Discrete particle modelling as a molecular dynamics tool to study elastic properties of water in clay

Presented by

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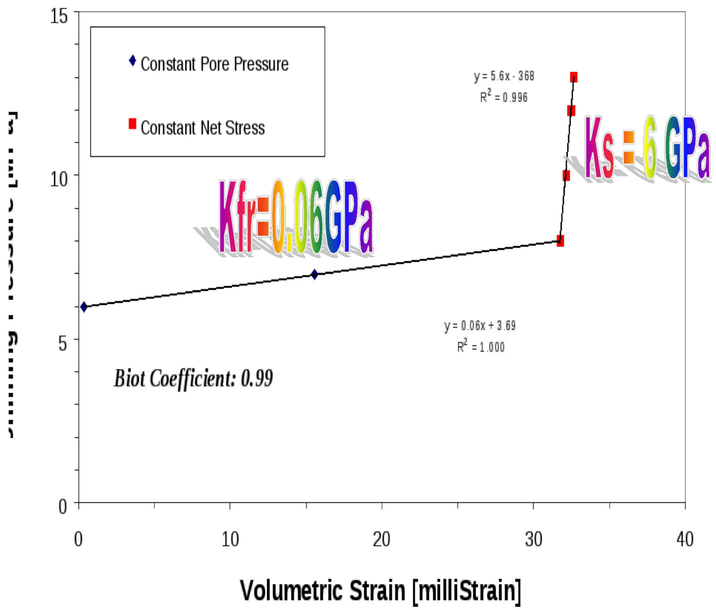
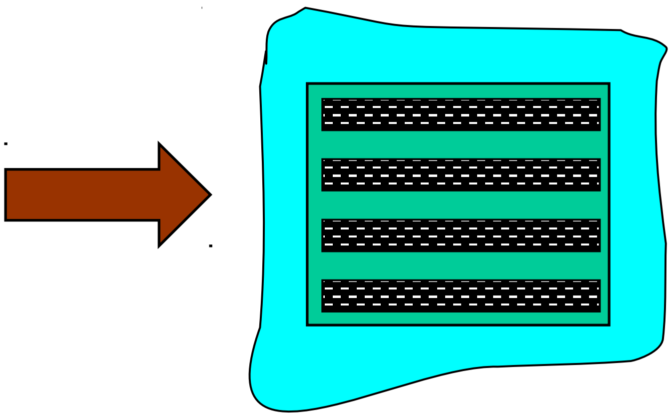
Outline

- Experimental results indicating the existence of bound water in unconsolidated clay.
- A Rock Physical Model for Shale
- Introduction of PFC
- Numerical simulations performed on a clay–water model in PFC
- Simulated measurements of the shear stiffness of bound water.

Experimental measurements indicating the existense of bound water in unconsolidated clay samples.



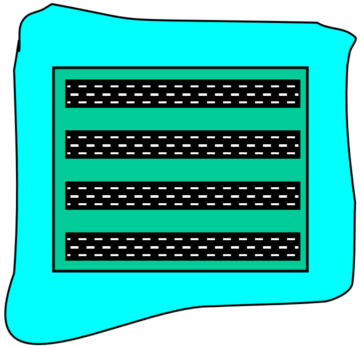


From Holt *et al*., EAGE 2009

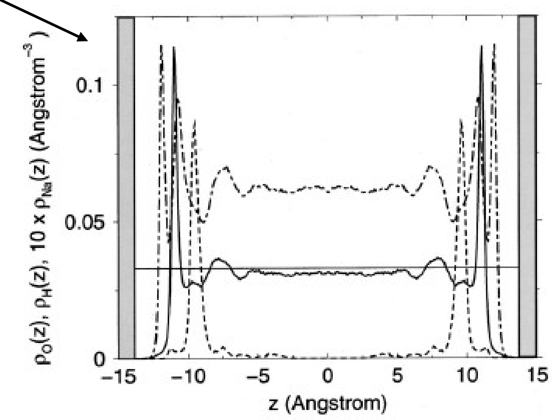
- K_s of Kaolinite < 10 GPa.
- Different experimental measurements (Prasad, Vanorio): K_s of dry clay ≥ 10 GPa
- Suggestion: Presence of bound water softens the grain bulk modulus.
  - The solid material is covered by a thin film of water molecules interacting with the solid surface.

A Rock Physics Model for Shale

- It is assumed that bound water in shale is
  - Attached to clay mineral surfaces and interstitial in swelling clay minerals
  - Equivalent to Debye thickness from electrostatic double-layer theory, or 1-2 monolayers thick ?
  - Because pore sizes are 2-20 nm and because of abundant clay minerals, bound water effects are much more important in shale than in other rock types
  - Amount depends on the clay surface area and surface charge density.
  - Strong hydrogen bonds with the clay surface

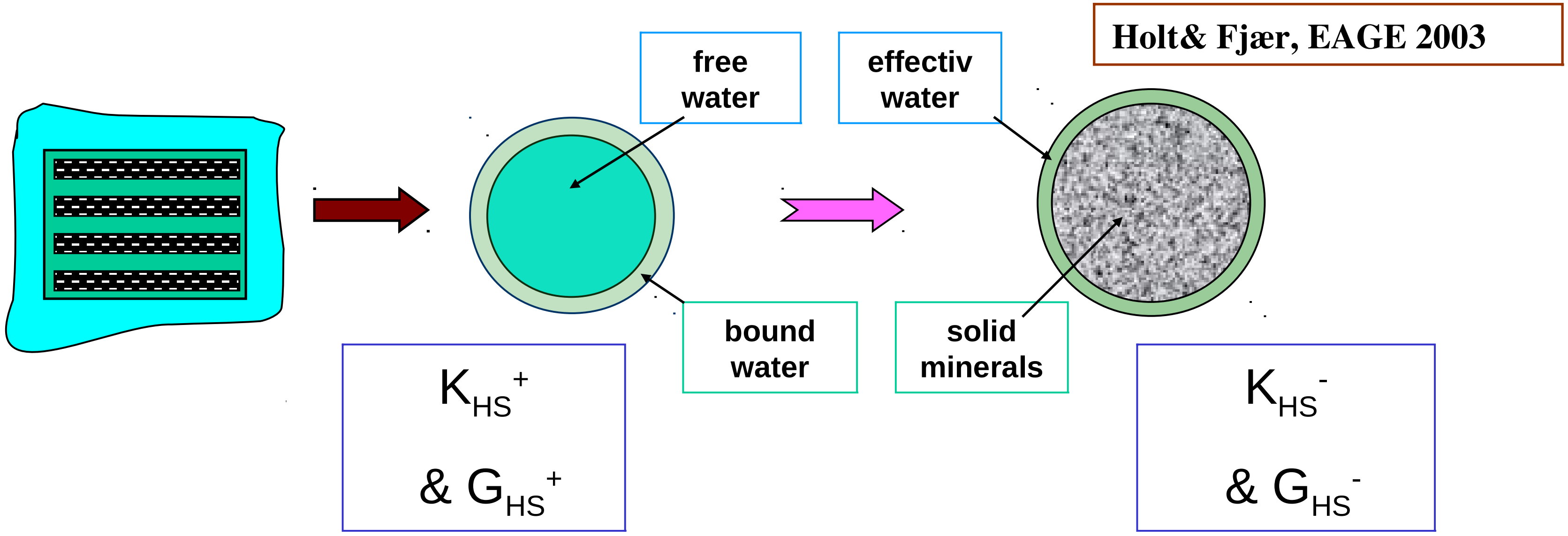


Holt& Fjær, EAGE 2003



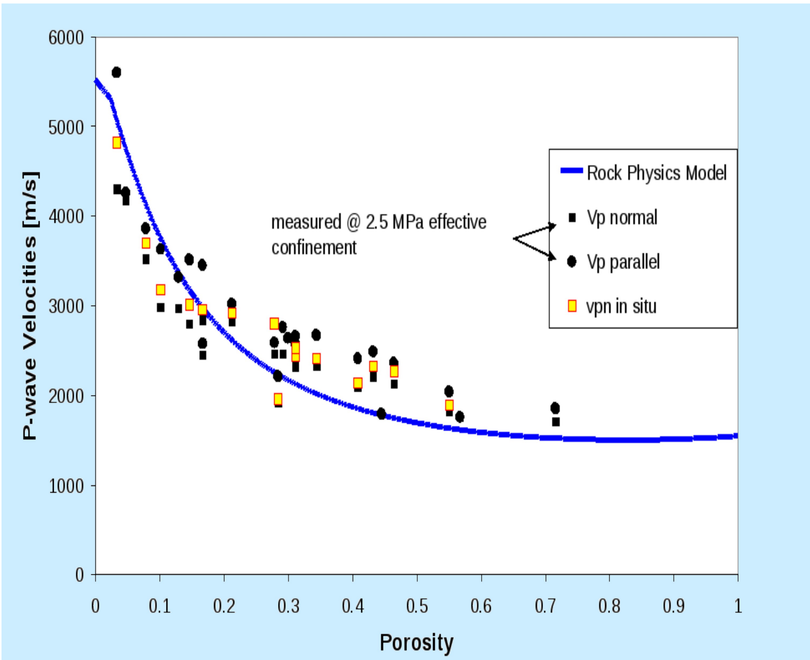
(Skipper, J.Chem.Phys.,Vol. 114, No. 8, 2001)

A Rock Physics Model for shale



- ***Application of Hashin-Shtrikman equations to shale***
  - ***Pore size in shale: 2-20 nm***
  - ***Intercalated water between the clay sheets on nm-scale***
  - ***Grain stiffness in shale : K and G < 20 GPa.***
  - ***K_{BW} and G_{BW} unknown parameters***
- **Bound water (with shear stiffness) needs to be accounted for**
  - **Tool for verification: Moleculer mechanics simulations**

A Rock Physics Model for shale



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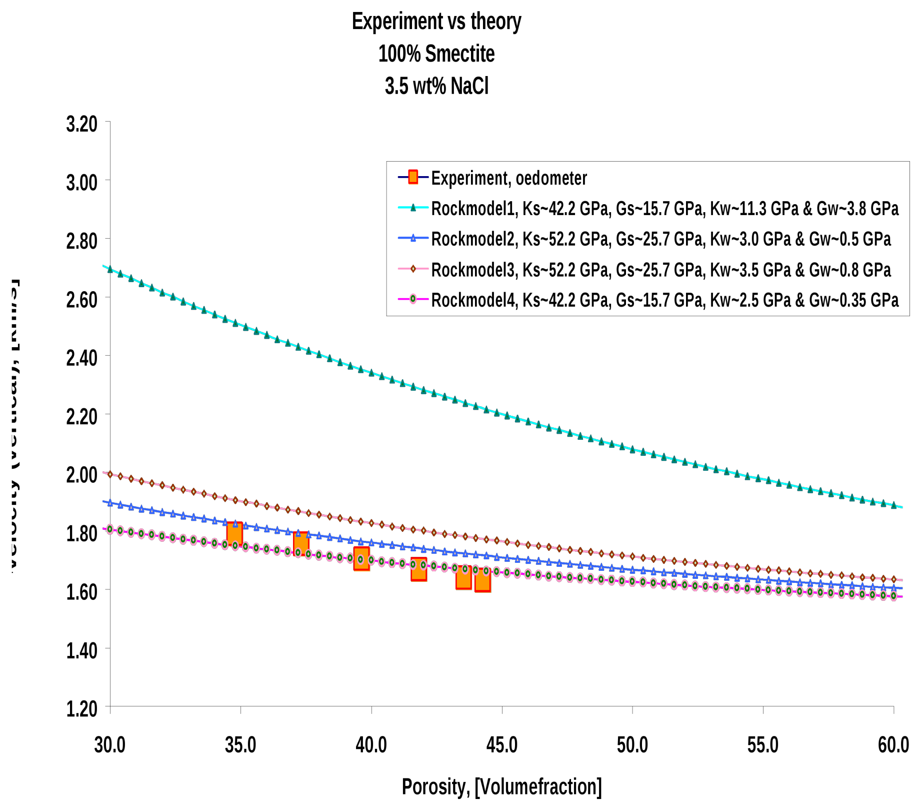
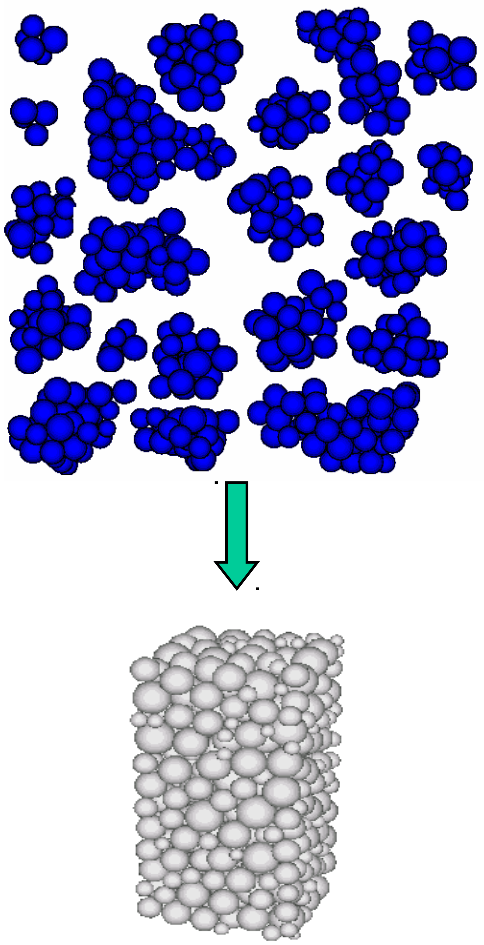


- Left side: Predictions from the model, with bound water properties K_{bw}=3.4 and G_{bw}=5.1 GPa.
- Right side: Predictions from the model, with different bound water properties.

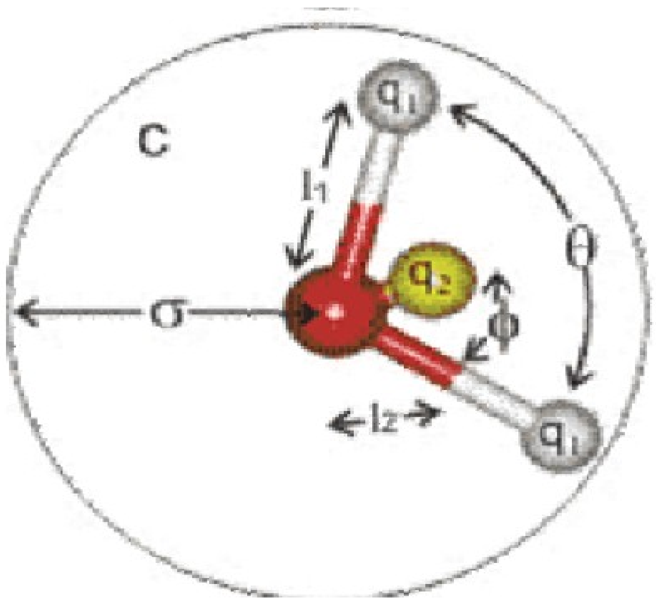
  Oedometer experiment on an unconsolidated smectite sample.

PFC : Introduction

- Real grains (abritrary shaped) :
- Created by either a
  - Cluster: Adjustable bond properties.
    - Soft grains.
  - Clump: Unbreakable bonds
    - Very stiff grains
- Bond strength distribution is implemented
  - Heterogeneity
- Algorithms for estimating bulk and shear moduli of porous rocks on the µm-scale available (http://www.itascacg.com)
  - Triaxal, biaxial, uniaxial stress tests

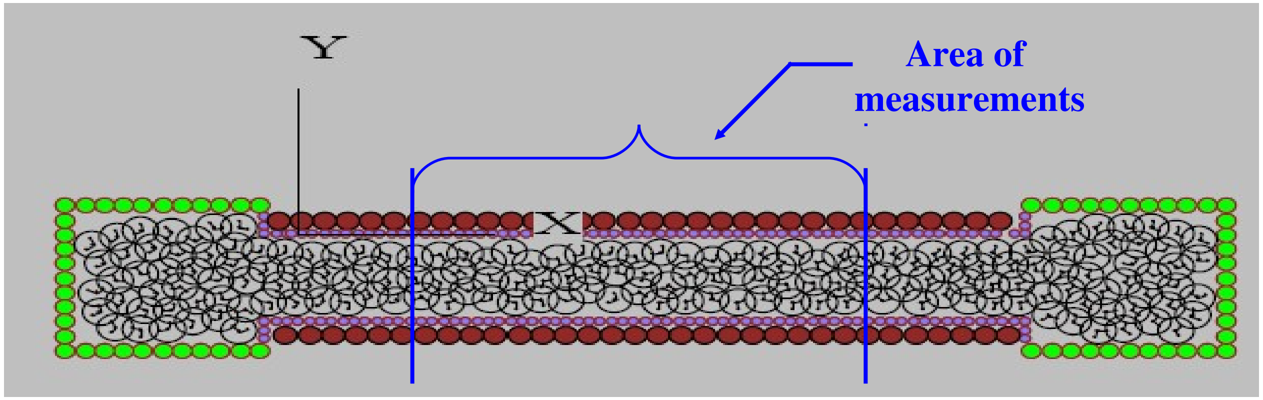


Numerical simulations performed on a clay–water model in PFC



- **The TIP4P water molecule model (4 sites)**
  - **Oxygen ion**
    - **Van der Waal site: Red ball**
    - **Coulomb site: Yellow ball**
      - ✓ **q_2= -1.04 e**
    - **Separation distance: 0.15 Angstrom**
  - **Hydrogen ions (white balls)**
    - **q_1 = 0.52 e**
  - **Θ = 104.52^0**
  - **L_1= L_2 = 0.9572 Angstrom**
- **Reproduces experimental thermodynamical and structural data of bulk water (Jorgensen et al, 1983)**
- **Extensively used in Monte Carlo simulation of clay-water systems (Skipper, Carvalho, Boek 1995-2008)**
- **Modeled as a PFC-clump (strong covalent bonds).**

Numerical simulations performed on a clay–water model in PFC



- ❑ Mineral surface:
  - Brown balls : Positive ions (+2e, unchanged)
  - Blue balls : Oxygen ions (changable charge)
  - Green balls : Interacts with H_2O only through van der Waal forces. Confines free water molecules.
- ❑ TIP4P water molecules confined between two planar and charged surfaces
  - Separation distance: 12.64 Angstrom (Boek, 1995)
  - Length of charged surface: 6.80 nm.
- ❑ Area of measurement: Between the blue lines → Avoid edge effects.

Numerical simulations performed on a clay–water model in PFC

- Potential energy function describing each pair interaction within the clay water system

Coulomb

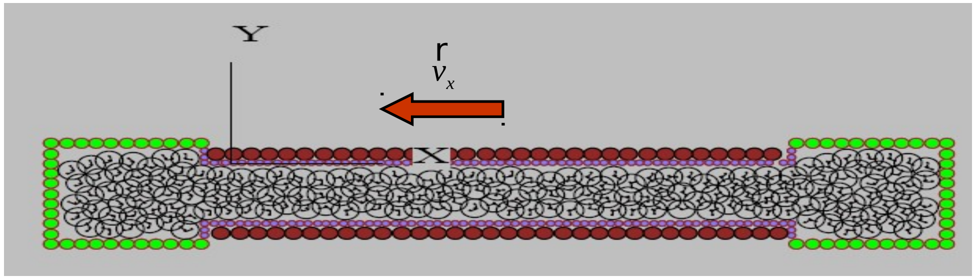
$$v_{ij} = \frac{kq_i q_j}{r_{ij}} + 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$

van der Waal

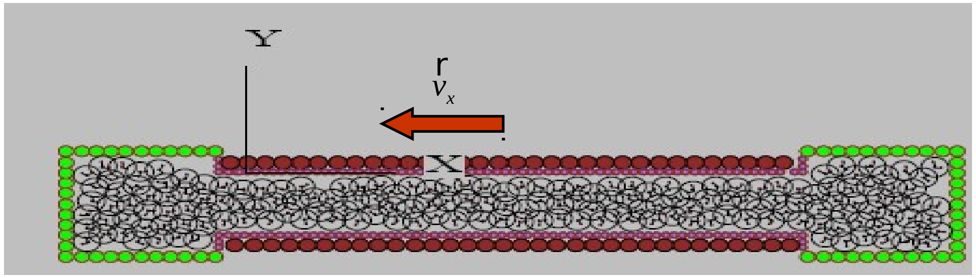
Lennard Jones potential

- **Parameters:**
  - **q_i = Charge of ion i**
  - **r_{ij} = Separation between interacting pair of ions i and j**
  - **ε_{ij} = Binding energy at equilibrium**
  - **σ_{ij} = Minimum separation distance between ions i and j.**

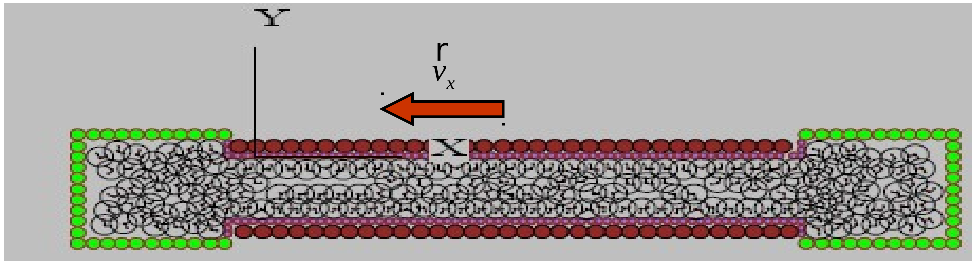
Numerical simulations performed on a clay–water model in PFC



Only van der Waal interaction



Surface charge density: -0.5 C/m^2



Surface charge density: -1.1 C/m^2

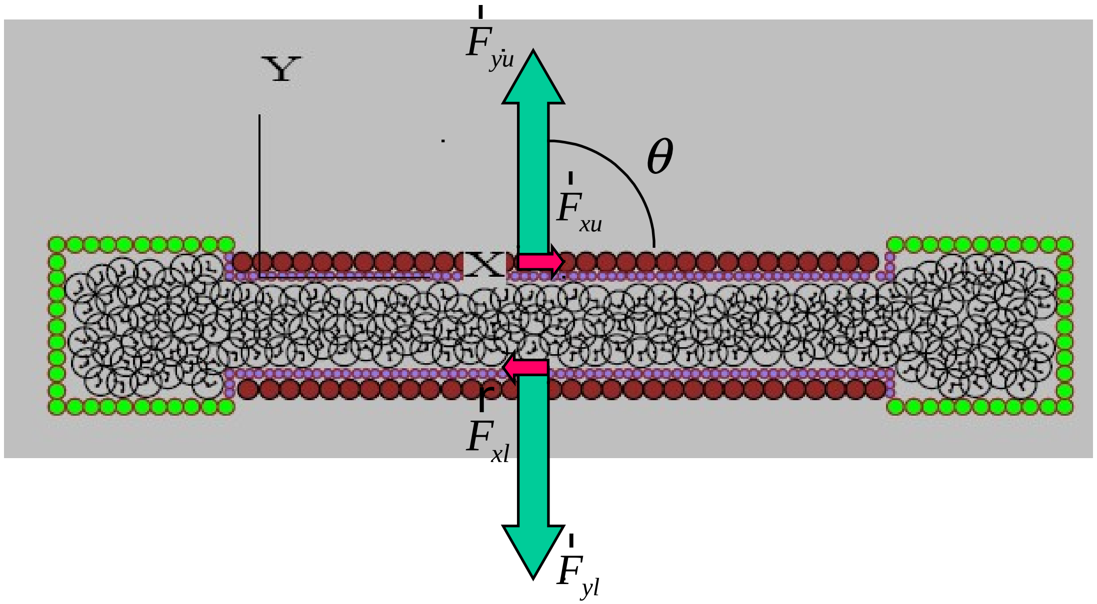
- Performed shearing experiment:
  - Upper surface move with constant velocity
  - Lower surface stationary
  - Negative charge density varying between 0 and -1.1 C/m^2.

- Results:
  - Enhanced ordering of the water molecule structure with increased negative surface charge density.

    ↓

  - Increased shear stiffness with increasing negative surface charge density.

Numerical measurements of the shear stiffness of bound water

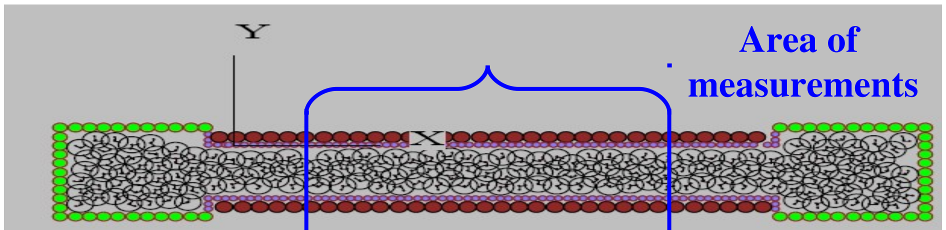


- $|\vec{F}_{xu}| \ll |\vec{F}_{yu}|$ **and** $|\vec{F}_{xl}| \ll |\vec{F}_{yl}| \Rightarrow \theta \approx 90^0$
- $|\vec{F}_{xu}| \neq 0$ **and** $|\vec{F}_{xl}| \neq 0 \Rightarrow$ **Shear stiffness ≠ 0**

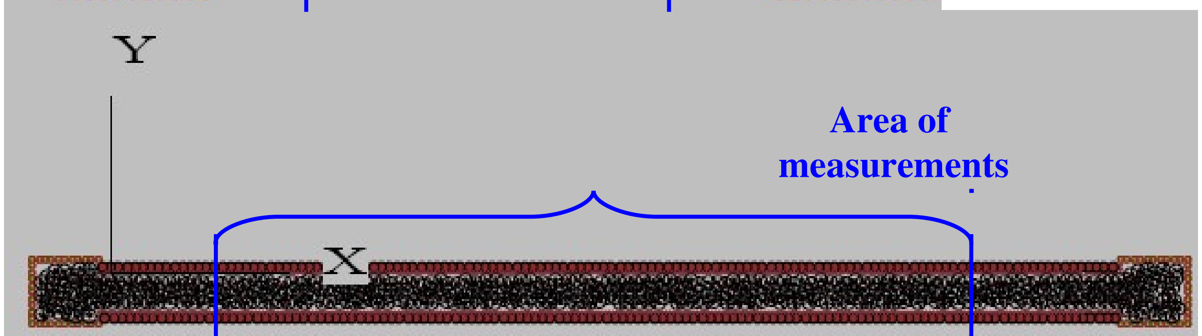
Numerical measurements of the shear stiffness of bound water

Three different sizes:

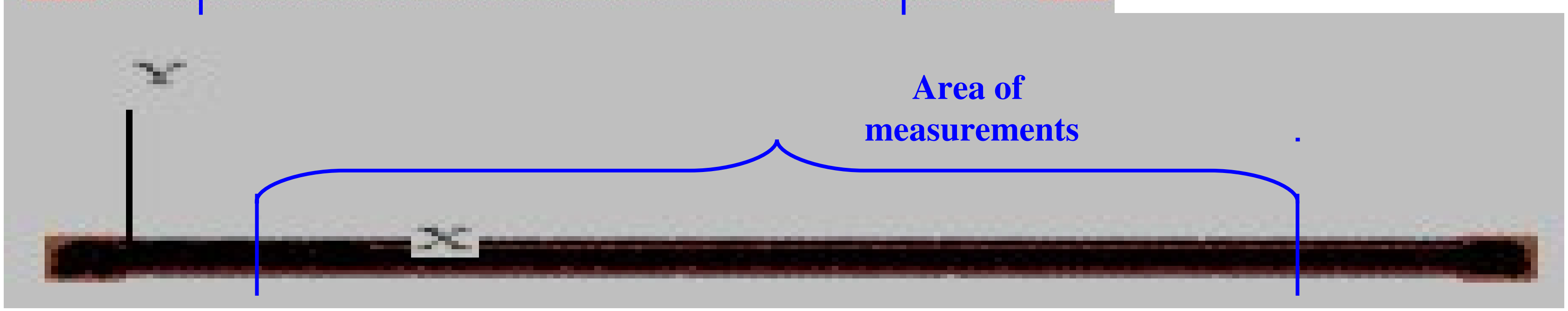
Negative surface charge density identical for all three models (-0.5 C/m^2).



Model 1: Length of channel: 6.8 nm.

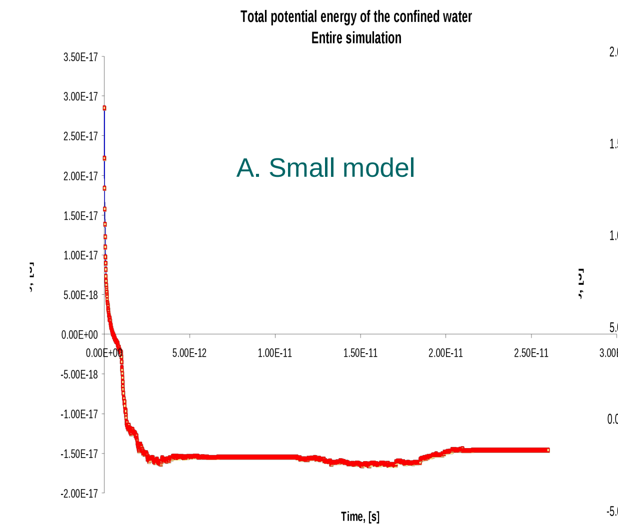


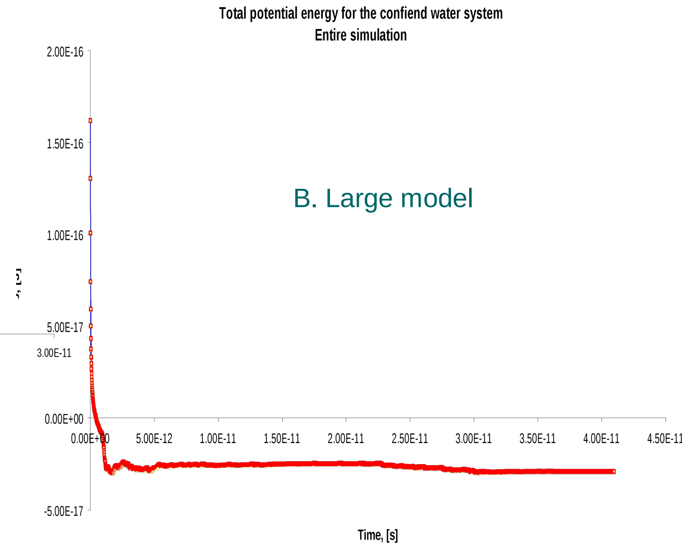
Model 2: Length of channel: 27.0 nm.

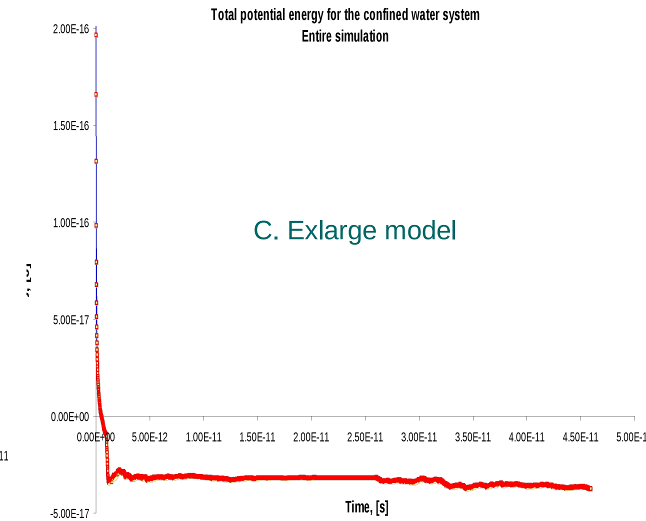


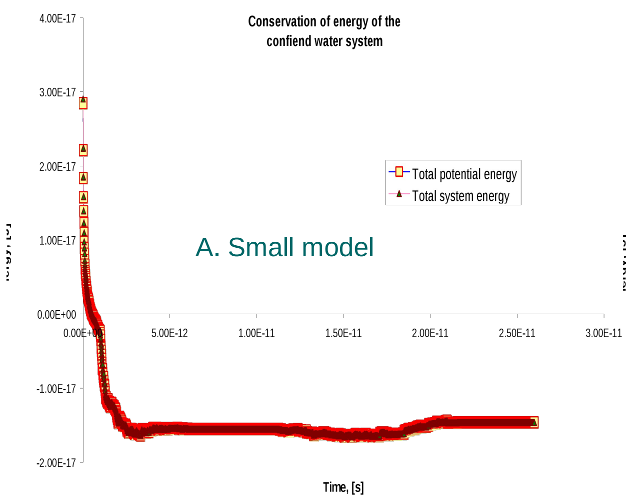
Model 3: Length of channel: 42.7 nm

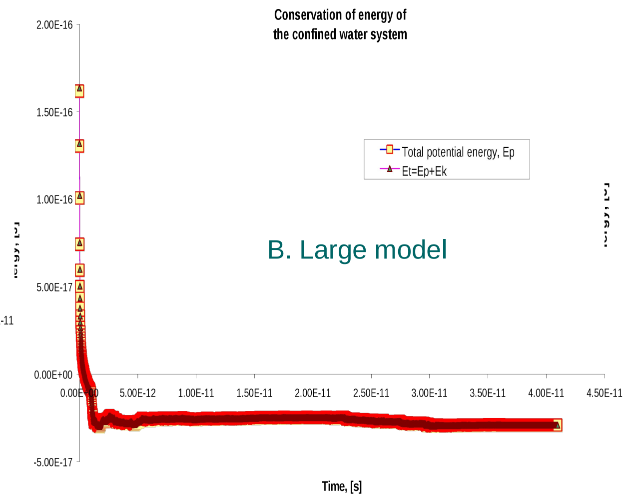
Numerical measurements of the shear stiffness of bound water

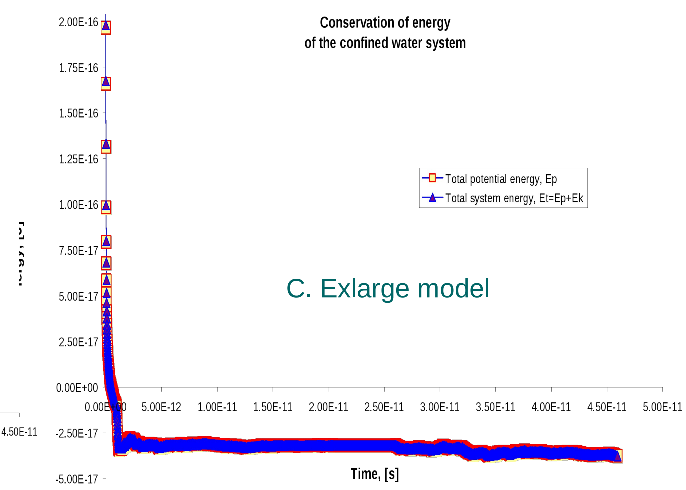




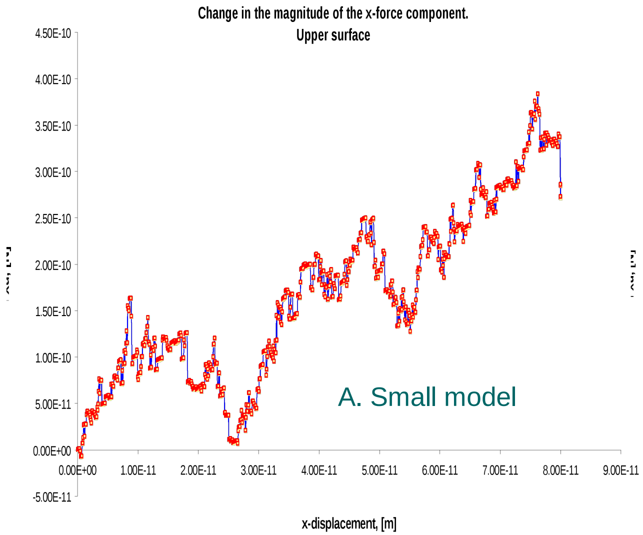


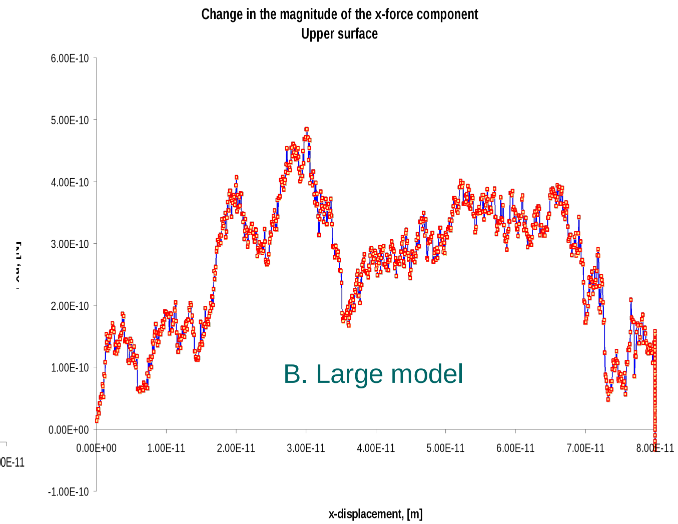


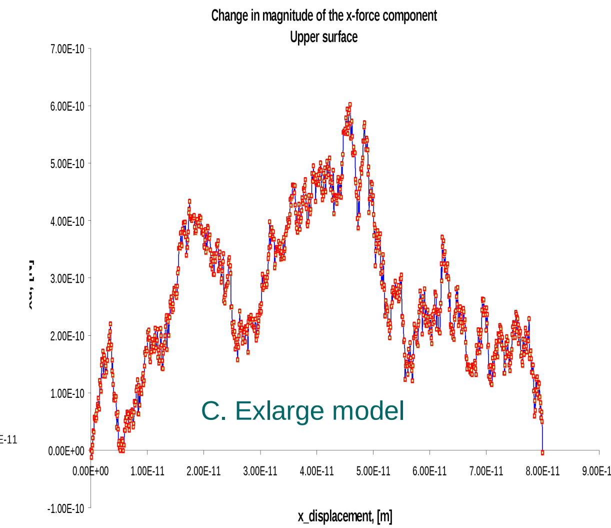


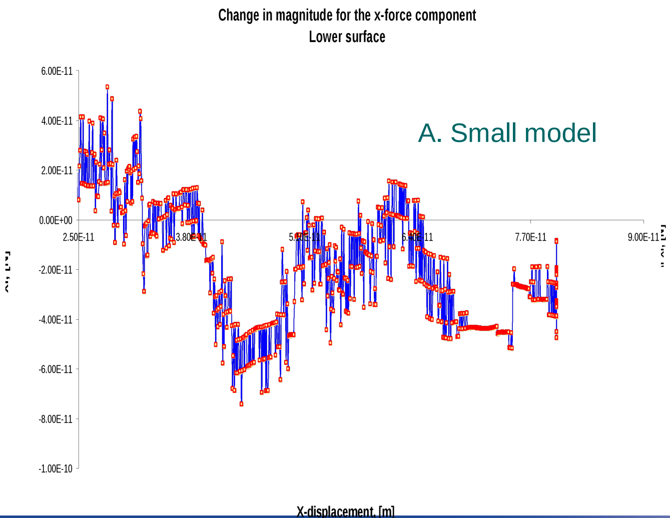


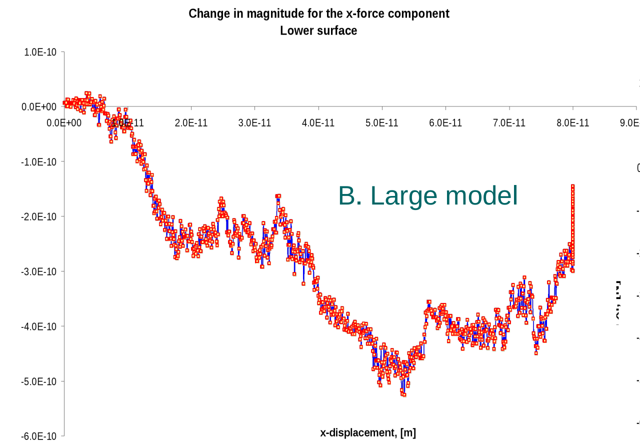
Simulated measurements of the shear stiffness of bound water.

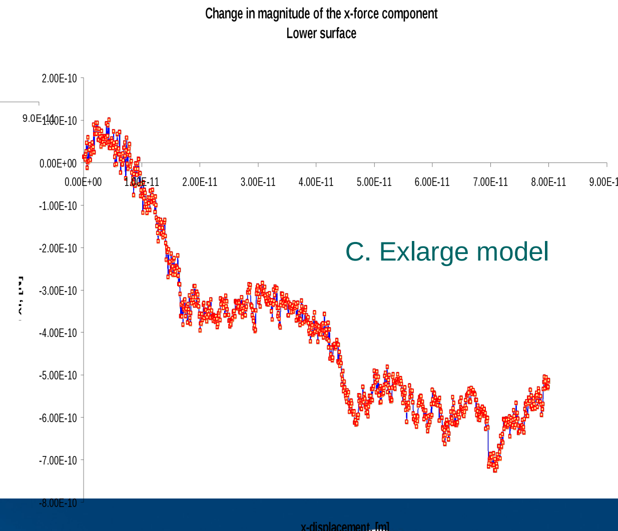




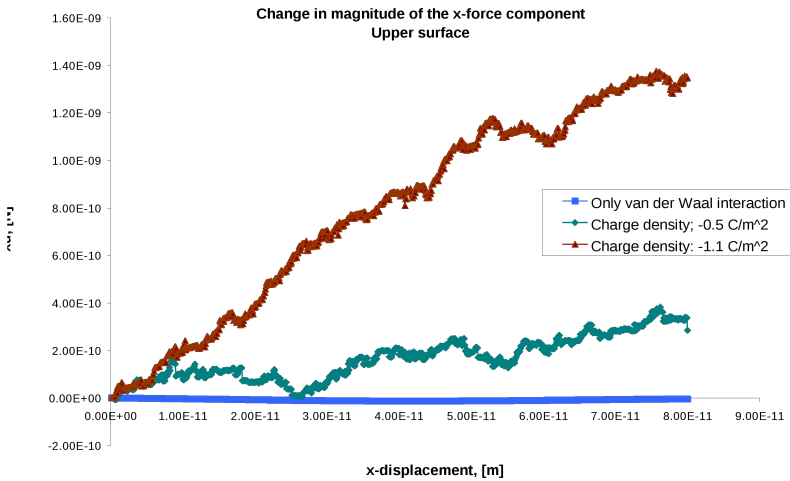


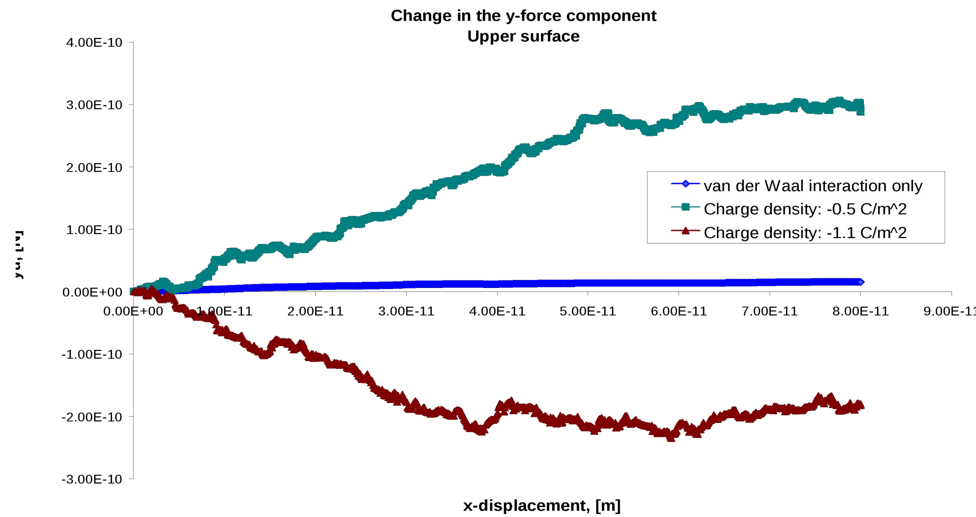


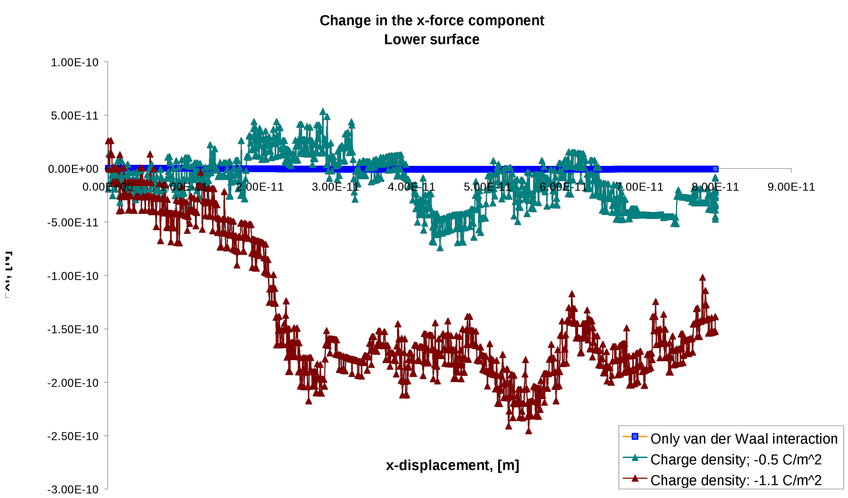


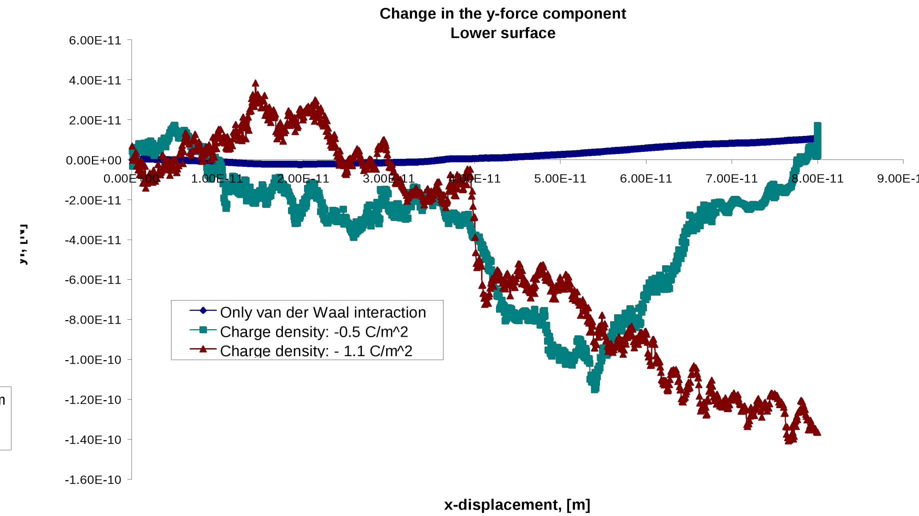


Simulated measurements of the shear stiffness of bound water.

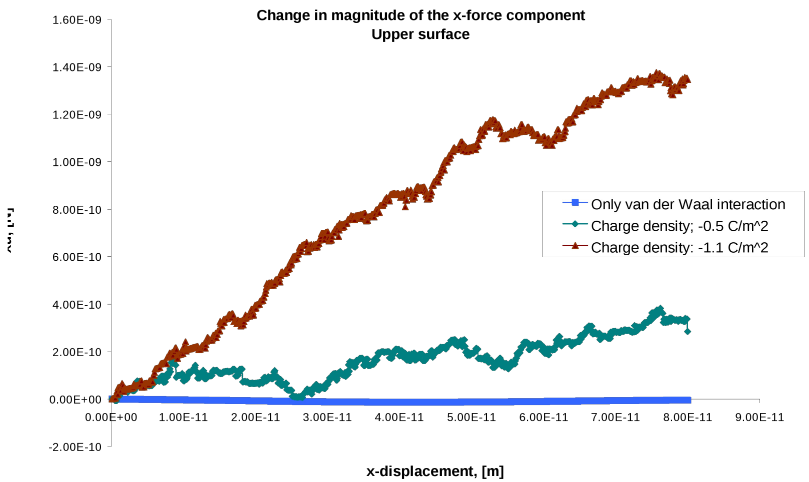


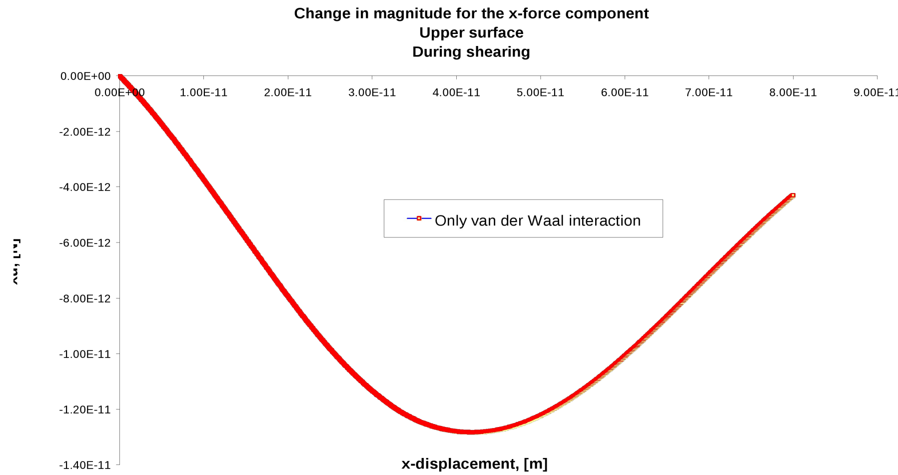


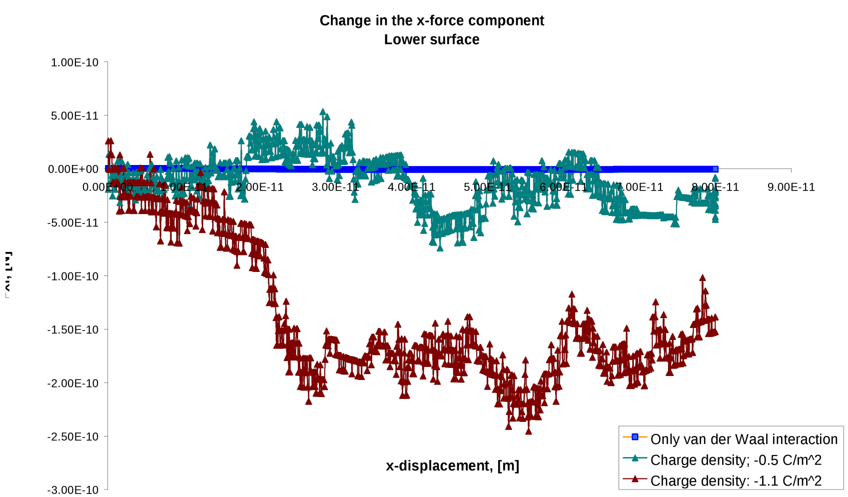


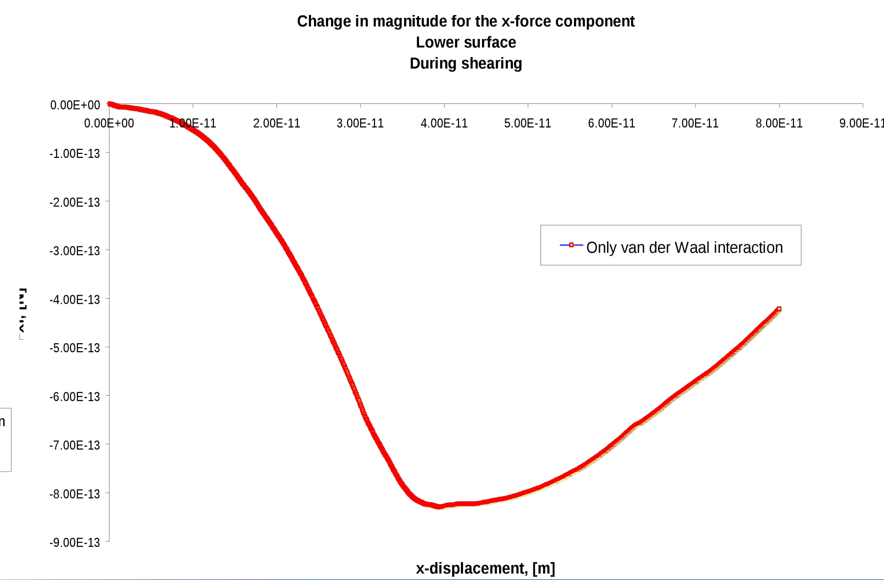


Simulated measurements of the shear stiffness of bound water.









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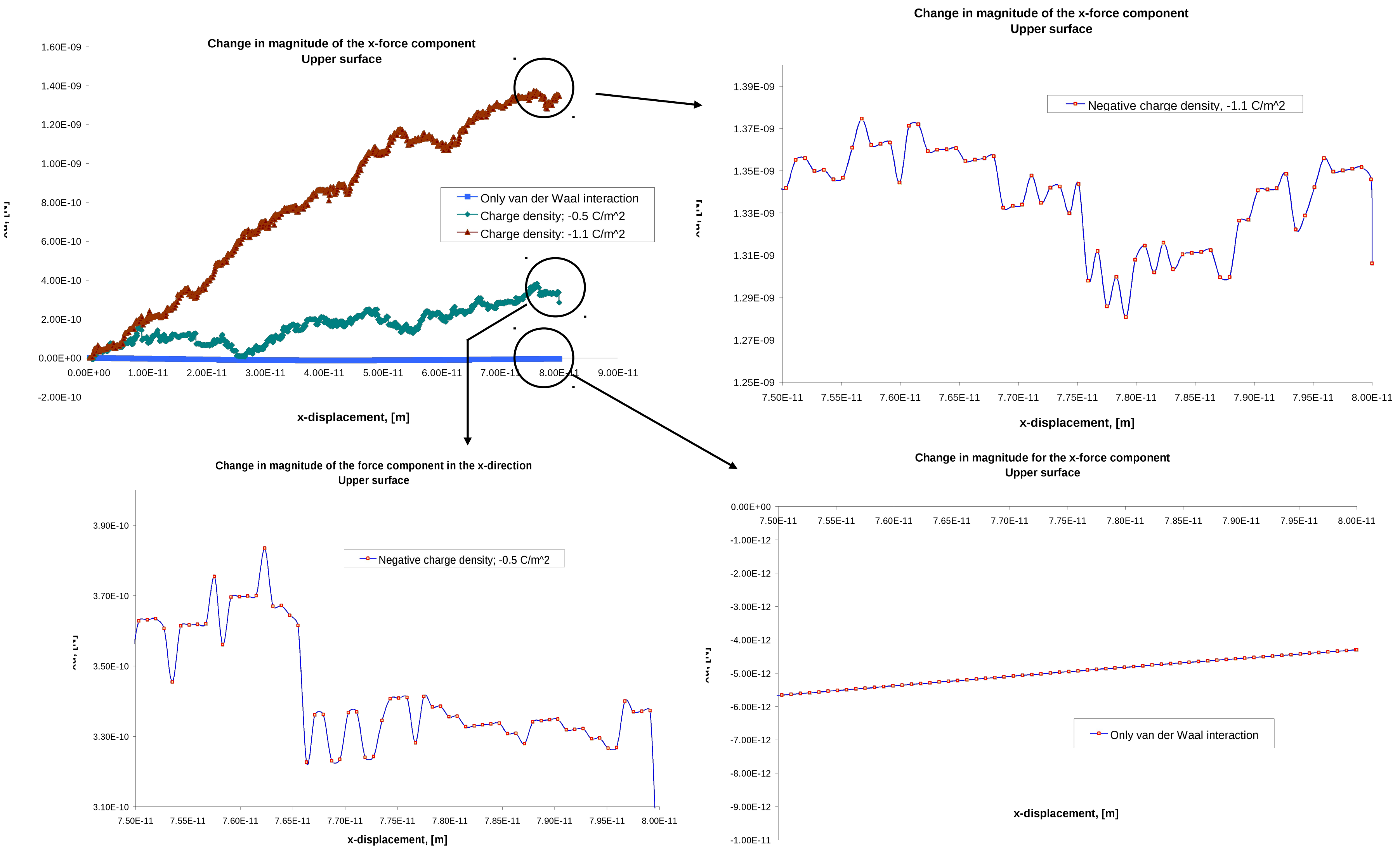
Simulated measurements of the shear stiffness of bound water.



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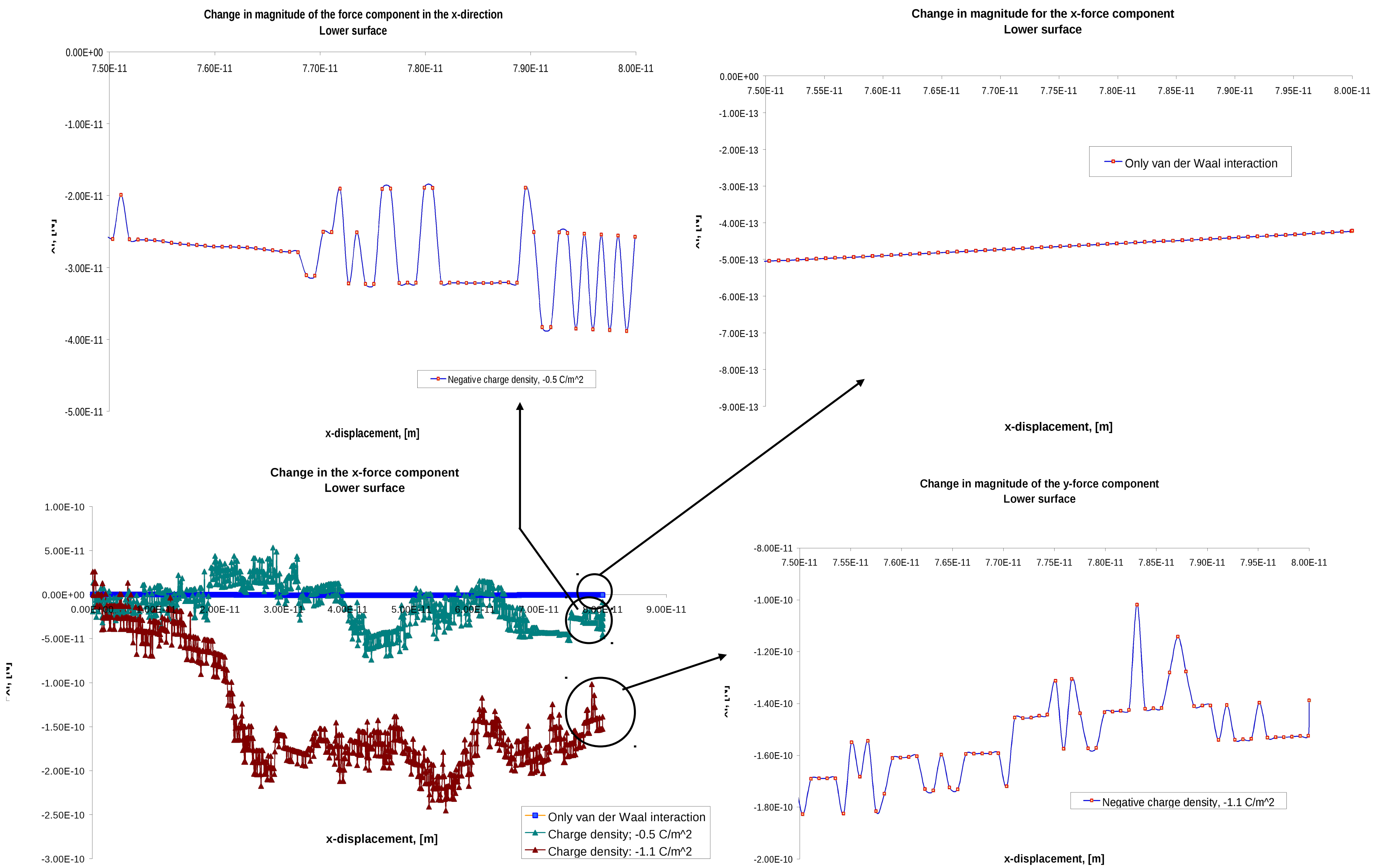

Summary

- Experimental data indicate that bound water exist in saturated unconsolidated clay samples.

- Molecular Mechanics-modelling of intercalated water in clay using PFC:
  - Separation distance between charged surfaces: nm-scale!
  - Increasing negative surface charge density
    - ✓ Enhanced ordering of the water molecule system
    - ✓ Increasing shear stiffness of the water molecule system with increasing negative surface charge density.
    - ✓ Only van der Waal interactions activated → Shear stiffness ≠ 0.