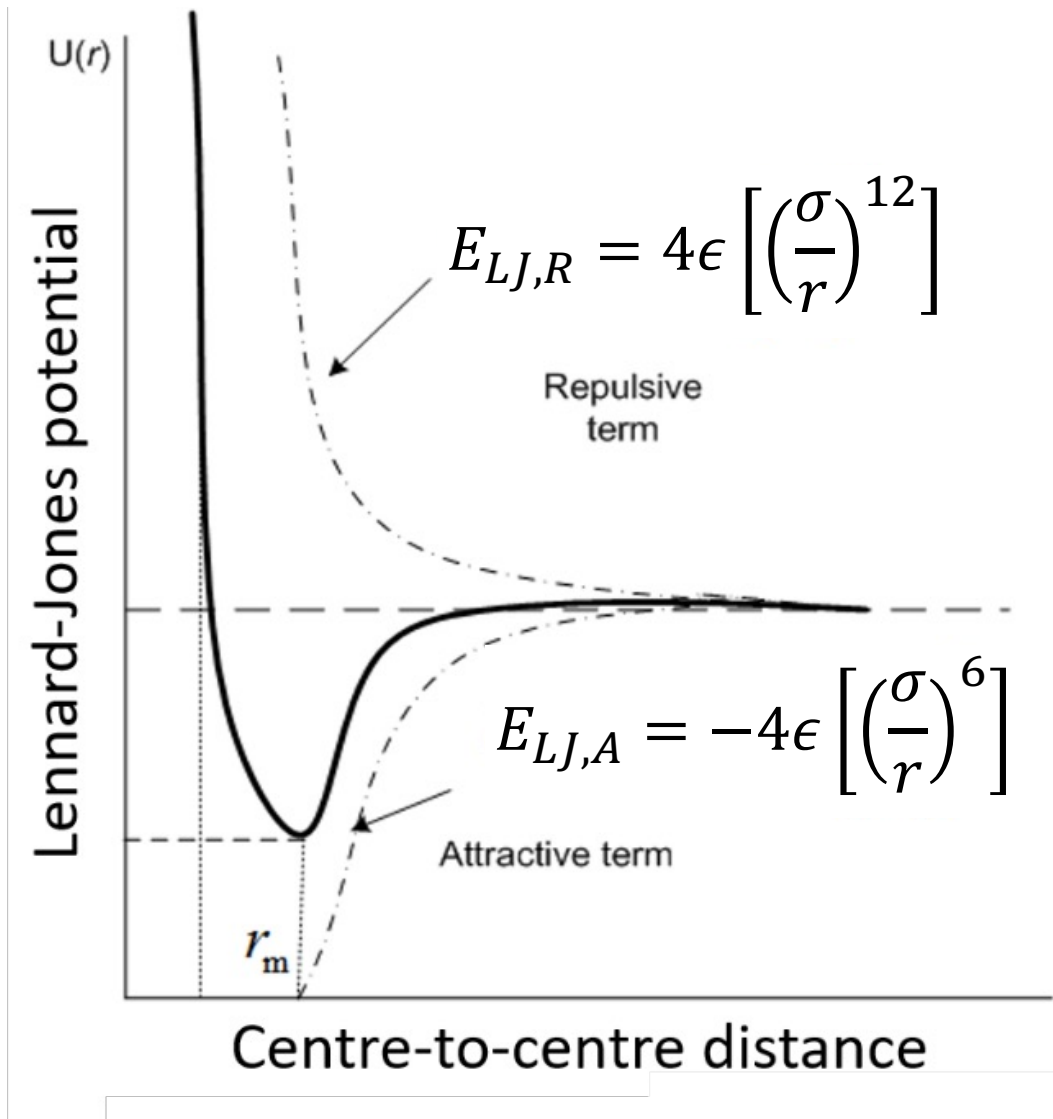


Lennard-Jones Potential



- Widely used in molecular dynamics simulations in a variety of studies for non-bonded interactions.
- First proposed by Lennard-Jones (1931) for investigating cohesive forces between ideal gas particles.
- Assumes spherical particles
- Useful to model colloids

Lennard-Jones Potential



$$E_{LJ} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

Repulsive term: $E_{LJ,R} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} \right]$

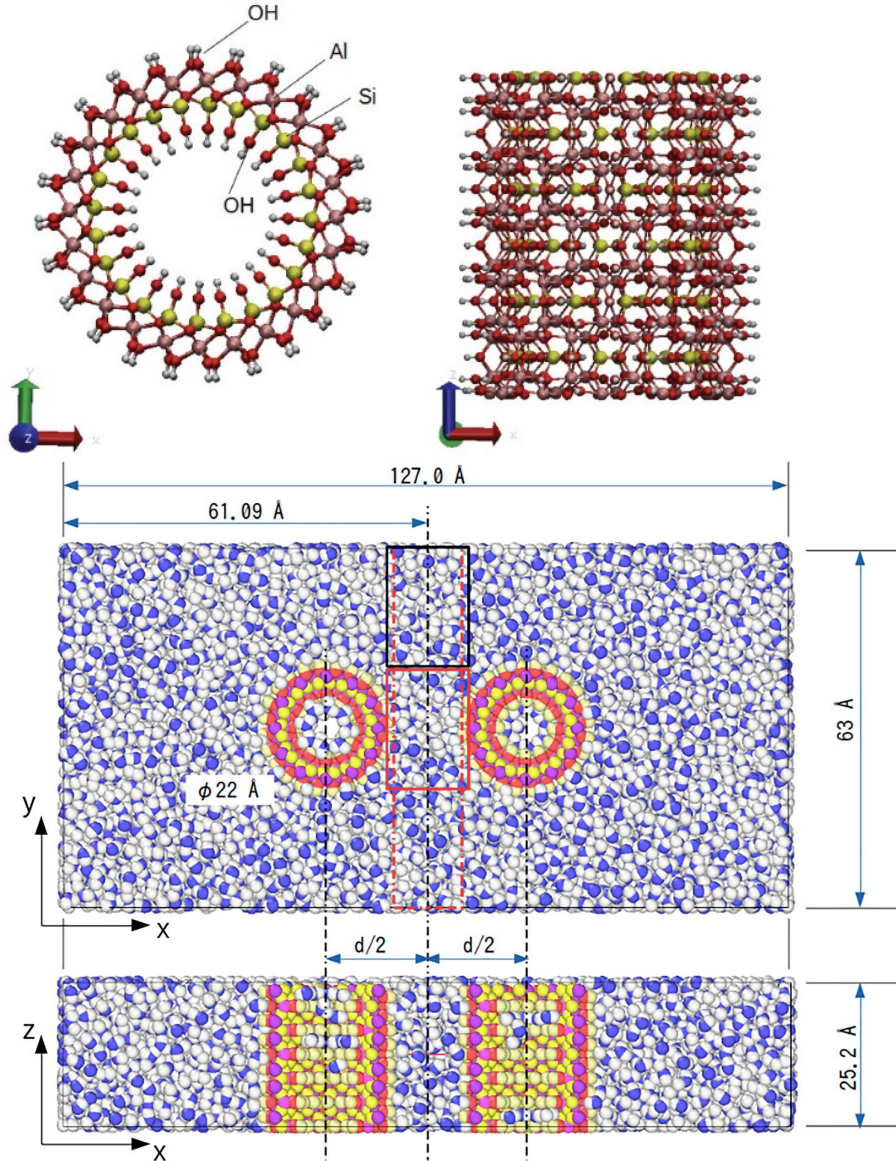
- Repulsive component of interaction
- Dominates at short distances

Attractive term: $E_{LJ,A} = -4\epsilon \left[\left(\frac{\sigma}{r} \right)^6 \right]$

- Van der Waals force
- Dominates at medium-large distances
- Exponent of 6 relates to equations for van der Waals force

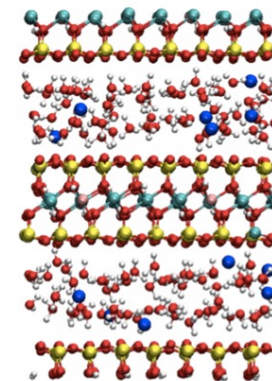
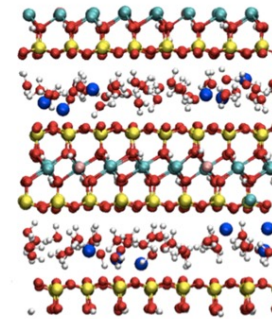
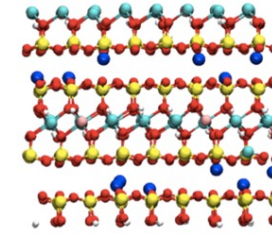
Part 2: Options to model clay

Modelling options – sub-platelet scale

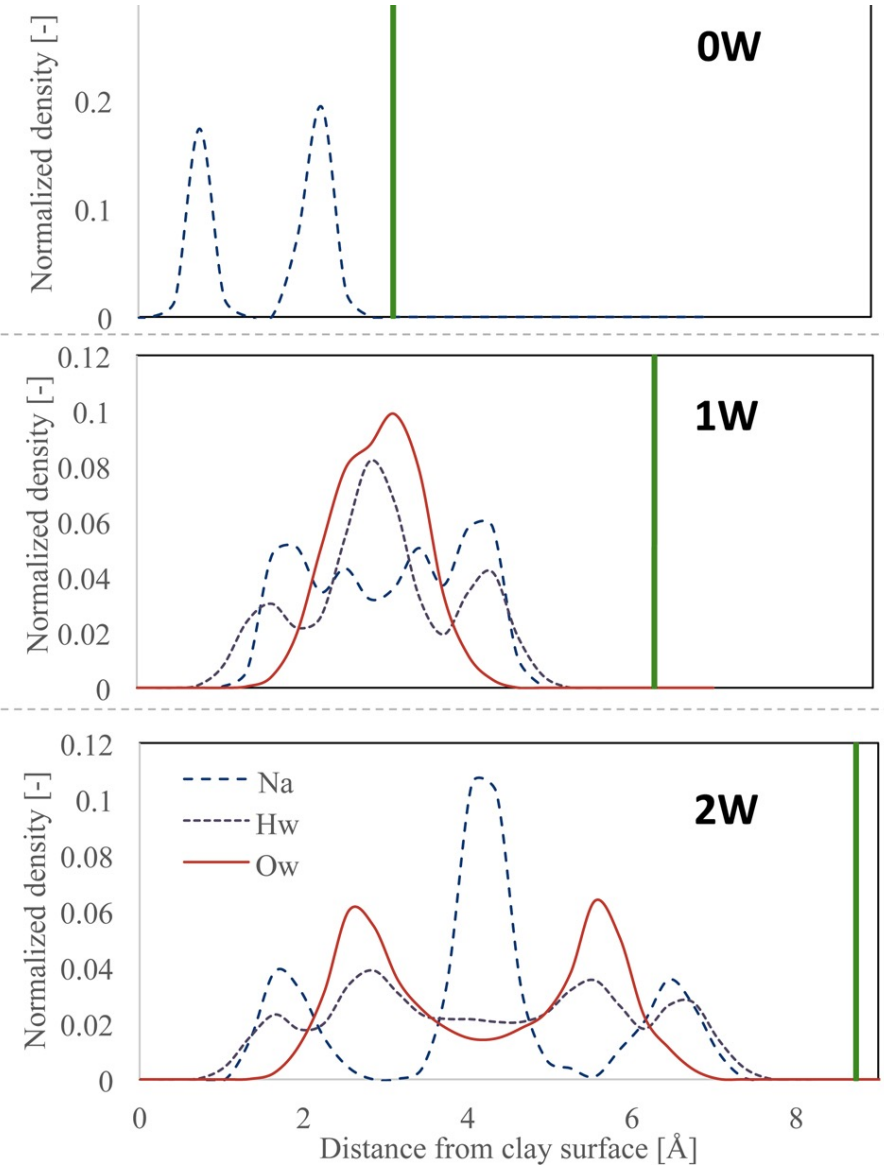


Imogolite

Zhu et al. (2019)

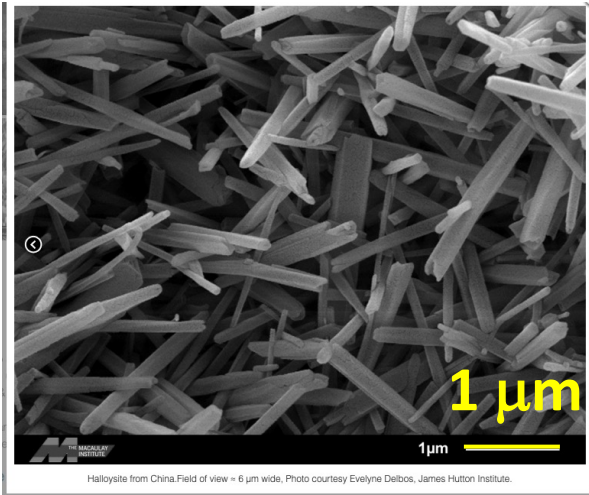


Smectite

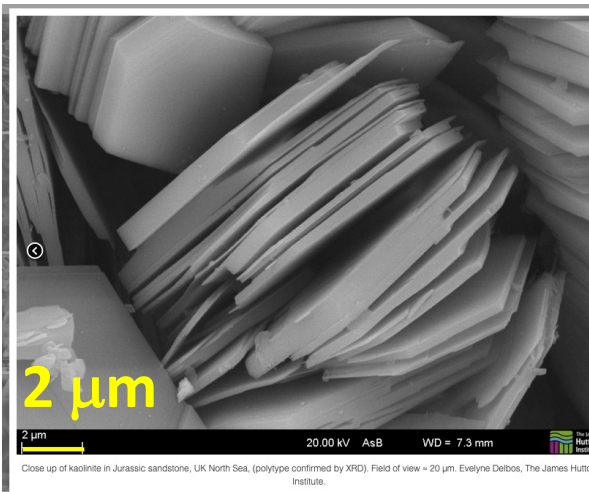


Honorio et al. (2017)

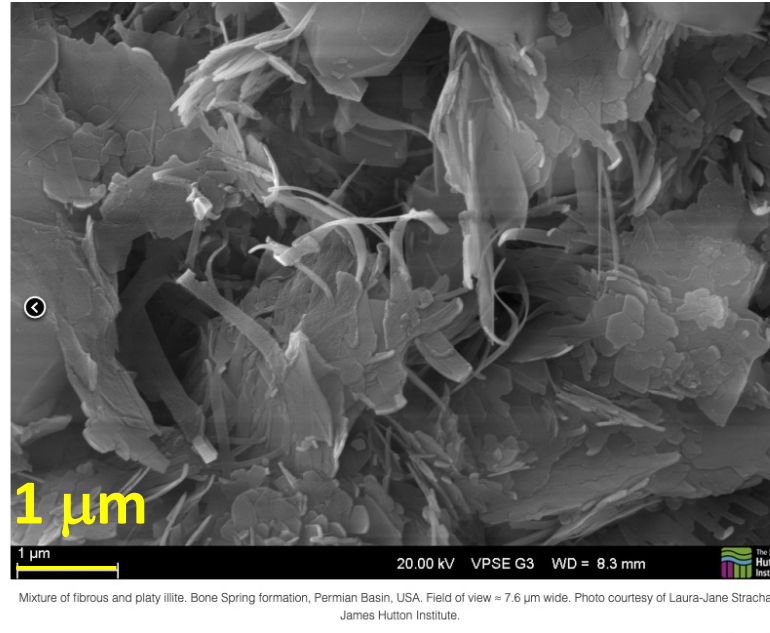
Clay minerals



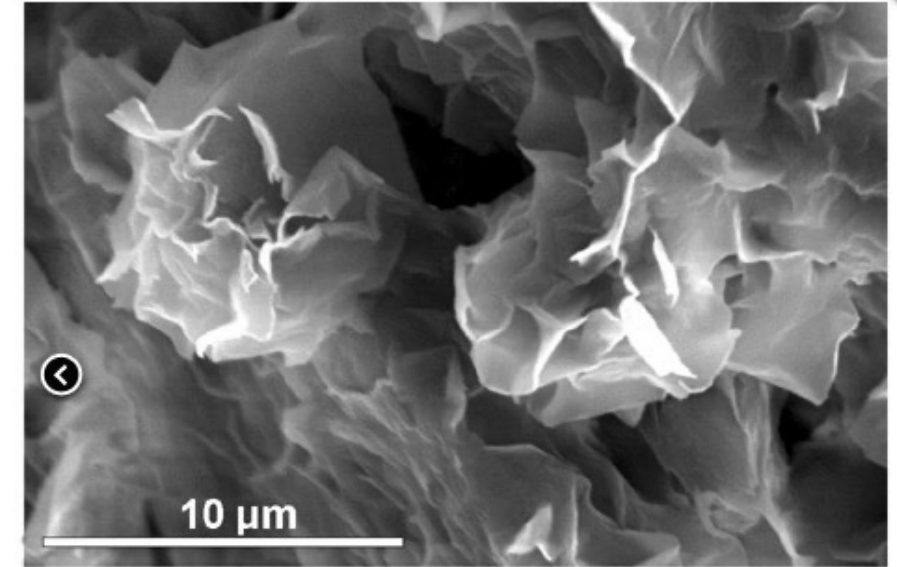
Hallosite



Kaolinite



Illite

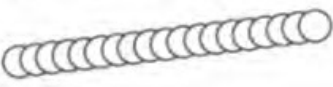
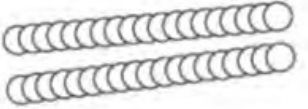
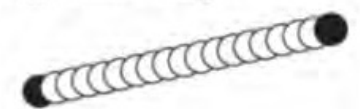



Montmorillonite

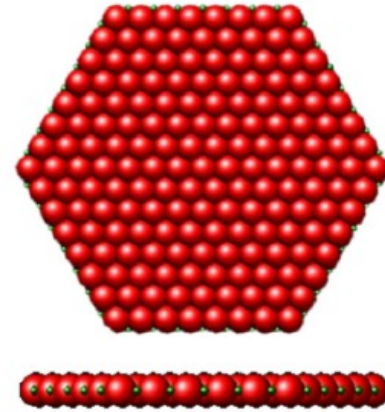
Montmorillonite showing a rose like texture, Miocene arkose, Madrid Basin, Spain. Fesharaki, O., García-Romero, E., Cuevas-González, J., López-Martínez, N. (2007) Clay mineral genesis and chemical evolution in the Miocene sediments of Somosaguas, Madrid Basin, Spain [DOI link](#). Field of view ≈ 22 µm wide. Photo courtesy of Emilia García-Romero, Universidad Complutense de Madrid, Spain.

‘Images of Clay Archive’ of the Mineralogical Society of Great Britain & Ireland and The Clay Minerals Society
<https://www.minersoc.org/images-of-clay.html>

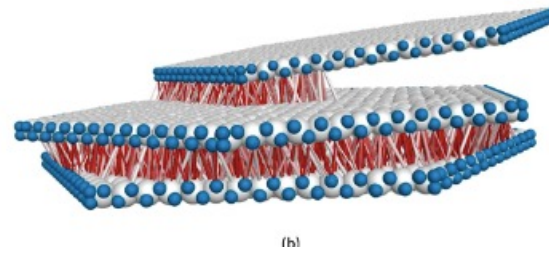
Modelling options – platelet scale

pH = 9	<p>— ○ Negative charge</p> 	<p>Face to face</p> 
pH = 4	<p>— ○ Negative charge + ● Positive charge</p> 	<p>Edge to face</p> 

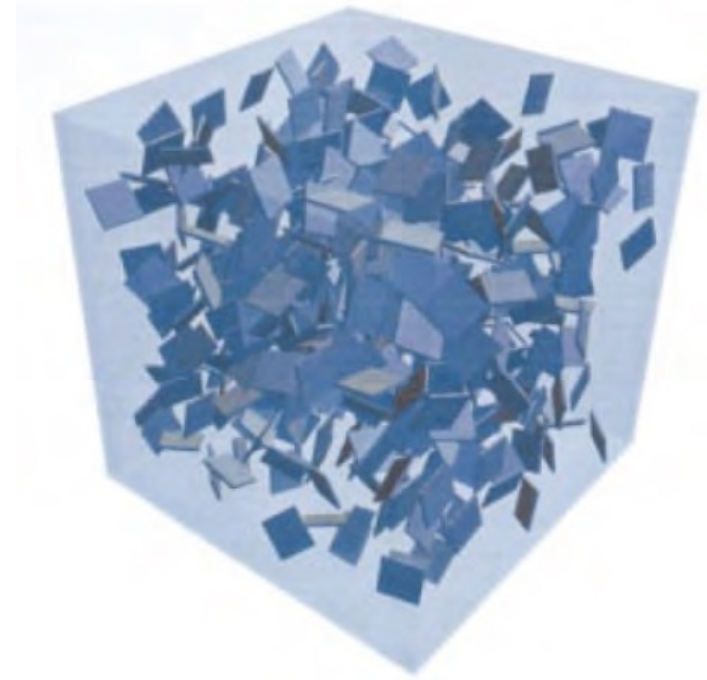
Pagano et al. (2020)



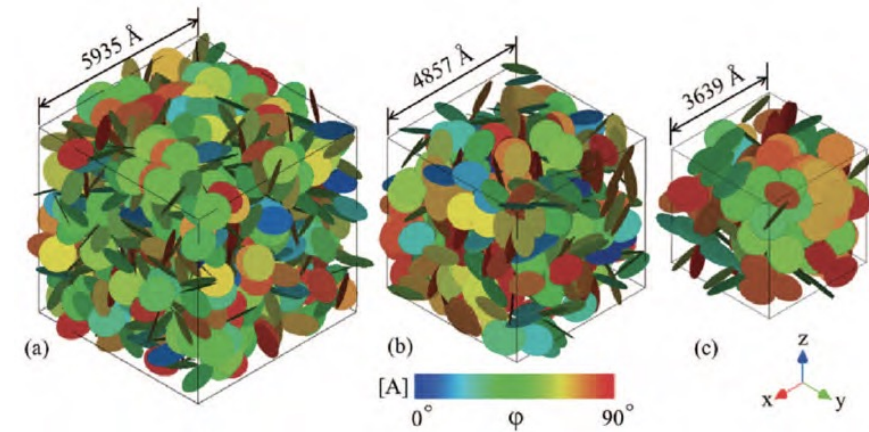
Sjoblom, 2015



deBono and McDowell (2002)
812 sub-spheres

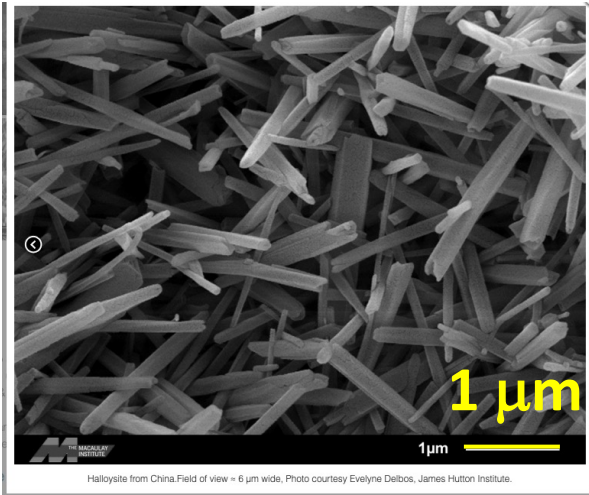


Yao and Anandarajah (2003)
Cuboids

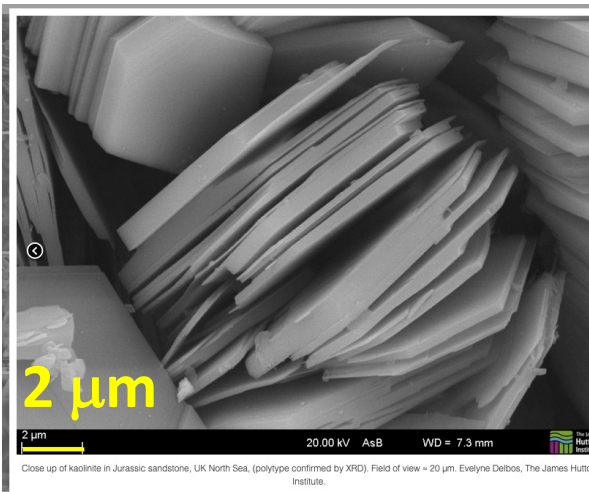


Bandera et al.(2021)
Flat ellipsoids

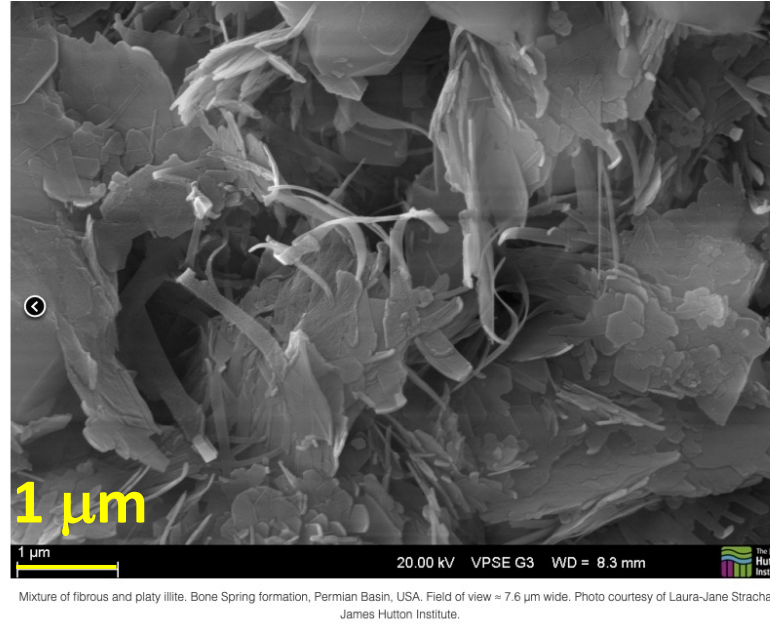
Clay “platelets” or “particles”



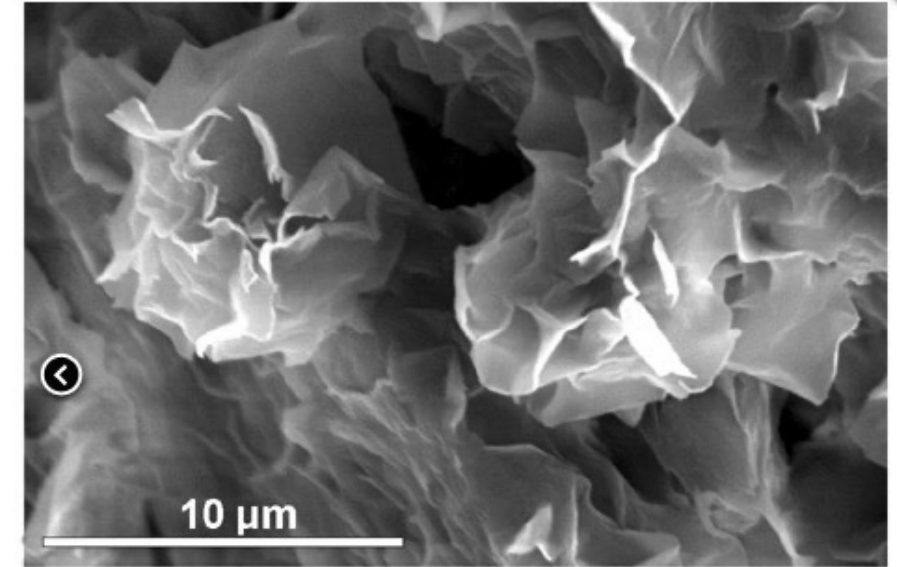
Hallosite



Kaolinite



Illite

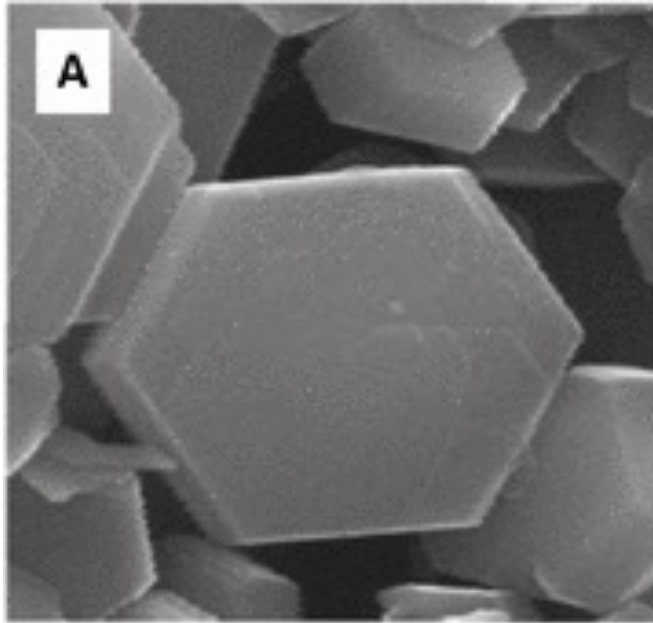


Montmorillonite

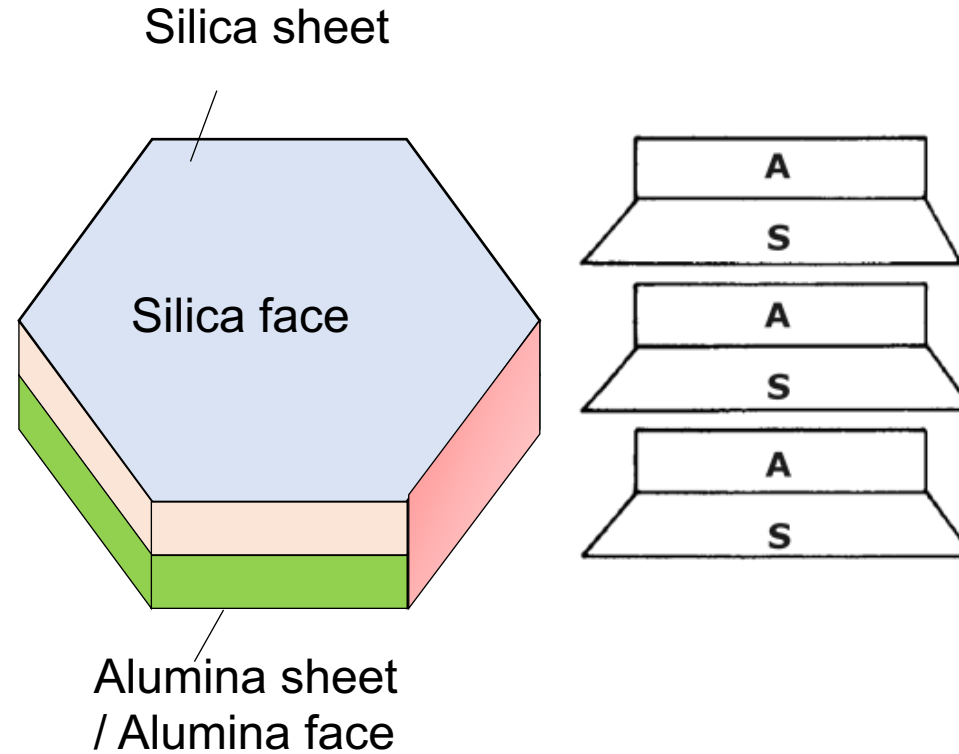
Montmorillonite showing a rose like texture, Miocene arkose, Madrid Basin, Spain. Fesharaki, O., García-Romero, E., Cuevas-González, J., López-Martínez, N. (2007) Clay mineral genesis and chemical evolution in the Miocene sediments of Somosaguas, Madrid Basin, Spain [DOI link](#). Field of view ≈ 22 μm wide. Photo courtesy of Emilia García-Romero, Universidad Complutense de Madrid, Spain.

‘Images of Clay Archive’ of the Mineralogical Society of Great Britain & Ireland and The Clay Minerals Society
<https://www.minersoc.org/images-of-clay.html>

Kaolinite particles

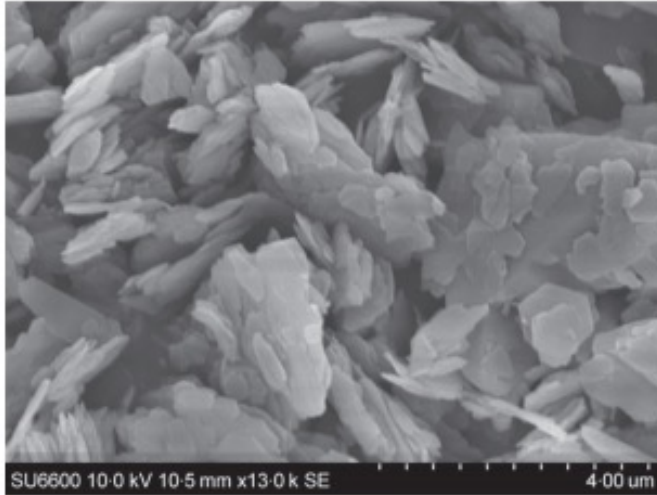


SEM image of single kaolinite particle
(Volkova et al., 2021)

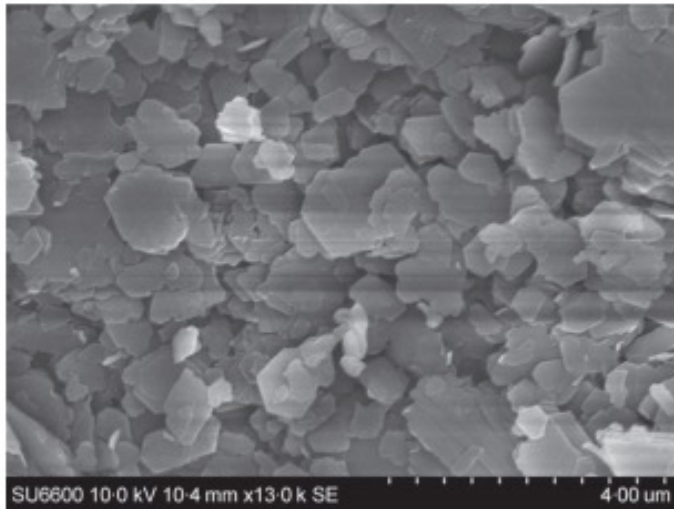


- One particle is 10 or more stacked units
- Particle dimensions circa 11 nm thick, 600 nm wide (Gupta, 2011)
- Shape hexagonal or pseudo hexagonal

Kaolinite



SEM image of
kaolinite
prepared with
acidic water
(pH < 5.5)



SEM image of
kaolinite prepared
with alkaline water
(pH > 5.5)

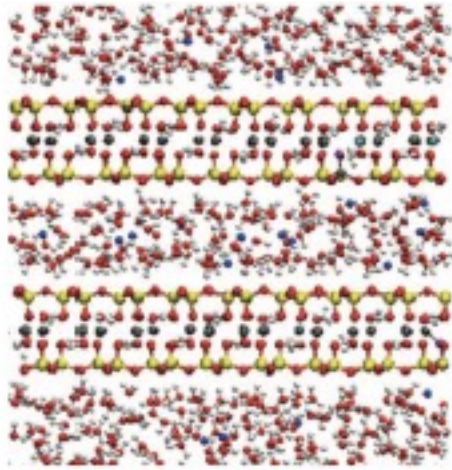
- Common clay mineral
- Surface chemistry depends on pore fluid (pH , salt concentration)
- Pore fluid characteristics influence overall mechanical behaviour
- Pore fluid characteristics influence fabric

Viable modelling framework
should capture sensitivity of
kaolinite to pore fluid chemistry

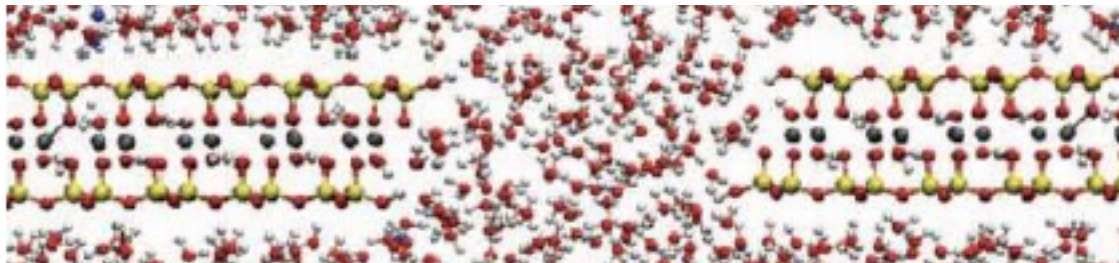
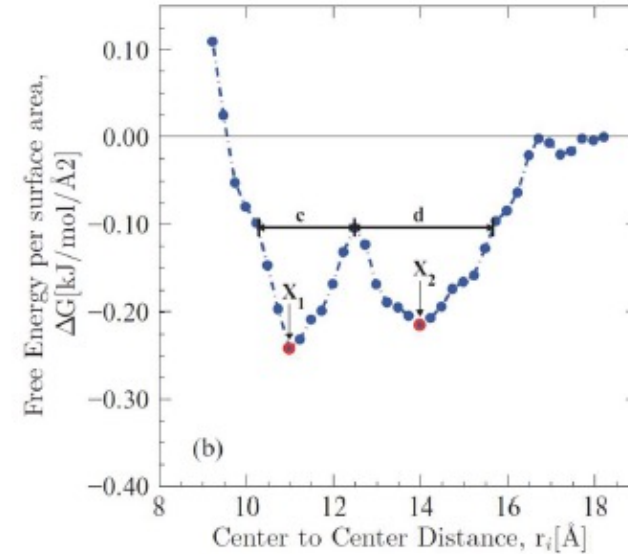
Electrolyte concentration negligible
(Pedrotti and Tarantino, 2017)

Part 3: Particle interactions

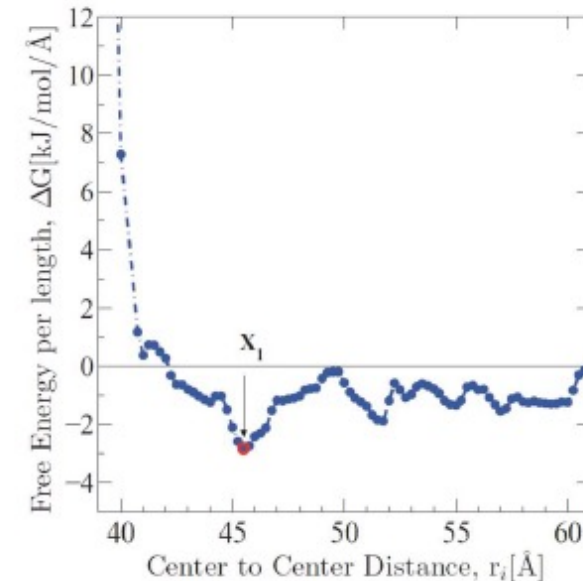
Use of atomistic MD to develop particle interactions



Face to Face Configuration

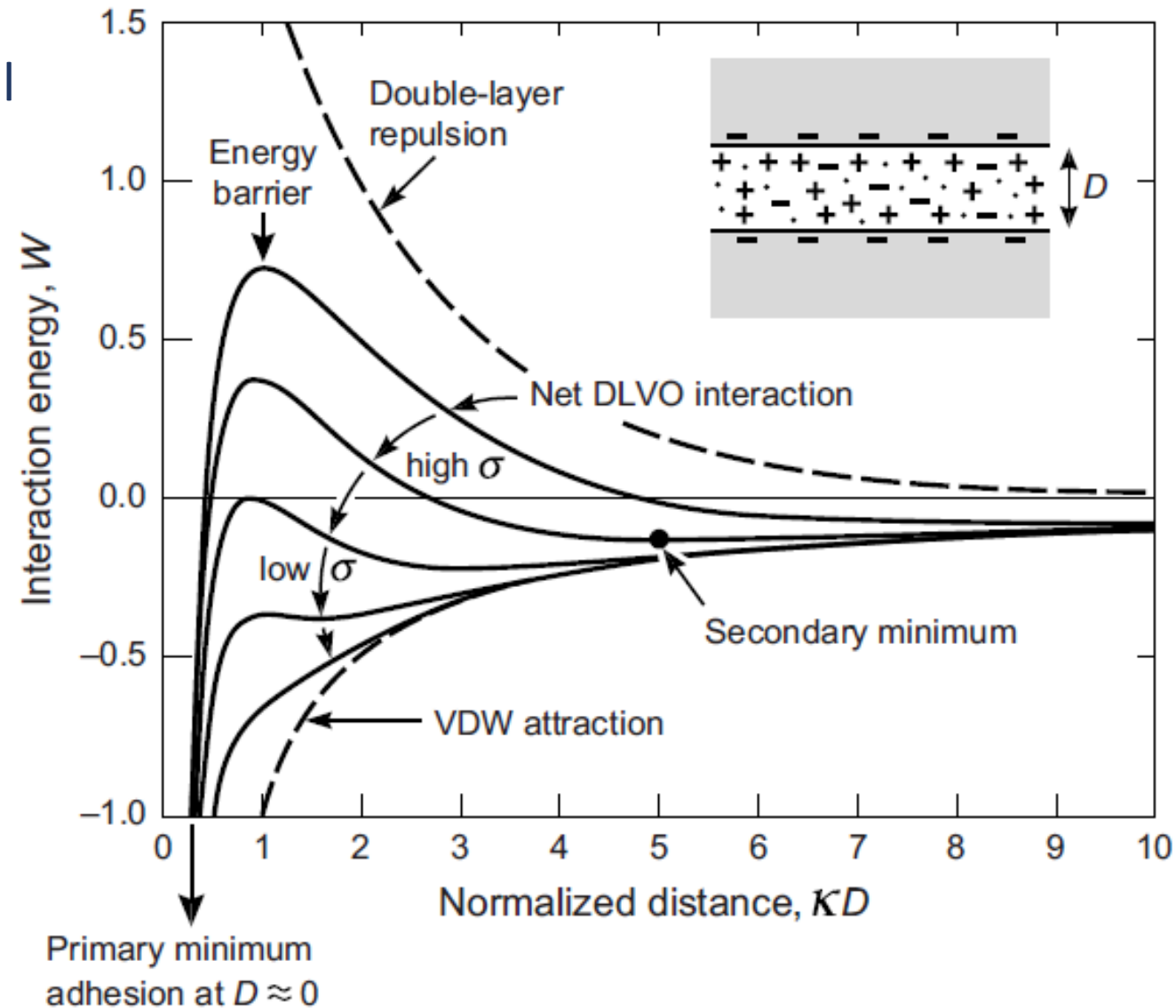


Edge to Edge Configuration



DLVO model

- Derjaguin-Landau-Vervey-Overbeek Model
- Developed to explain colloidal behaviour-equilibrium of colloids in solution
- Dates from 1950s
- Generally accepted in soil mechanics
- Gives force / energy per unit area



DLVO model

Electro-chemical forces:

Electrostatic forces

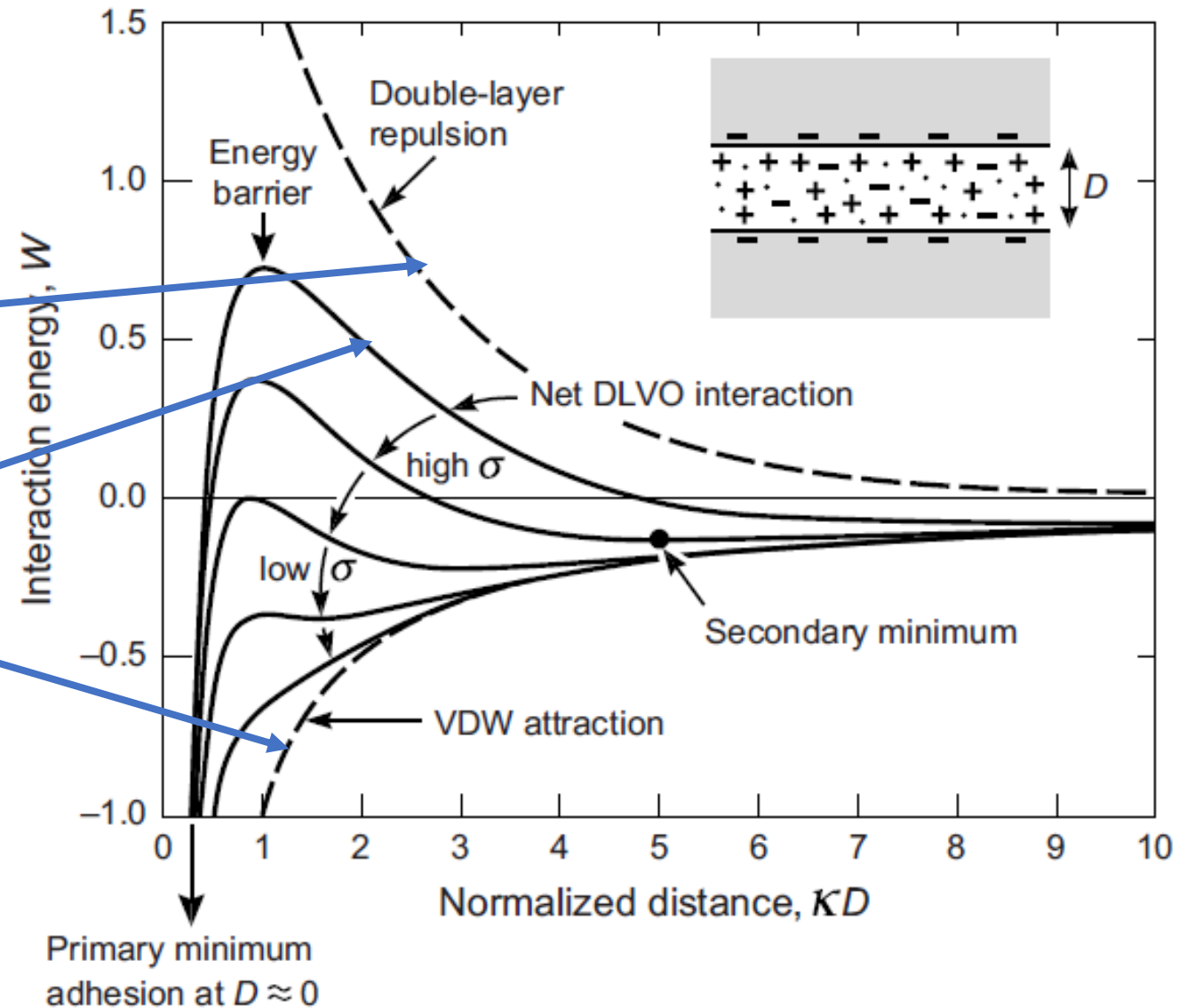
Van der Waals forces

DLVO
model

$$E_{\text{total}} = E_{\text{vdv}} + E_{\text{Coulumb}}$$

E_{vdv} = van der Waals energy

E_{Coulumb} = Electrostatic energy



Van der Waals Energy

- Attractive force (in case of colloids)

$$E_{vdv} = \frac{A_H}{12\pi} \left[\frac{1}{h^2} + \frac{1}{(h + \delta_1 + \delta_2)^2} - \frac{1}{(h + \delta_1)^2} - \frac{1}{(h + \delta_2)^2} \right]$$

Assume two
infinite parallel
plates

- h = separation distance
- Mineralogy of the clay considered and type of solvent through Hamaker Constant A_H
- Thickness of interacting particles δ_i

**Model
parameters** ✓

Electrostatic Energy

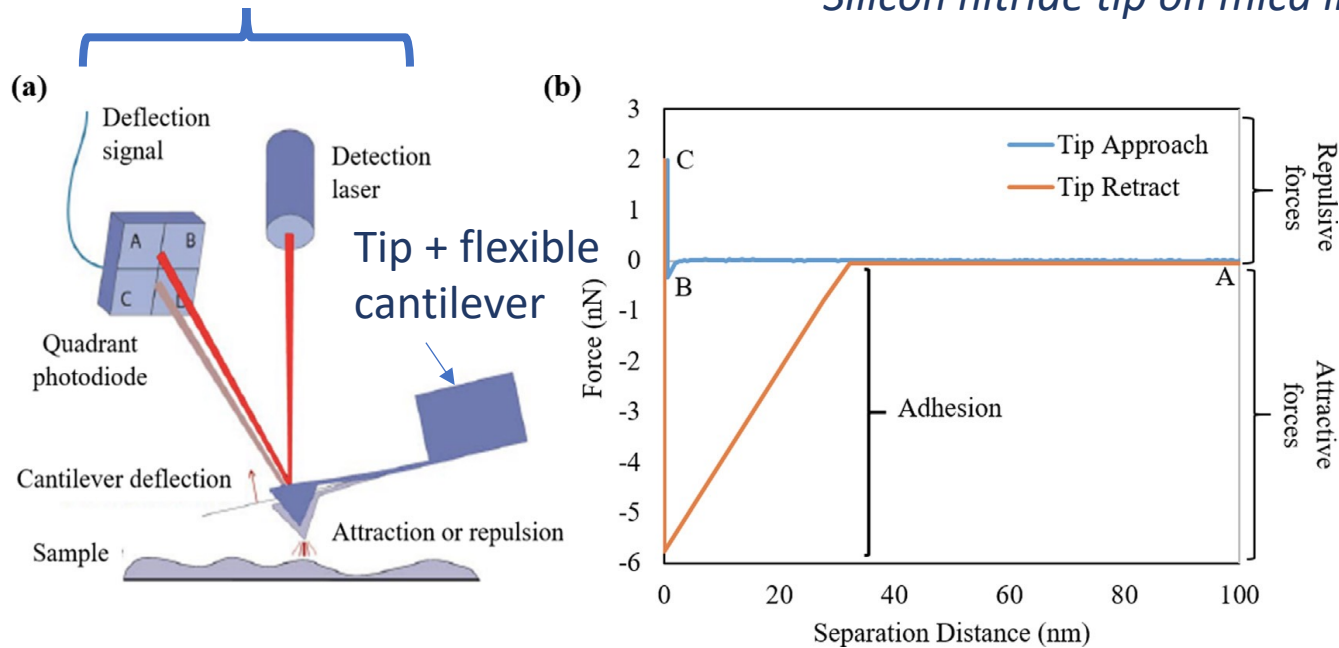
$$E_{\text{Coulumb}} = \epsilon_r \epsilon_0 \kappa \left[\frac{2\psi_1 \psi_2 \exp(\kappa h) - \psi_1^2 - \psi_2^2}{\exp(2\kappa h) - 1} \right]$$

- Dielectric permittivity ϵ_r ✓
- κ - Debye length which depends on salt concentration ρ_s ✓
- Surface potential ψ_i
- Graham equation links surface potential and surface charge

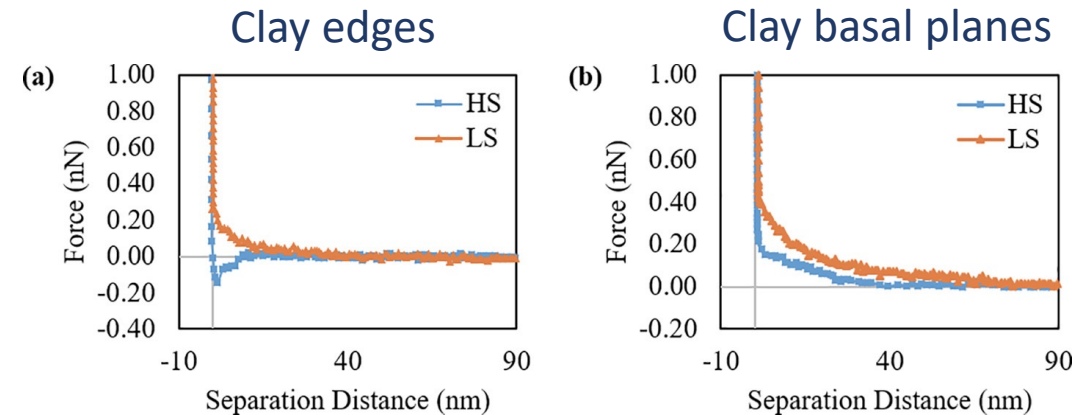
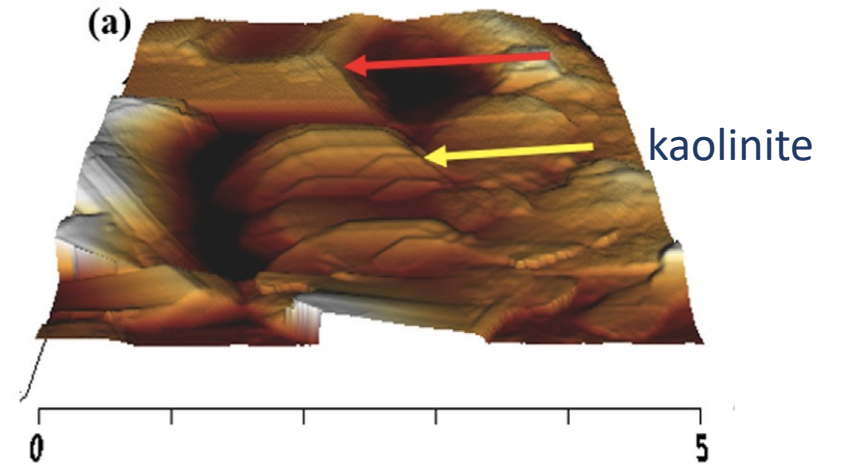
Challenging to determine accurately

Atomic Force Microscopy (AFM)

System to determine cantilever bending moment



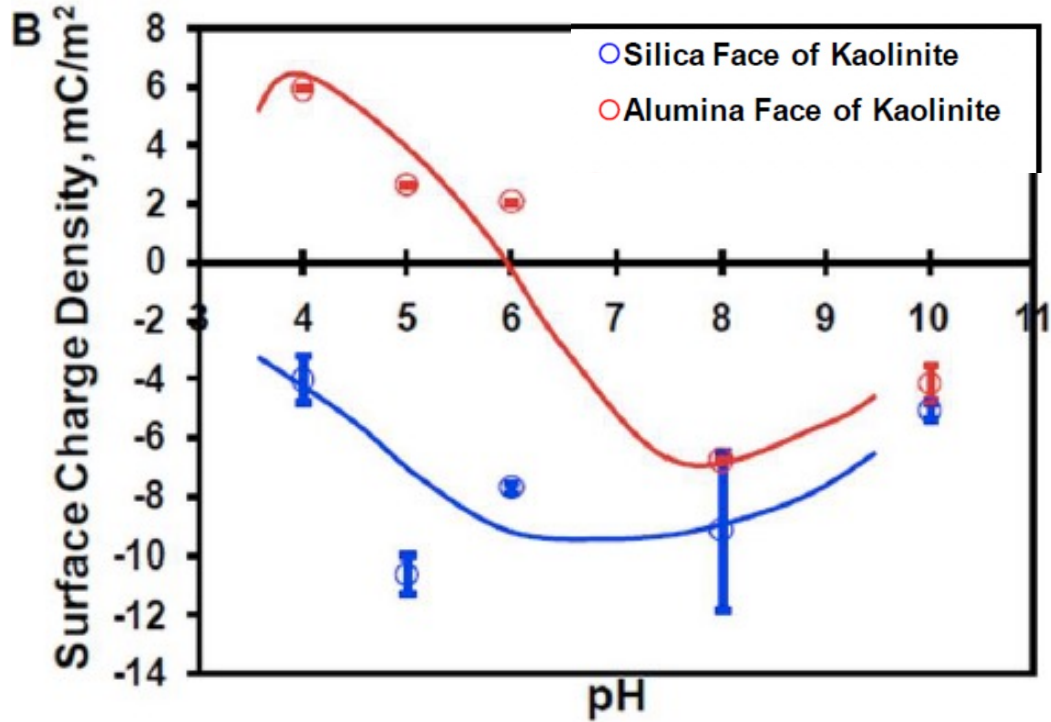
AFM → topography, stiffness and adhesion



Forces on kaolinite:
HS – high salinity, LS -Low salinity

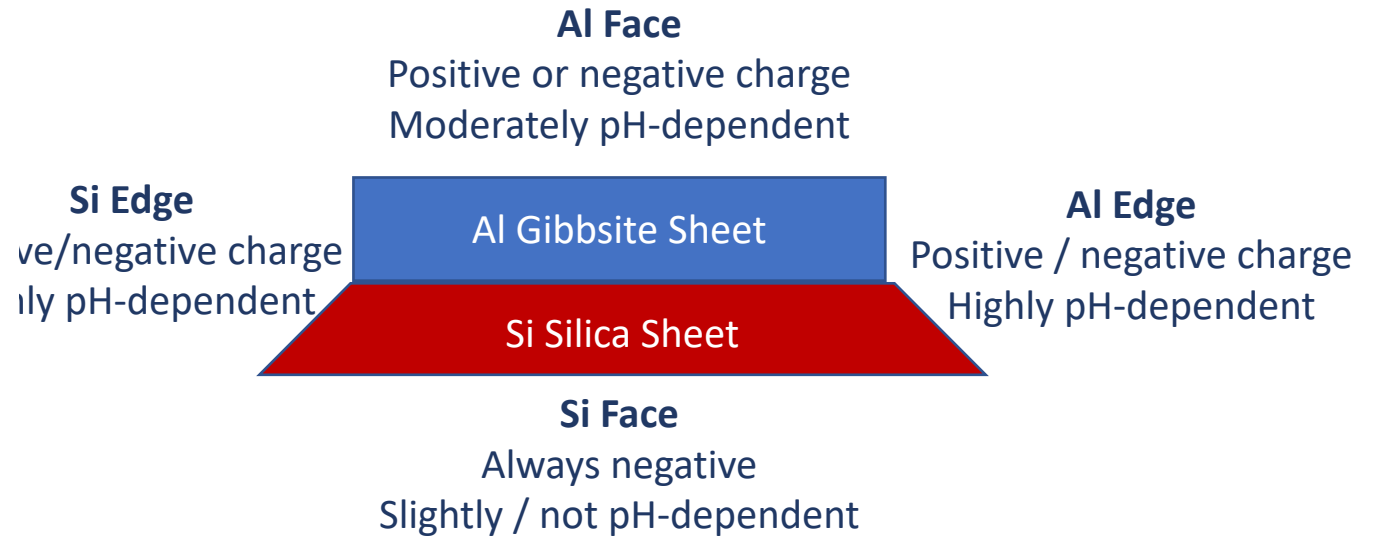
Surface charge

- Influenced by salt concentration and acidity of environment

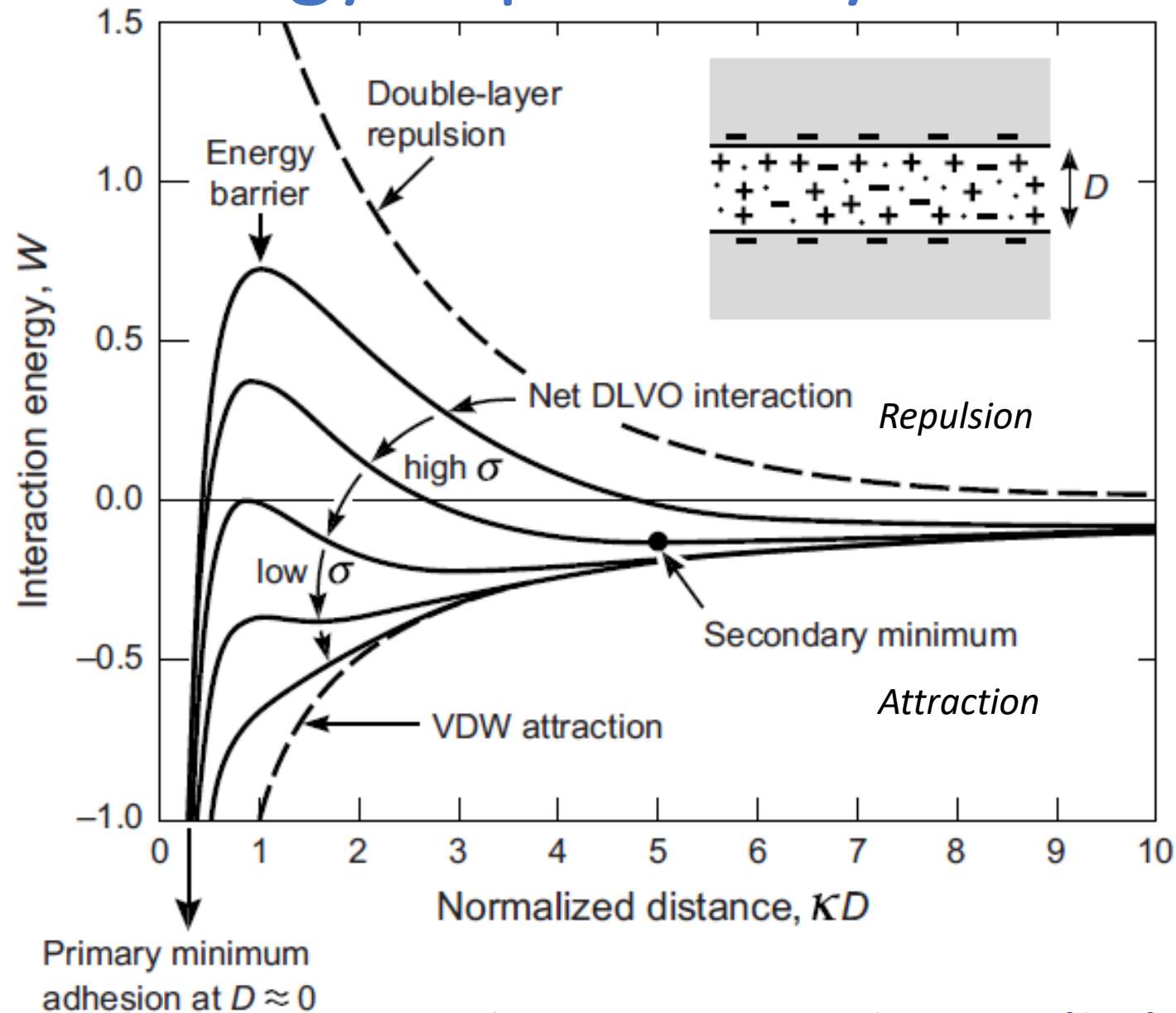


Atomic Force Microscopy (AFM) measurements
from Gupta (2011)

1mMol KCl

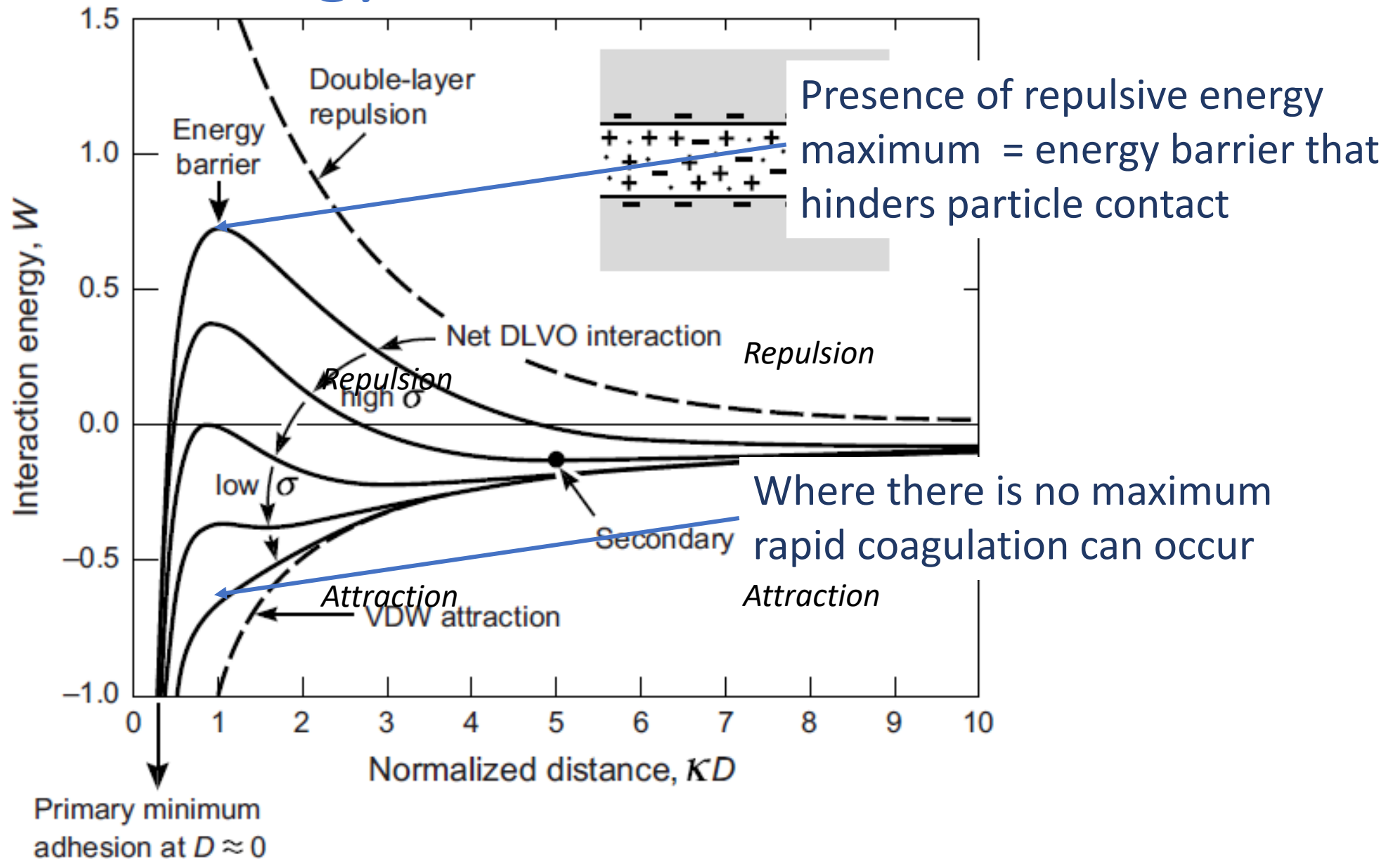


Interaction energy dependency on surface charge




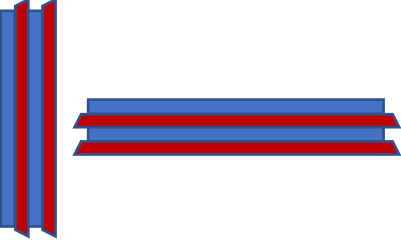
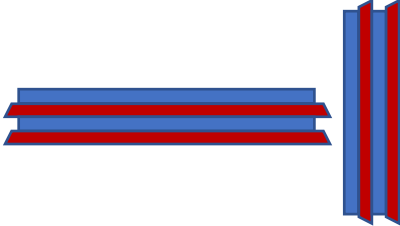
Schematic energy versus distance profile of DLVO model (Israelachvili, 2011)

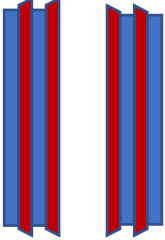
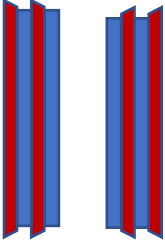
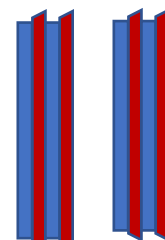
Interaction energy



Schematic energy versus distance profile of DLVO model (Israelachvili, 2011)

Kaolinite – 6 interaction scenarios

Edge-edge	
Edge-silica face	
Edge-alumina face	

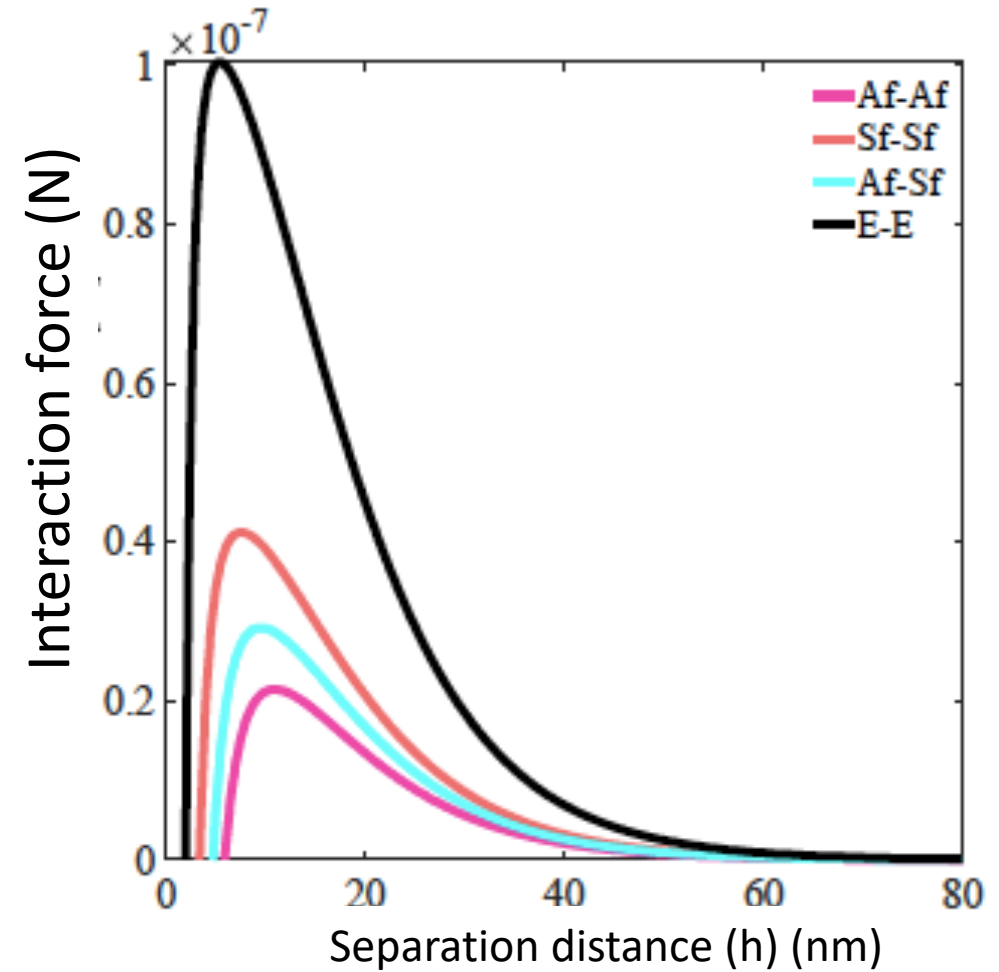
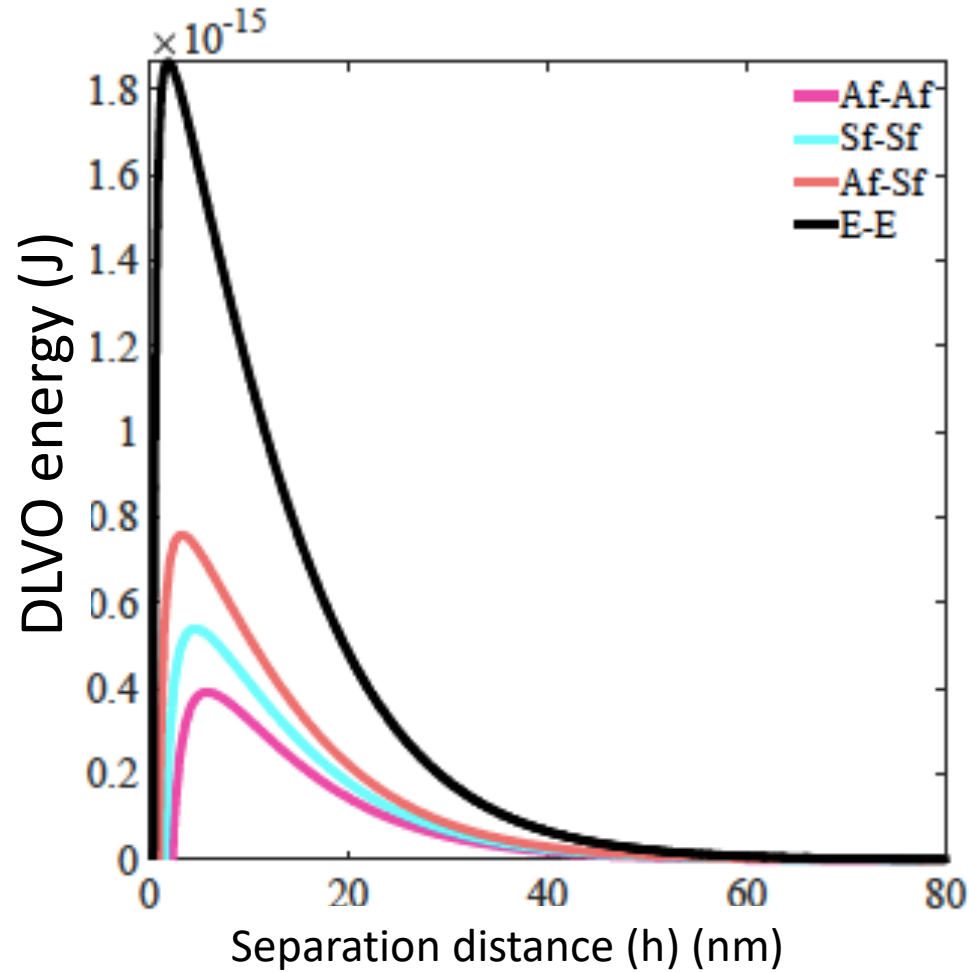
Silica face-silica face	
Alumina face-alumina face	
Silica face-alumina face	

> 6 interaction scenarios when pH varied

Edge-edge	Repulsive
Edge-silica face	Attractive pH \leq 4 Repulsive pH $>$ 4
Edge-alumina face	Repulsive pH=4 Attractive pH=5-6 Repulsive =8-10

Silica face-silica face	Repulsive
Alumina face-alumina face	Repulsive
Silica face-alumina face	Attractive pH \leq 6 Repulsive pH $>$ 6

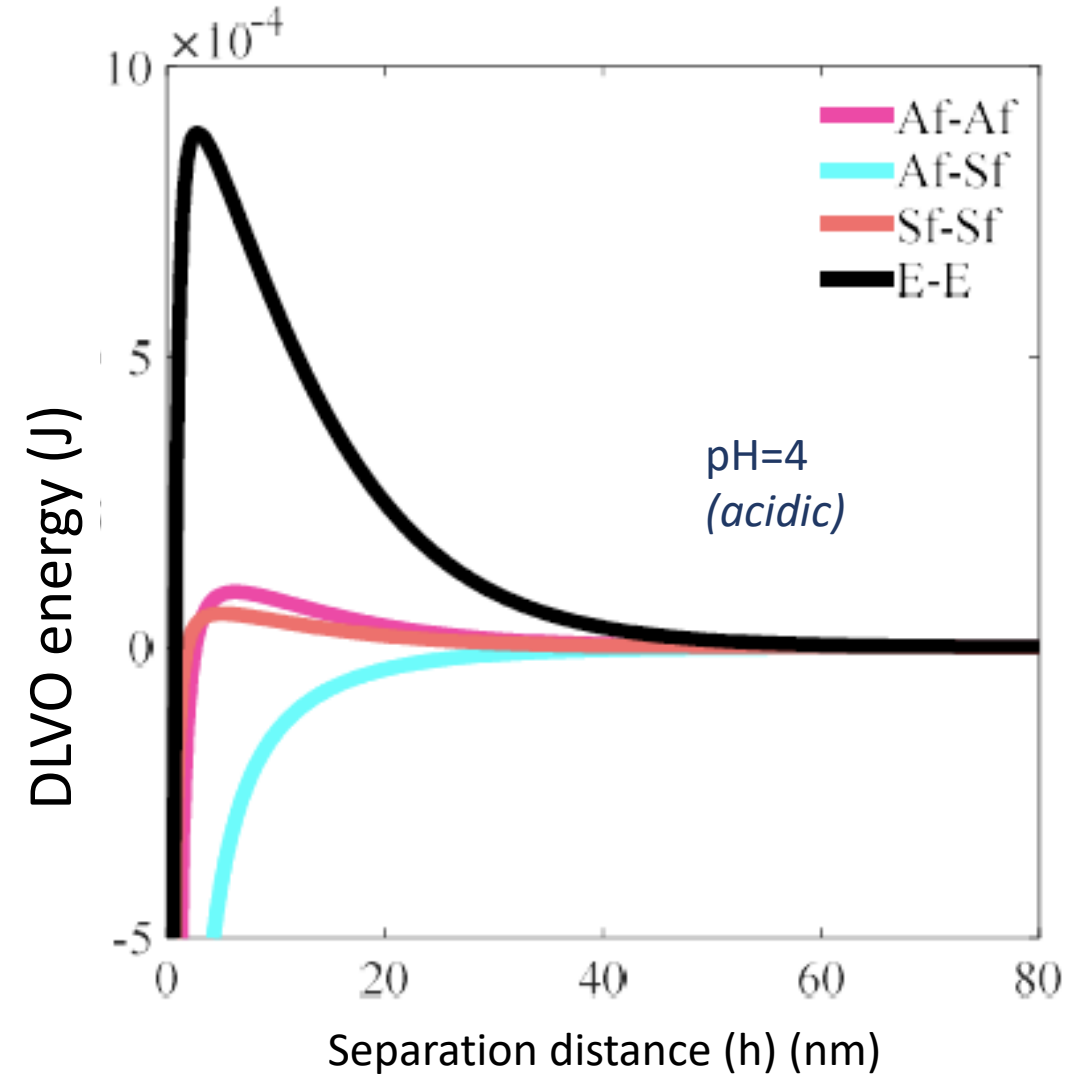
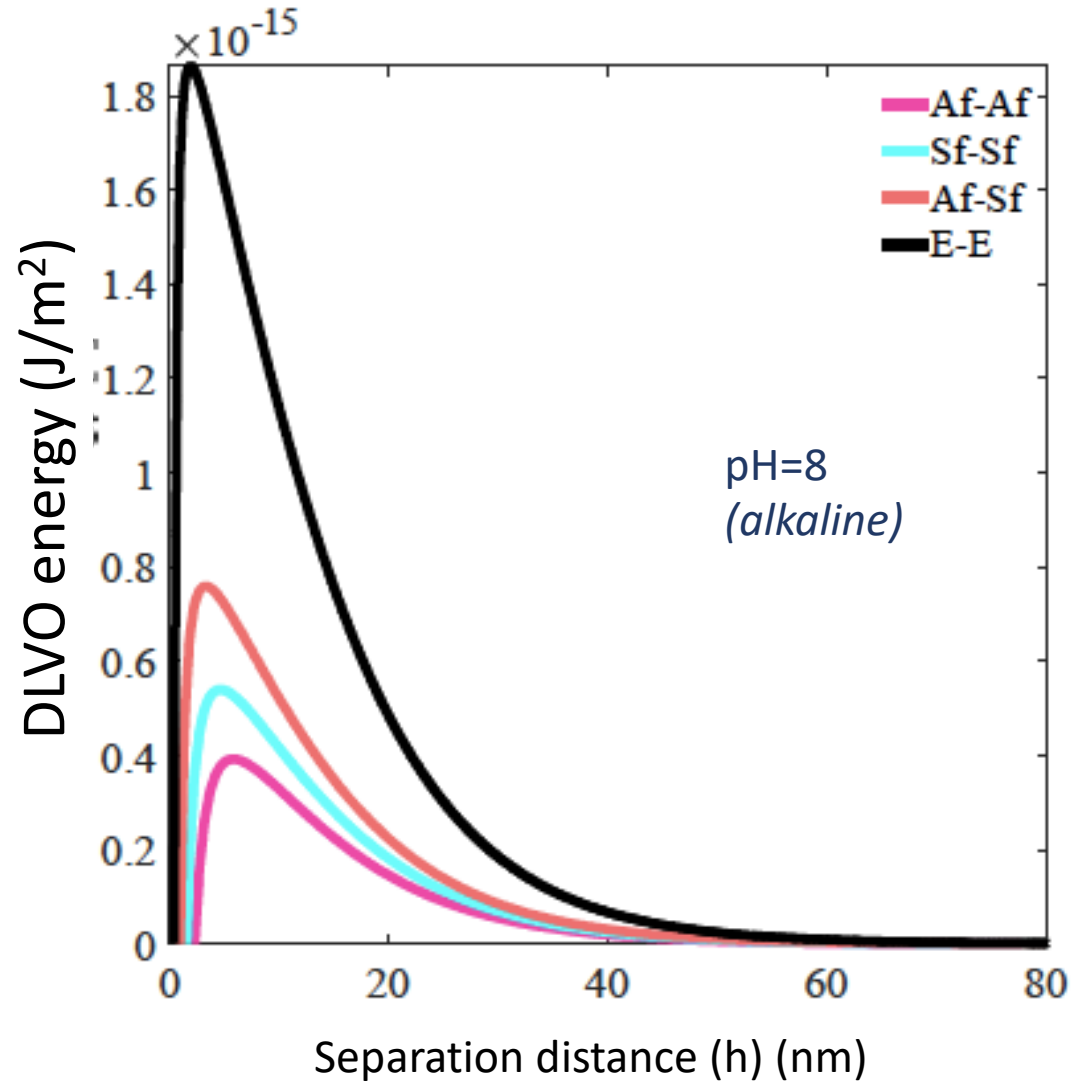
DLVO predicted interaction energy and force



Af = Alumina face
Sf = Silica face
E = Edge

Monodisperse system, pH=8, 1mM KCl electrolyte

DLVO predicted interaction energy and force



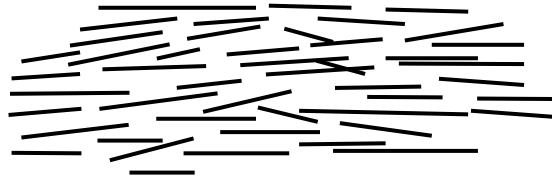
Monodisperse system, pH=8, 1mM KCl electrolyte

pH dependency of kaolinite particle interactions

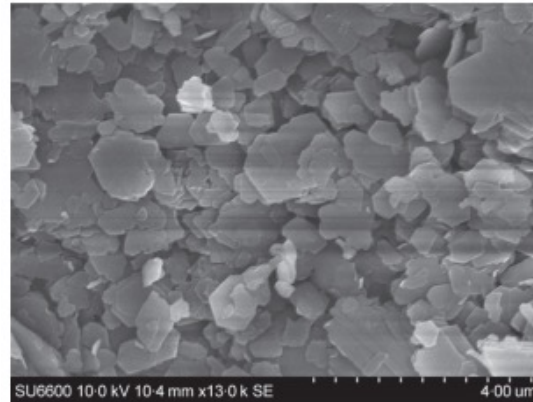
Alkaline conditions (pH>5,5)

Net interaction:

- Face-face: repulsion
- Face-edge : repulsion



Dispersed fabric

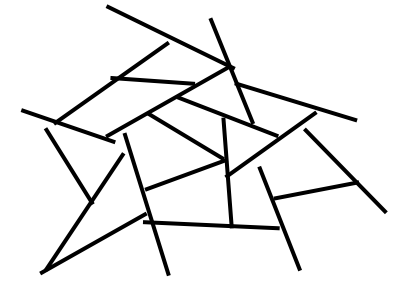


Kaolinite prepared with
alkaline water
(Pedrotti and Tarantino,
2017)

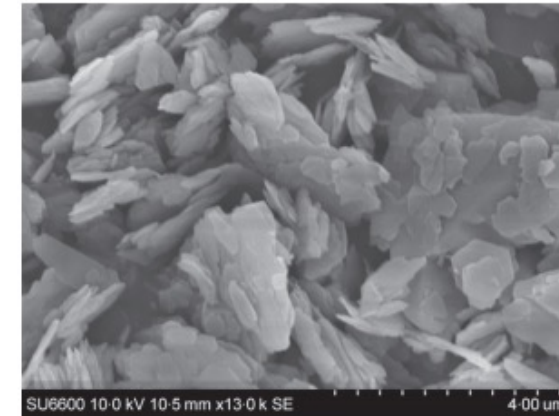
Acidic conditions (pH<5,5)

Net interaction:

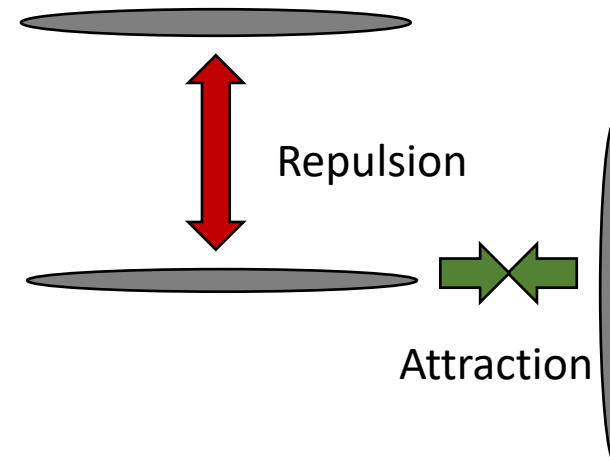
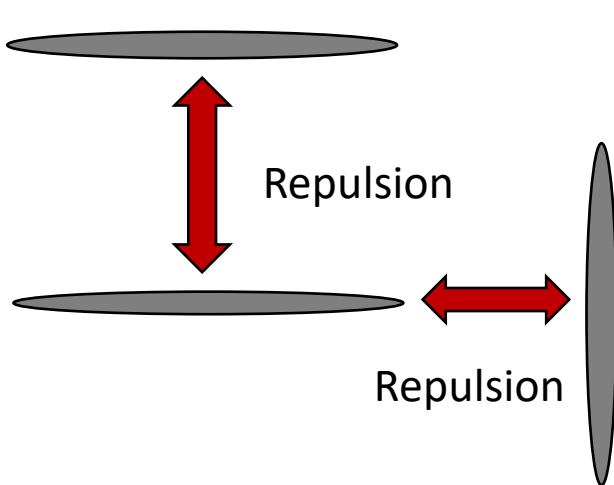
- Face-face: repulsion
- Face-edge - attraction



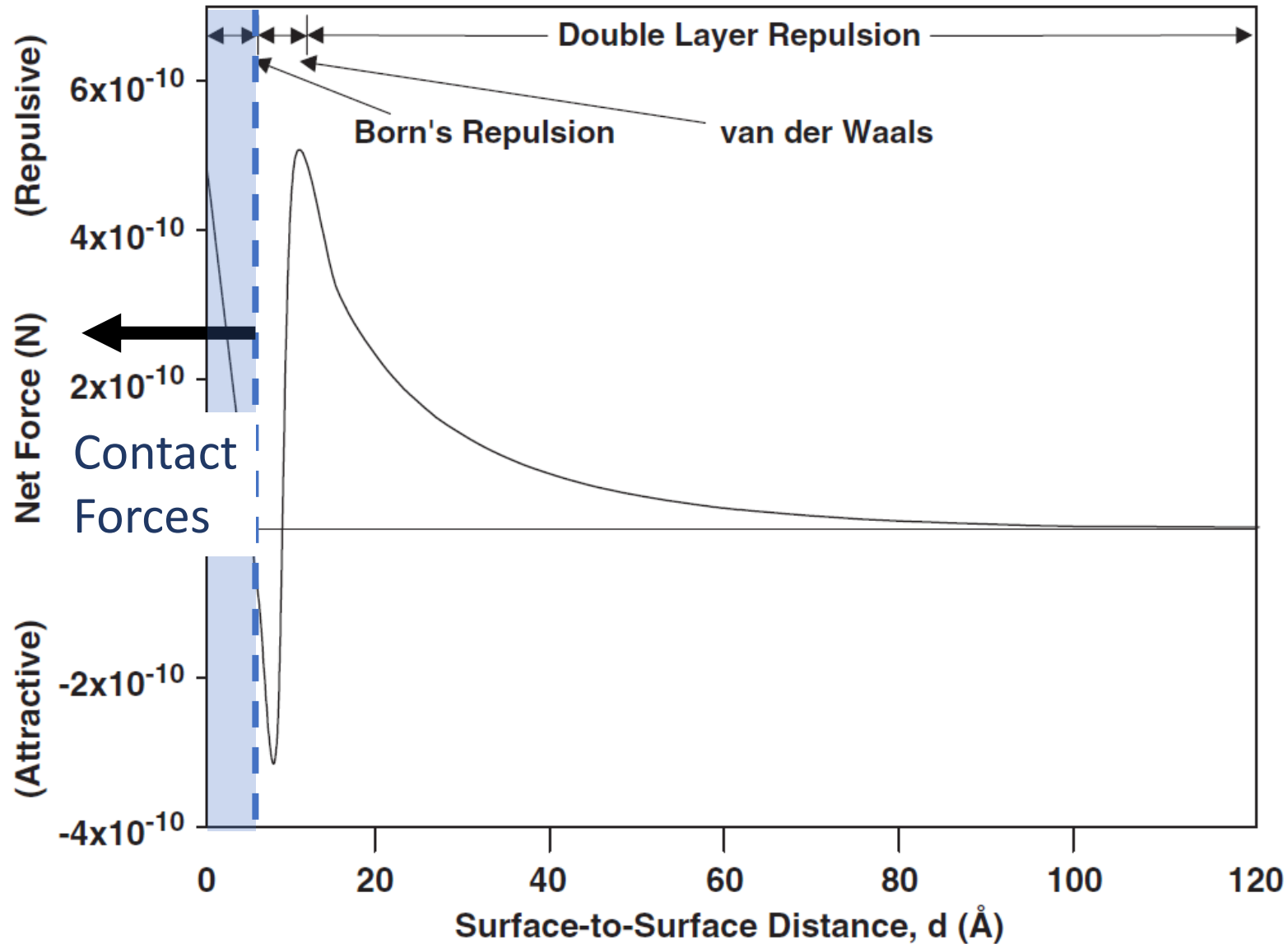
Cardhouse fabric



Kaolinite prepared with
acidic water
(Pedrotti and Tarantino,
2017)



Contact forces

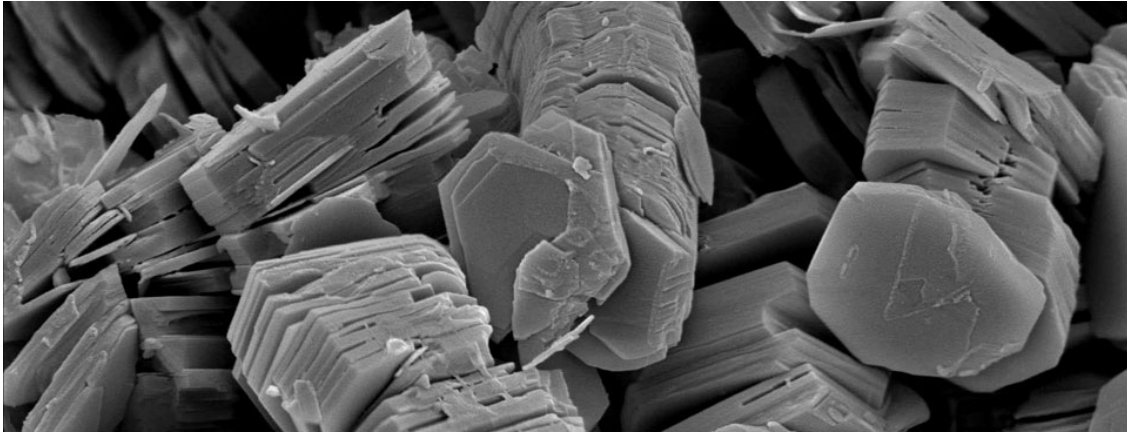


Mechanical forces:
Born's repulsion

Net interaction force between two clay particles (Liu et al., 2008)

Part 4: System level response

Overall aim

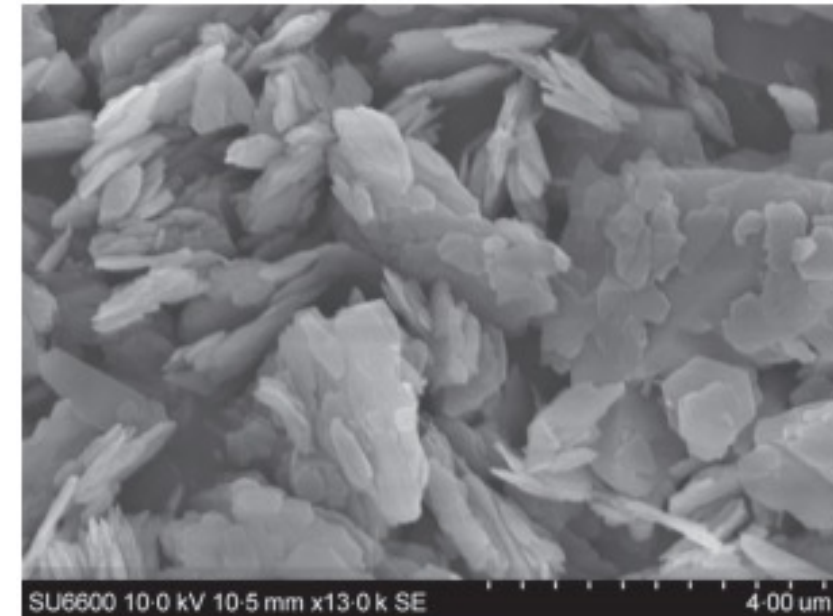
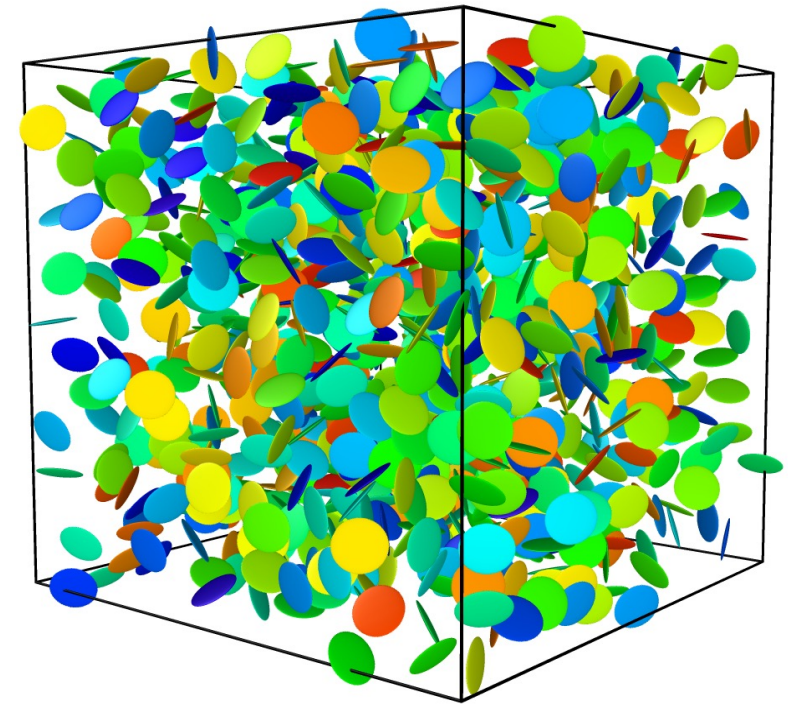


Scanning Electron Microscope (SEM) image of kaolinite (British Mineralogical Society)

- Develop effective framework to model clay at the particle scale
- Advance understanding of link between particle scale parameters and fabric
- Link fabric to overall mechanical behaviour

DLVO Model

- Direct use of DLVO theory in a molecular dynamics code complicated by lack of consideration of directional dependency of interactions
- Equations typically considered are for parallel planar surfaces or spheres
- Not capable of modelling particles with general morphology and orientation
- Seek framework to include DLVO contact interactions in multi-particle simulation environment



Particle scale model

Determine particle scale parameters

- Hamaker constant, particle size (E_{vdv})
- Dielectric permittivity, surface potential, Debye length ($E_{Coulomb}$)

Calculate energy-separation relationship as predicted by DLVO

- Need to consider face-face, edge-face, edge-edge

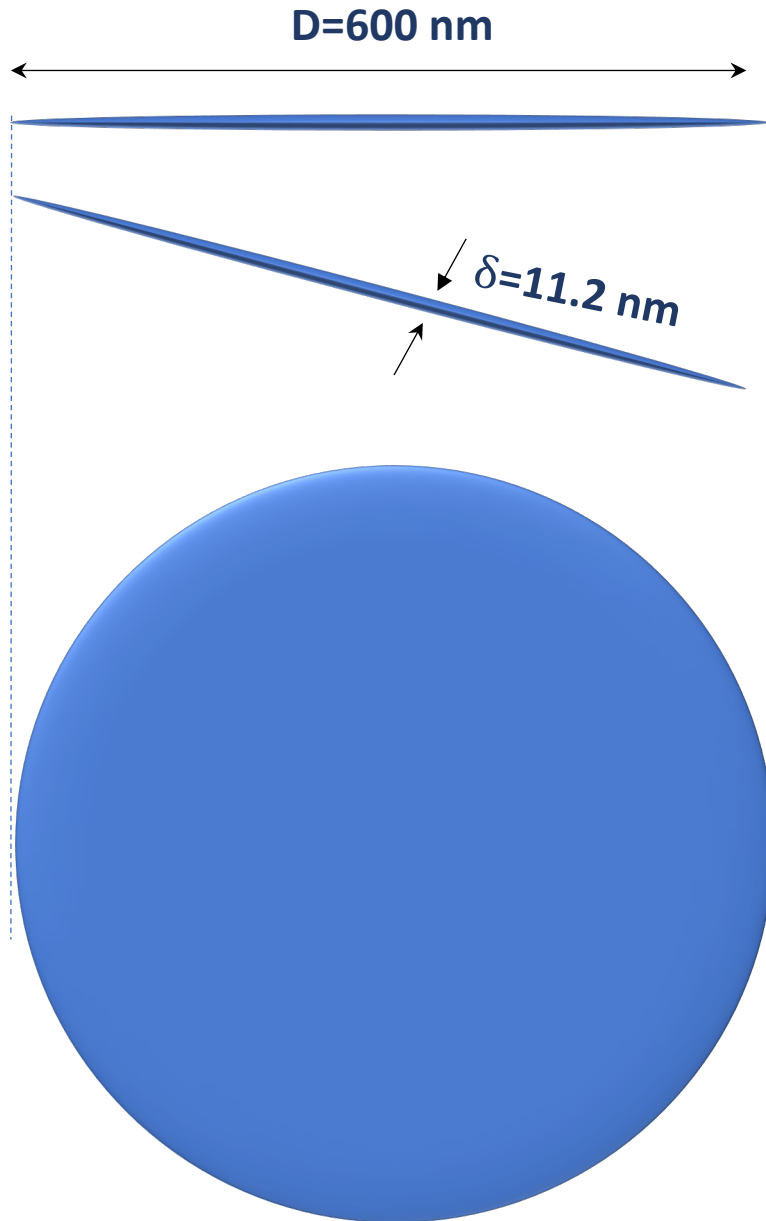
Calibrate Gay-Berne potential against DLVO predictions

- 5 parameters to calibrate for axisymmetric particles
- Need to consider face-face, edge-face, edge-edge

Input Gay-Berne parameters in multi-particle MD simulation

- Develop initial assembly
- Equilibrate
- Simulate compression tests

Ellipsoidal particles



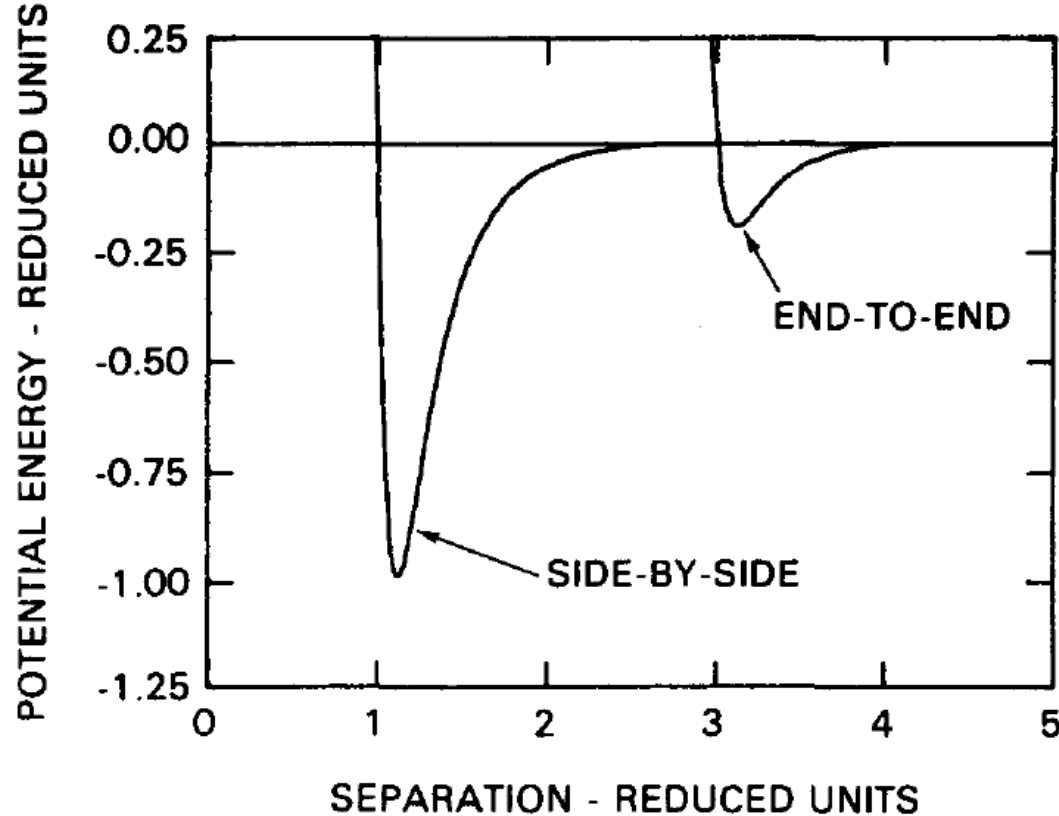
Tang-Tat Ng demonstrated benefits of using ellipsoids to model sand grains

Ebrahimi (2014) demonstrated viability of using ellipsoids to model clay particles

Requires use of generalized Leonard-Jones potential \rightarrow Gay-Berne potential

Ellipsoid dimensions from particle dimensions from SEM work of Gupta (2011)

Gay-Berne potential



Gay and Berne, 1981

- Introduced to study the anisotropic interaction of two large, rigid, ellipsoidal particles.
- Based upon Leonard Jones potential

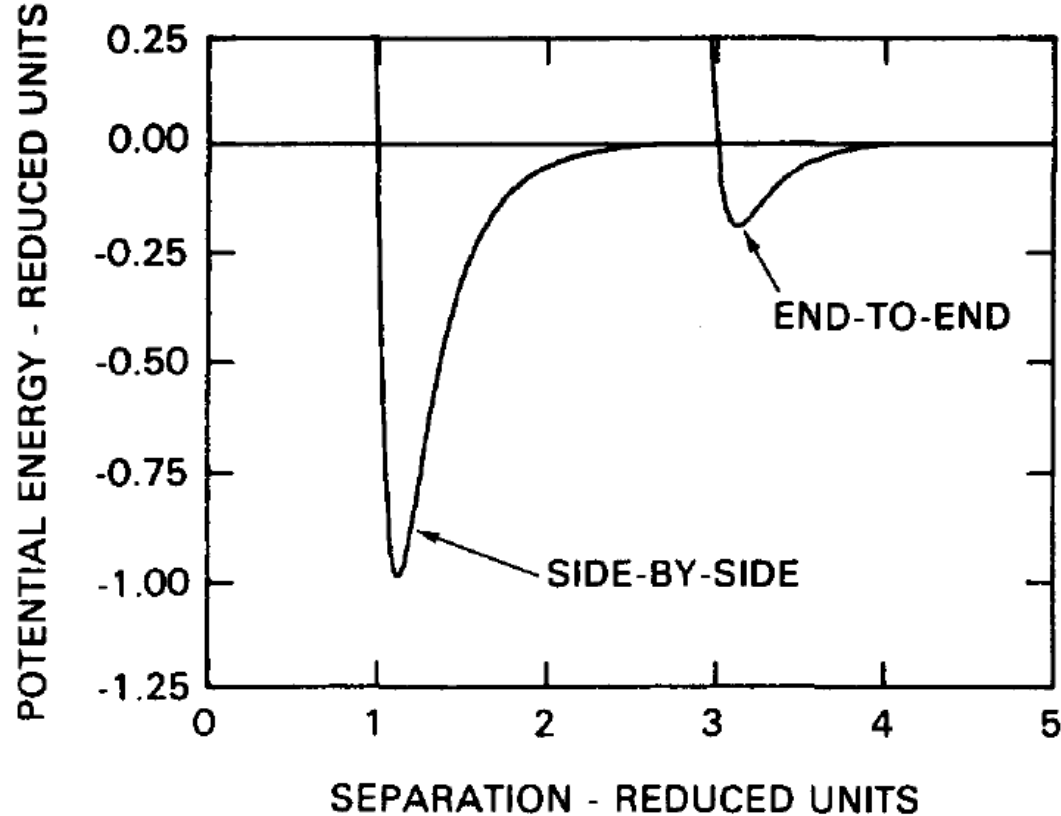
$$E_{LJ} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$



$$E_{GB} = 4\epsilon \left[\left(\frac{\sigma}{h_{12} + \gamma\sigma} \right)^{12} - \left(\frac{\sigma}{h_{12} + \gamma\sigma} \right)^6 \right] \times \eta_{12} \times \chi_{12}$$

- Additional model parameters account for variation in interaction with orientation
- Model parameters determined by curve fitting – empirical model

Gay-Berne potential



Gay and Berne, 1981

- Introduced to study the anisotropic interaction of two large, rigid, ellipsoidal particles.
- Based upon Leonard Jones potential

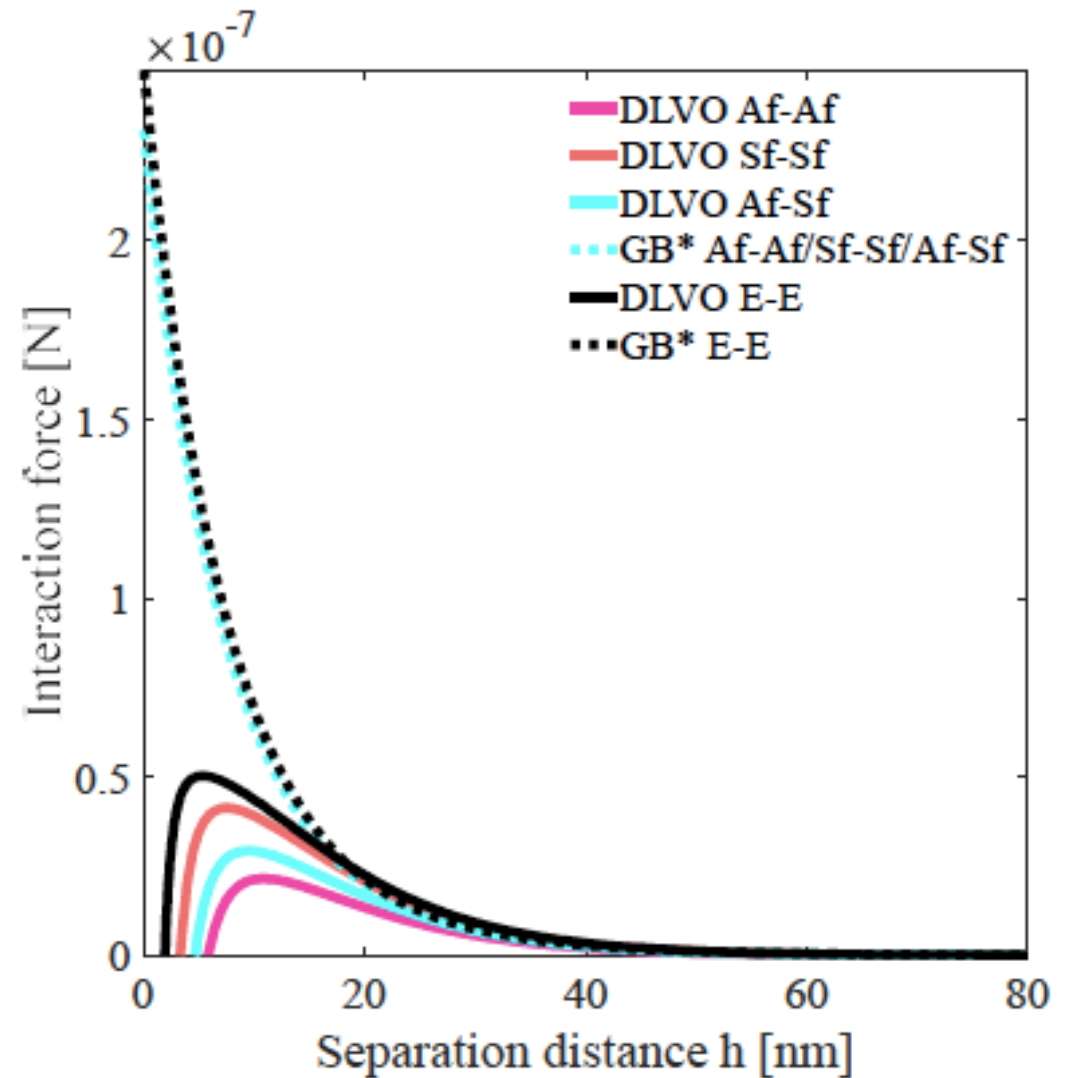
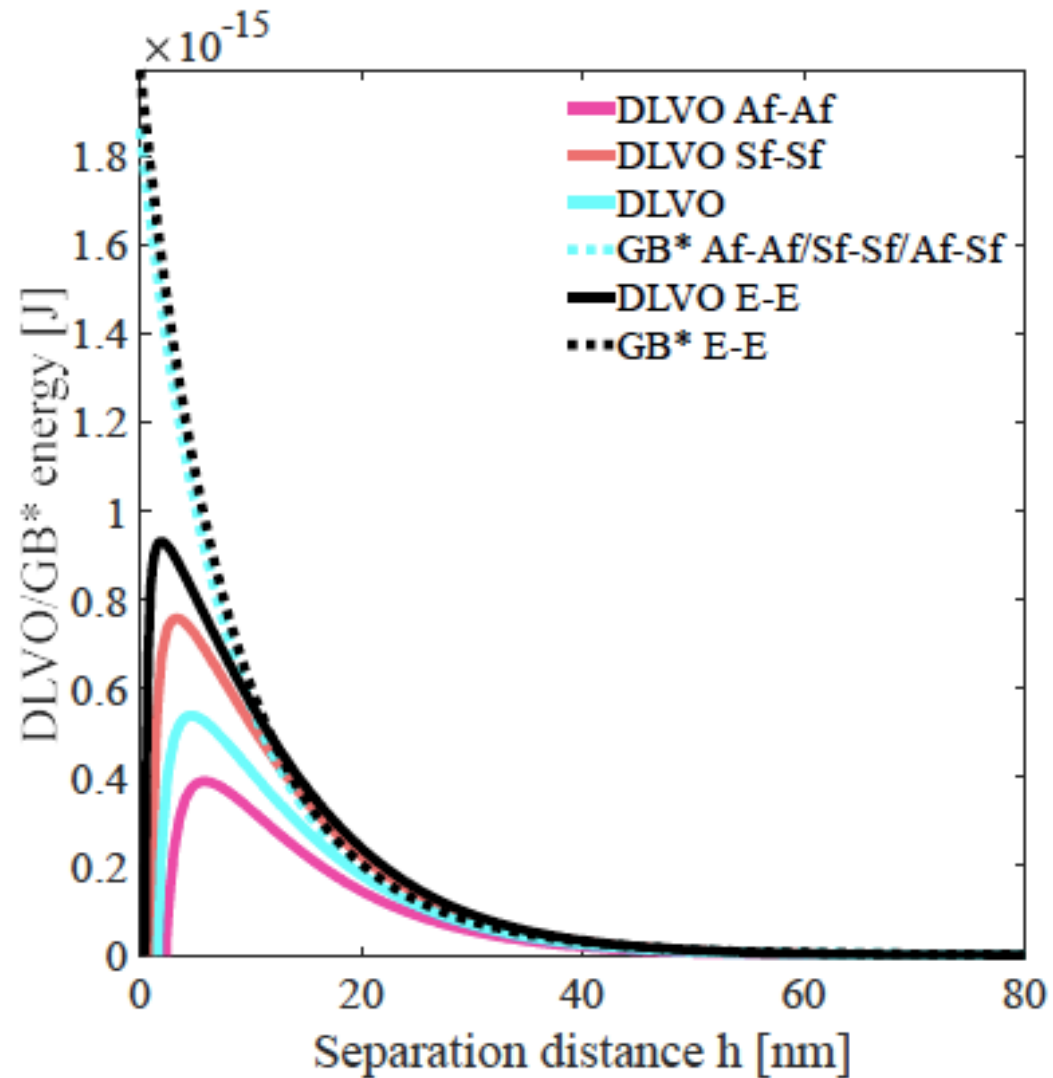
$$E_{LJ} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$



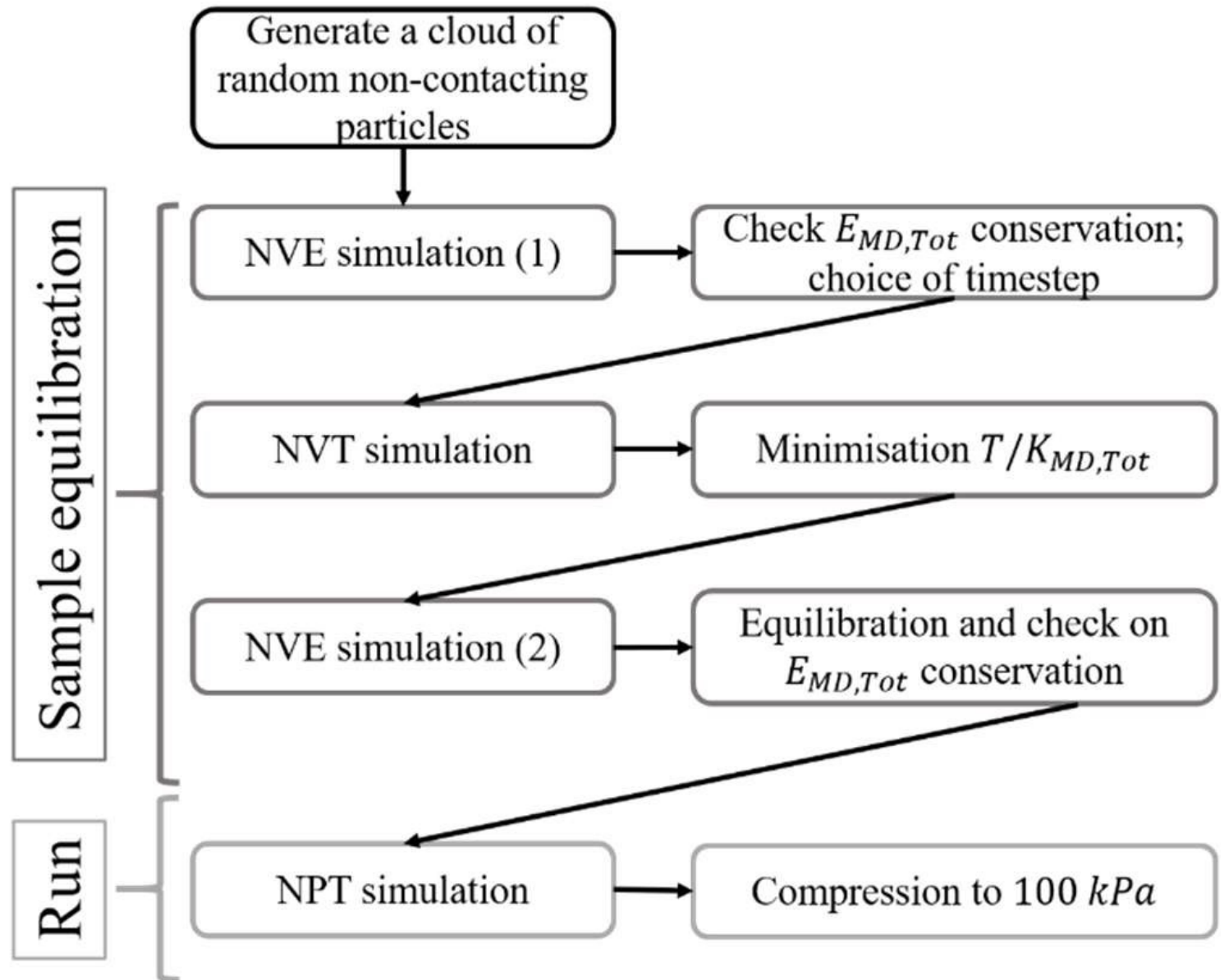
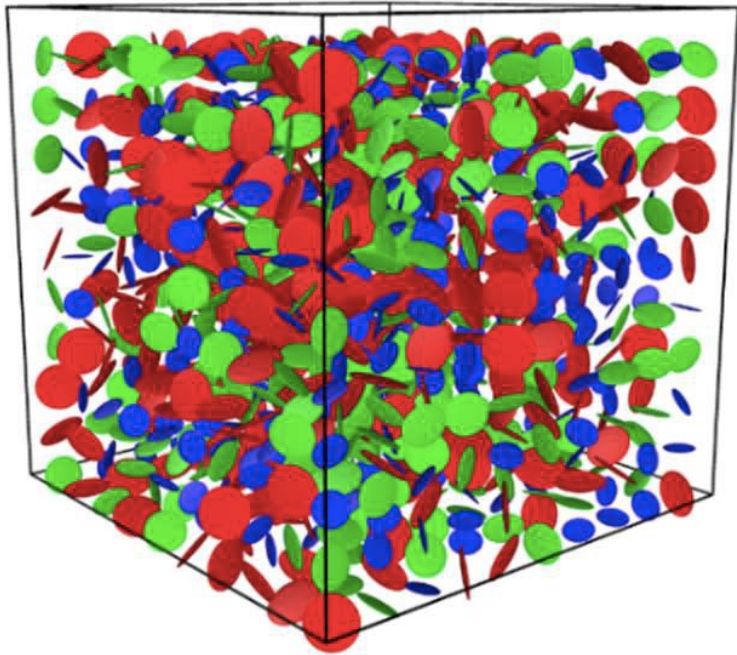
$$E_{GB} = 4\epsilon \left[\underbrace{\left(\frac{\sigma}{h_{12} + \gamma\sigma} \right)^{12}}_{\text{repulsive term}} - \left(\frac{\sigma}{h_{12} + \gamma\sigma} \right)^6 \right] \times \eta_{12} \times \chi_{12}$$

For alkaline pH isolate
repulsive term

Calibrated model

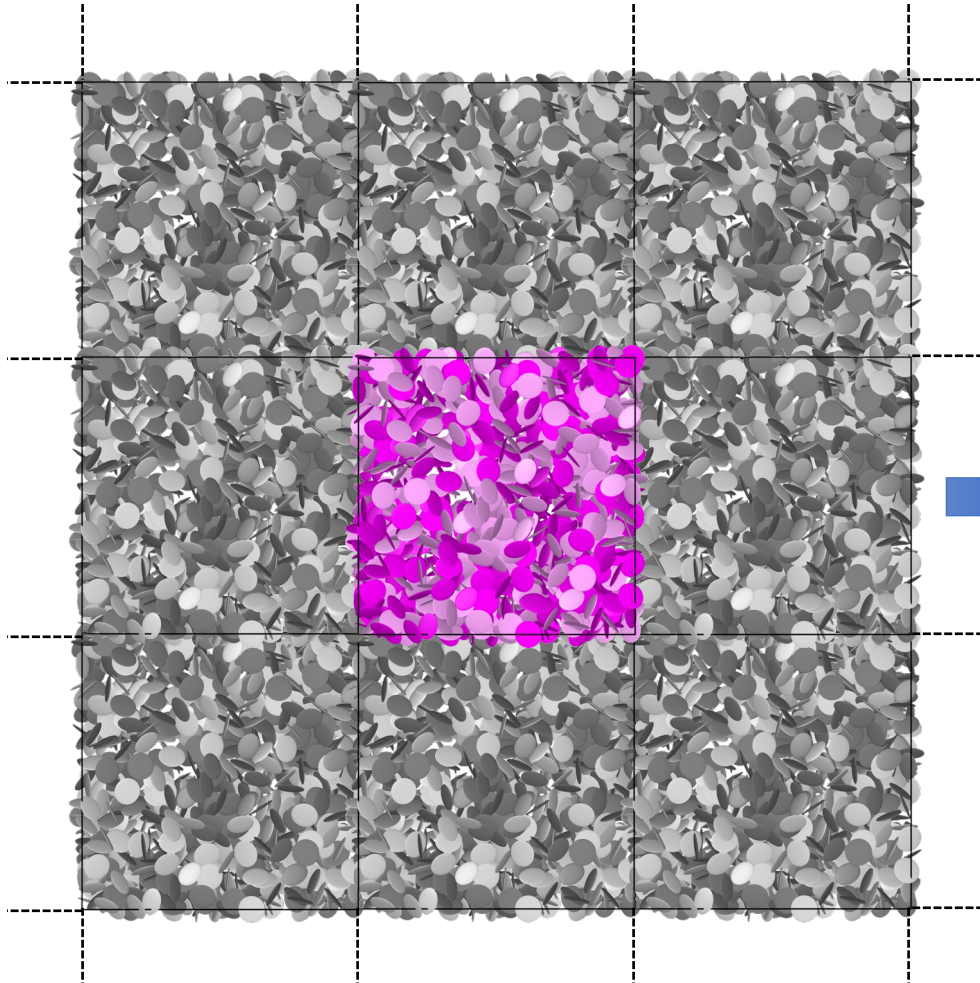


System level response



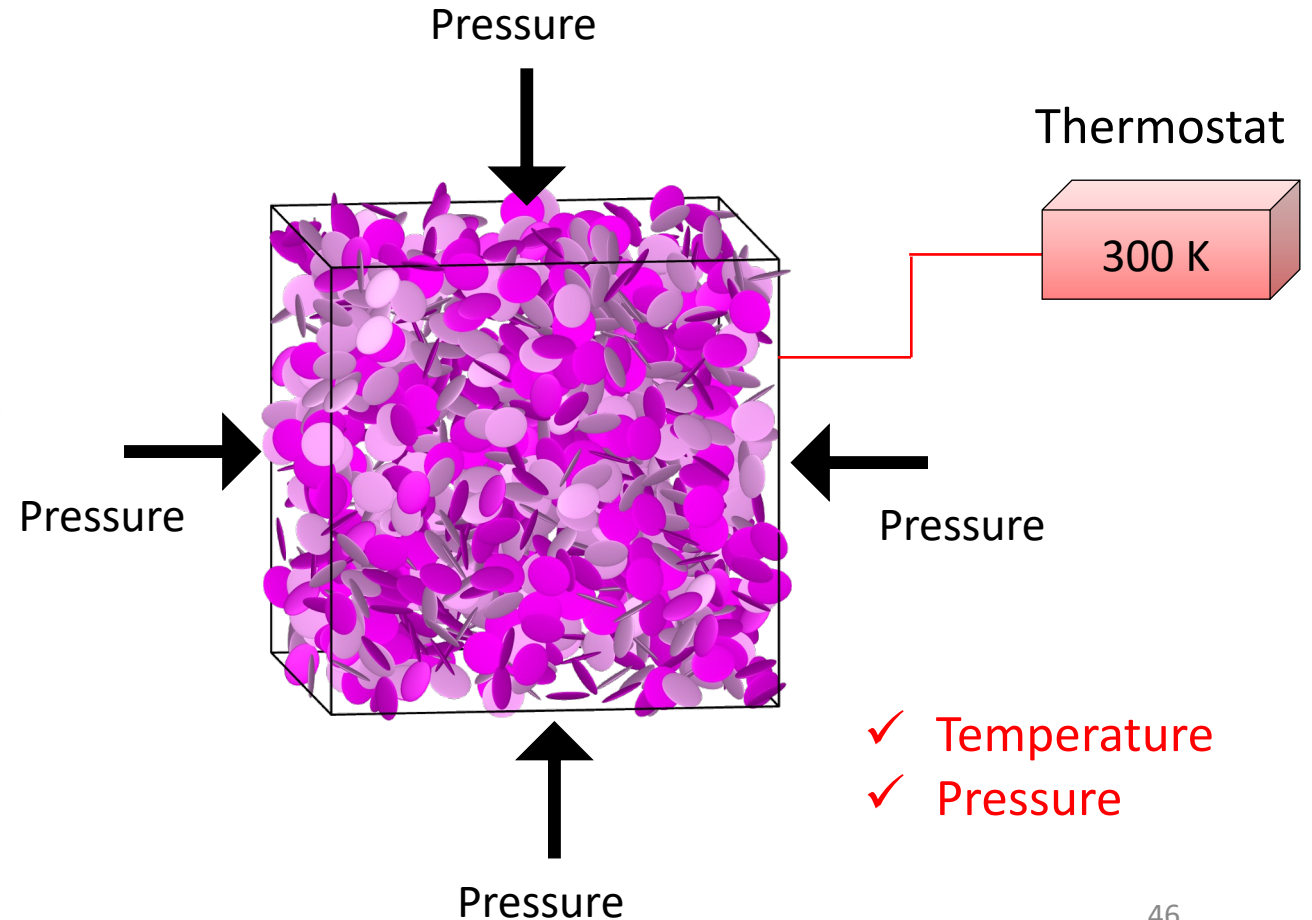
System level response

Periodic boundary condition

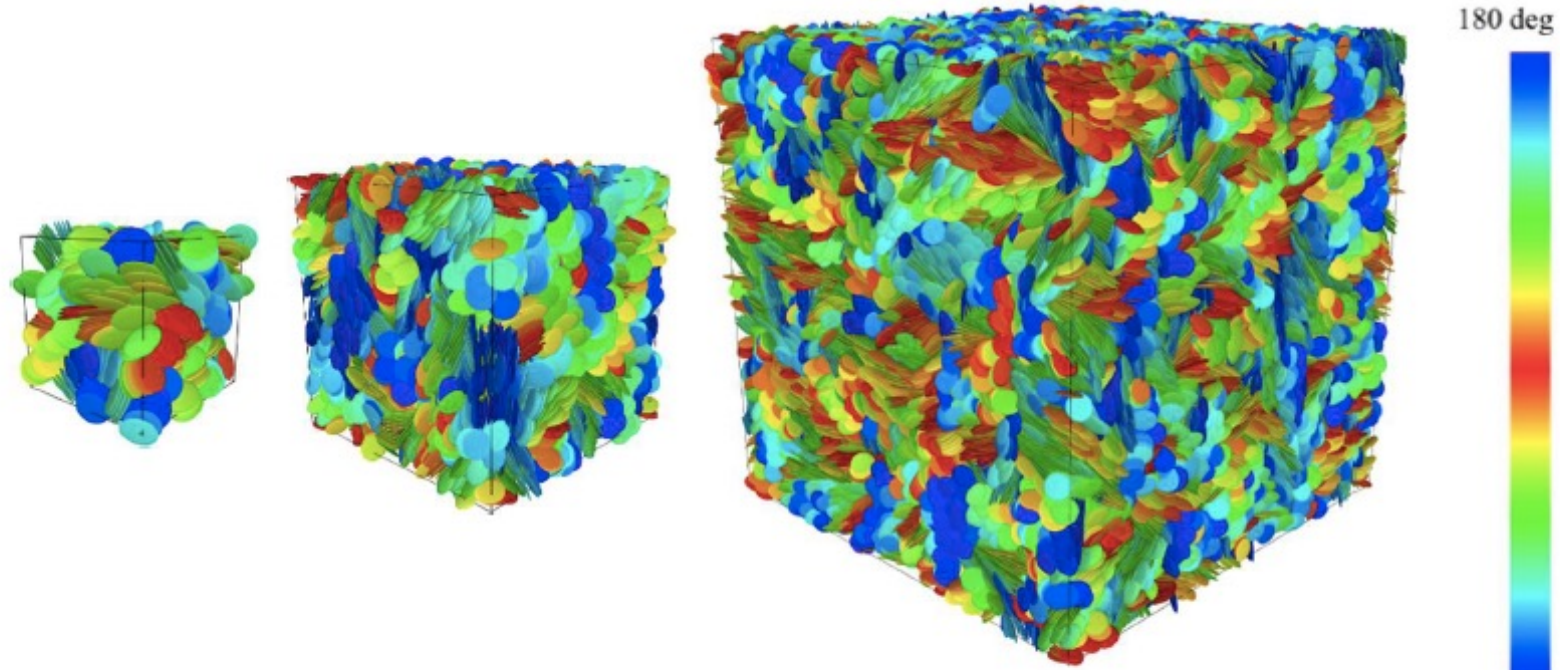
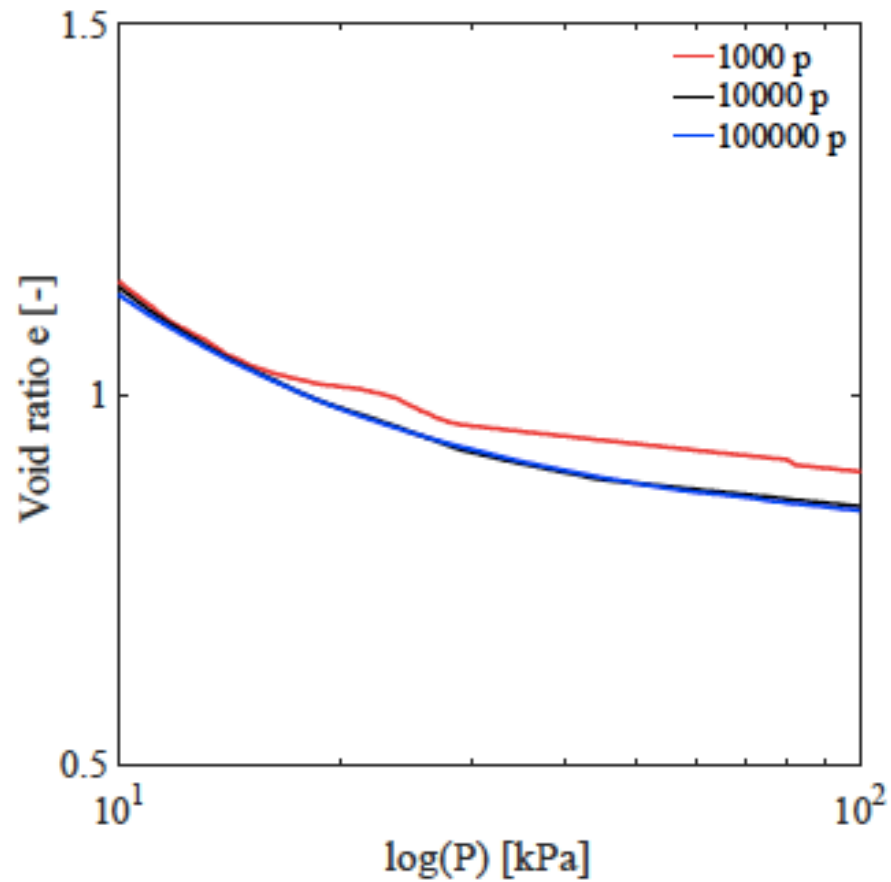


NPT ensemble

N: number of particles
P: pressure
T: temperature

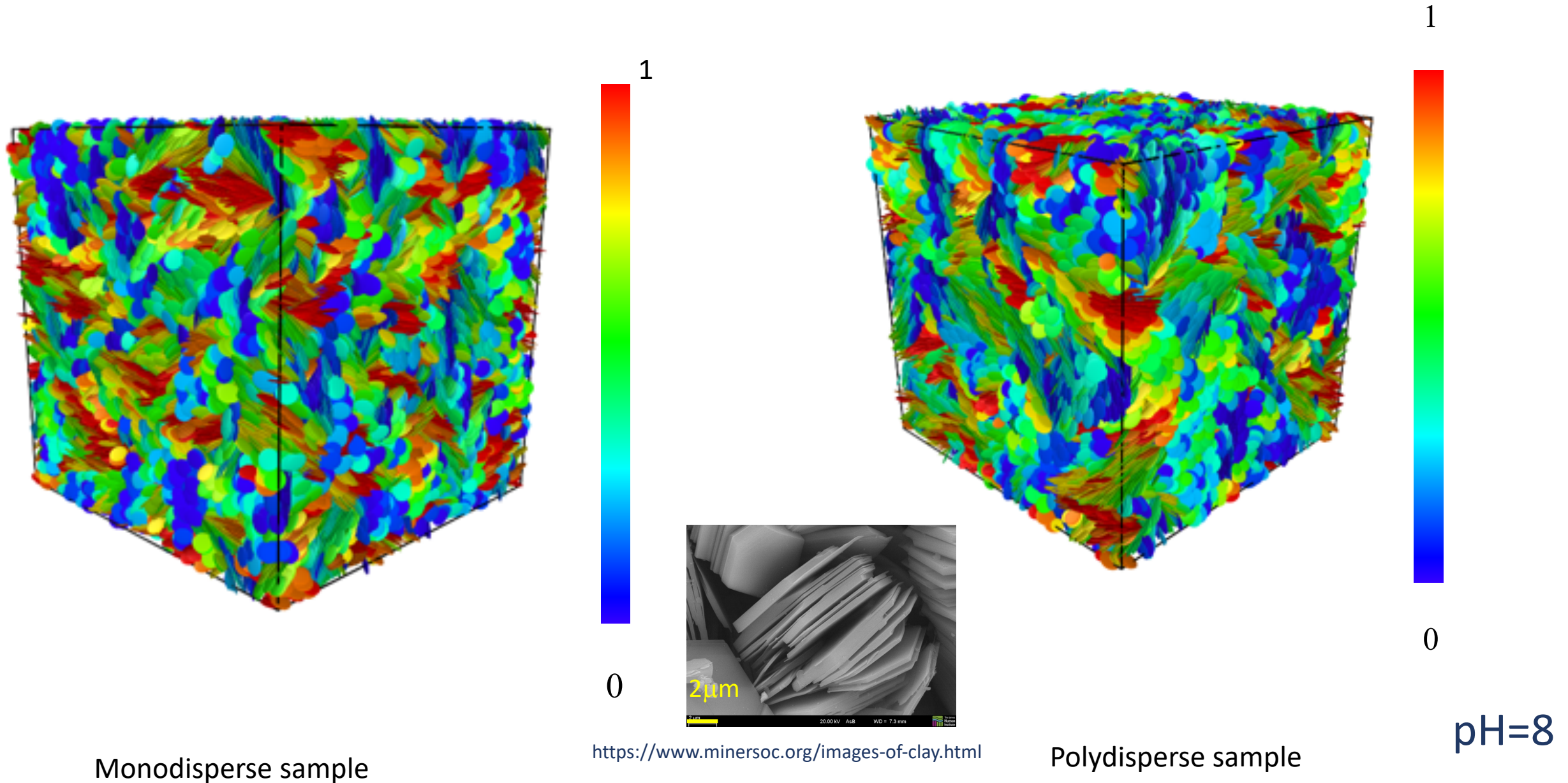


System response – isotropic compression



pH=8

System response – isotropic compression



Conclusions

- Link between clay particle interactions and mechanical behavior not well formed.
- Kaolinite is ideal material to develop a modelling framework
- Accepting validity of DLVO model Gay Berne potential can be calibrated to model clay particle interactions
- Need to consider large systems of particles
- Gay Berne framework is viable but needs modification

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