Theoretical Studies with Density Functional Theory (DFT) on Ca/ Na Montmorillonite: Structure, Forces and Swelling Properties

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Outline

- **Research Background**
- **Methods**
- **Results**
- **Conclusions and applications**

Research Background

- **Swedish KBS-3 disposal concept**

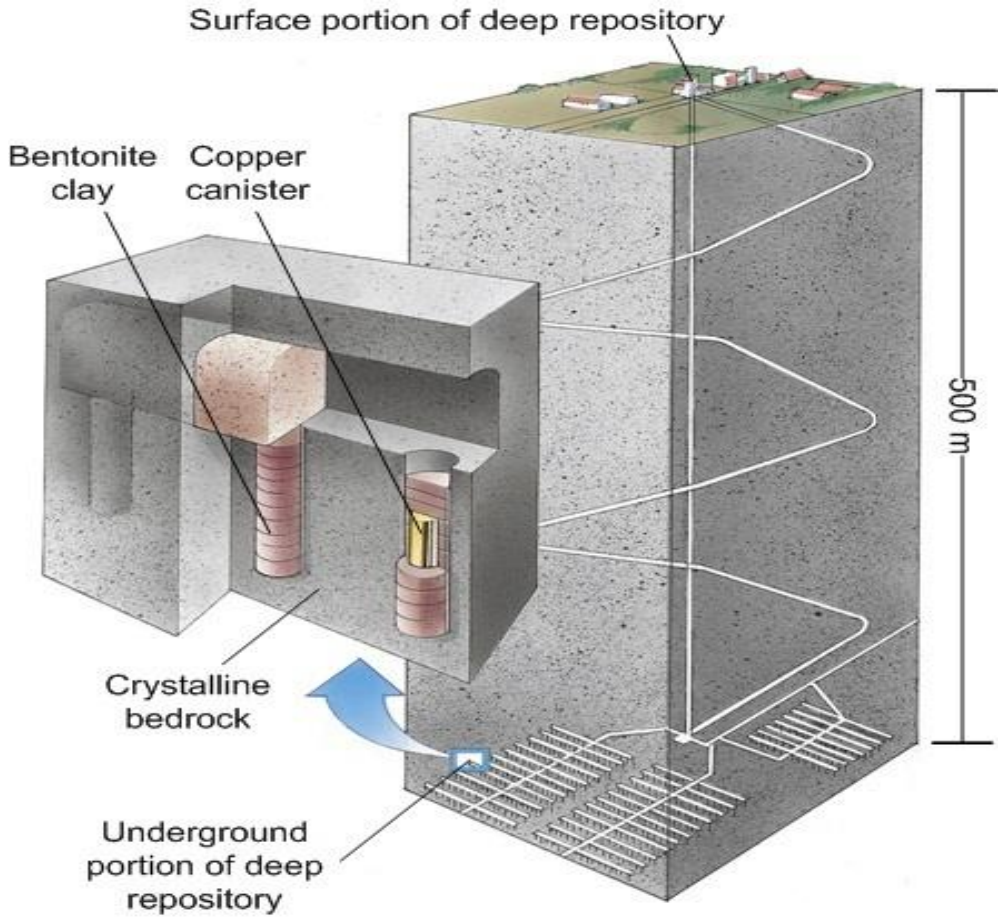


Fig 1. Swedish KBS-3 repository design

Research Background

- **Structure of Ca/ Na-bentonite**

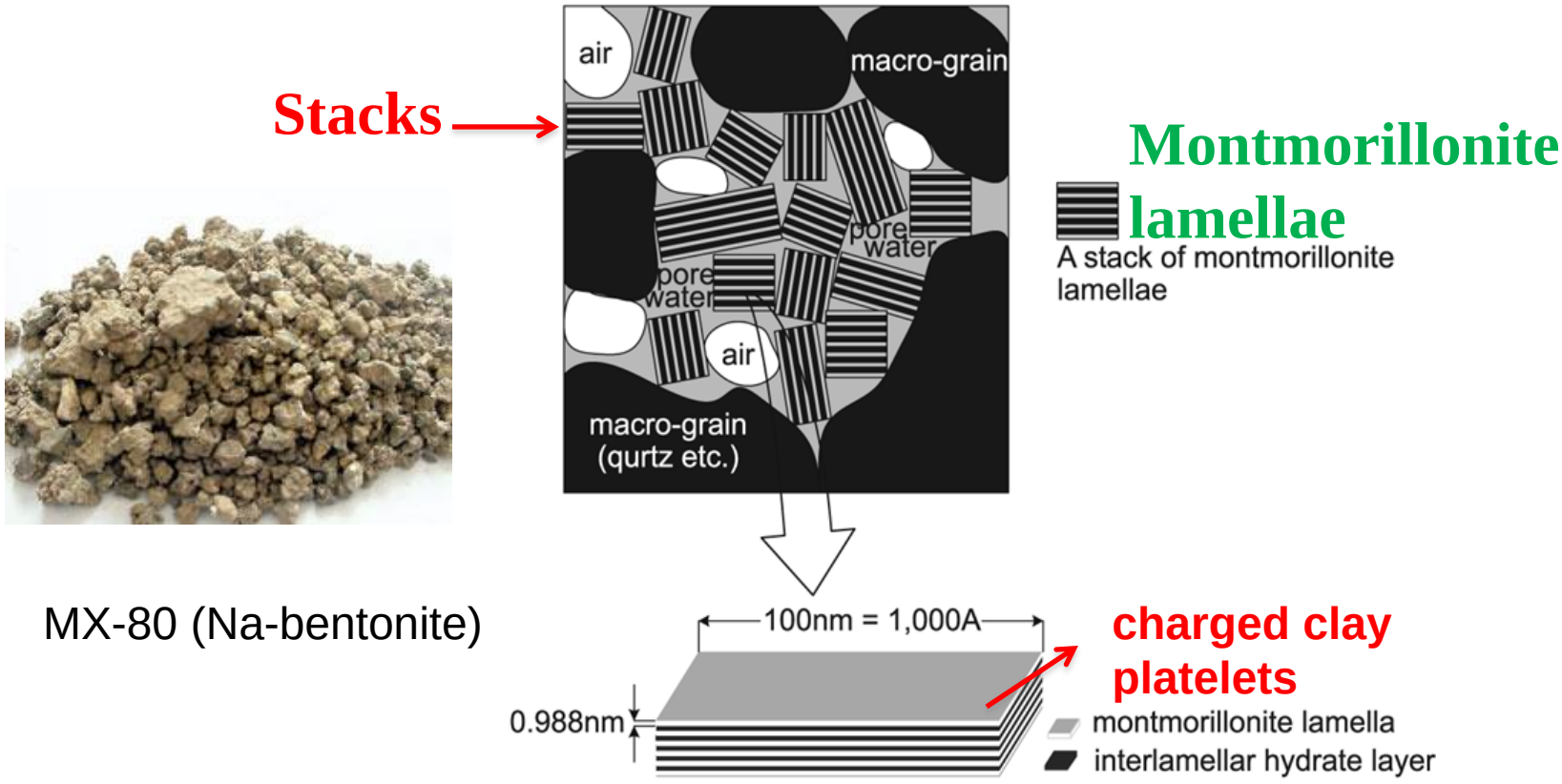


Figure 2. Structure of bentonite buffer

Research Background

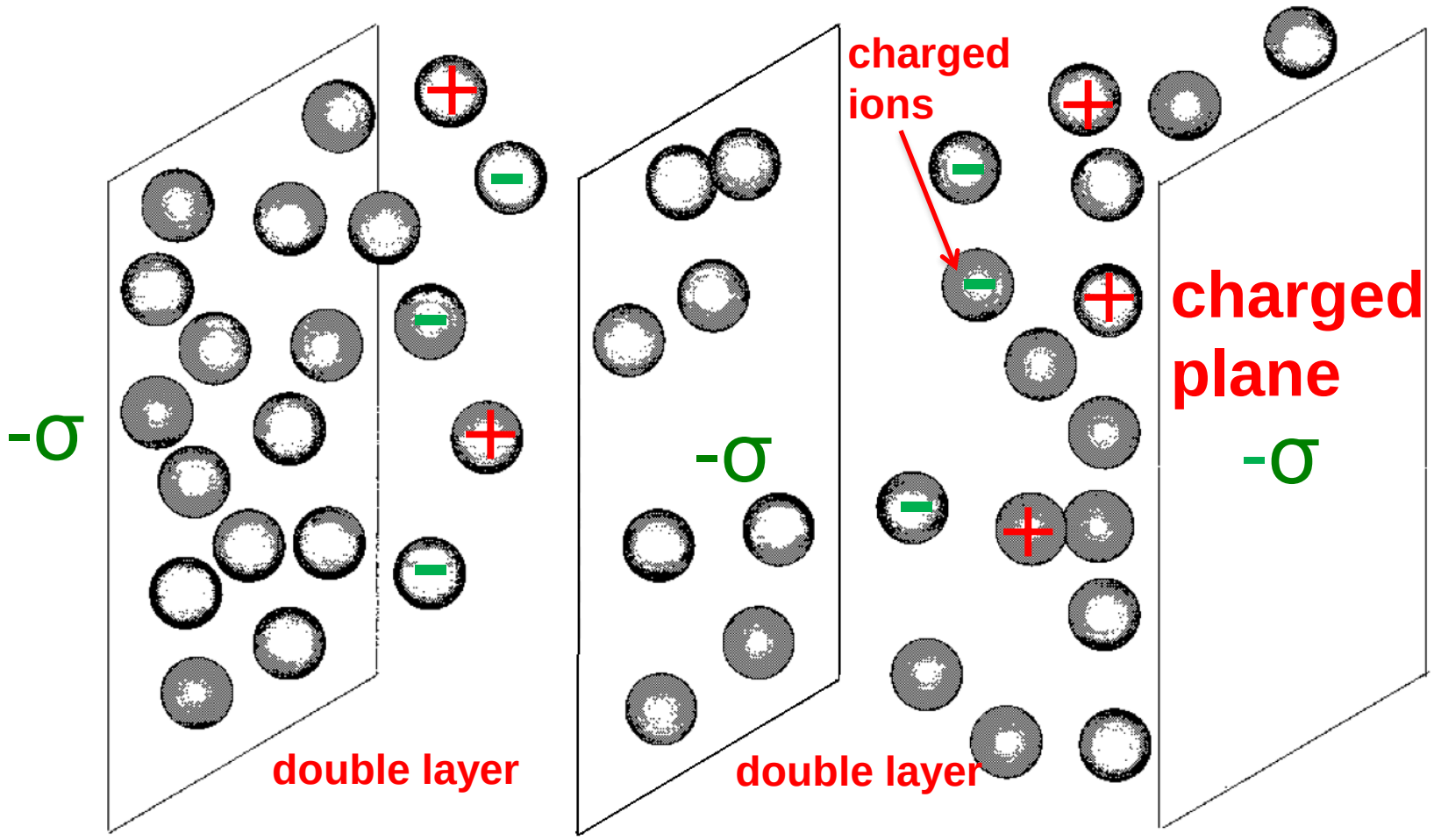


Fig 3. Schematic picture of a stack of montmorillonite lamella

Research Background

- **Swelling ability of bentonite(smectites)**

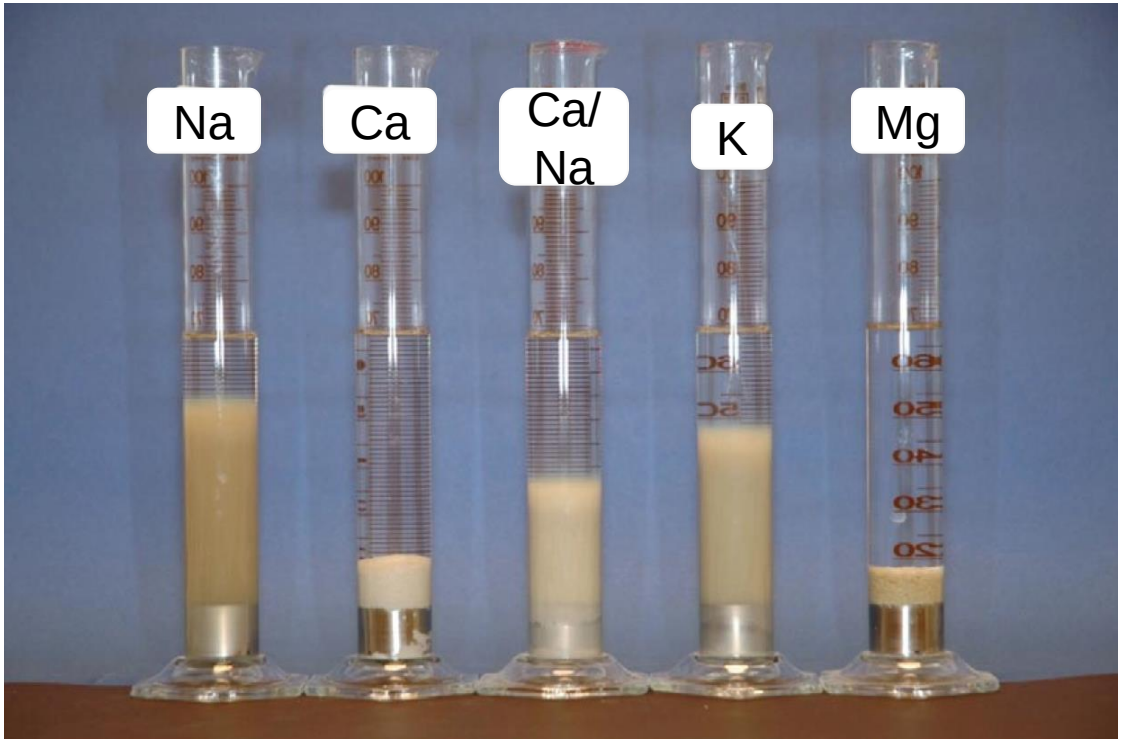


Fig 4. Free swelling tests with pure montmorillonites.
Birgersson et al. 2009

Research Background

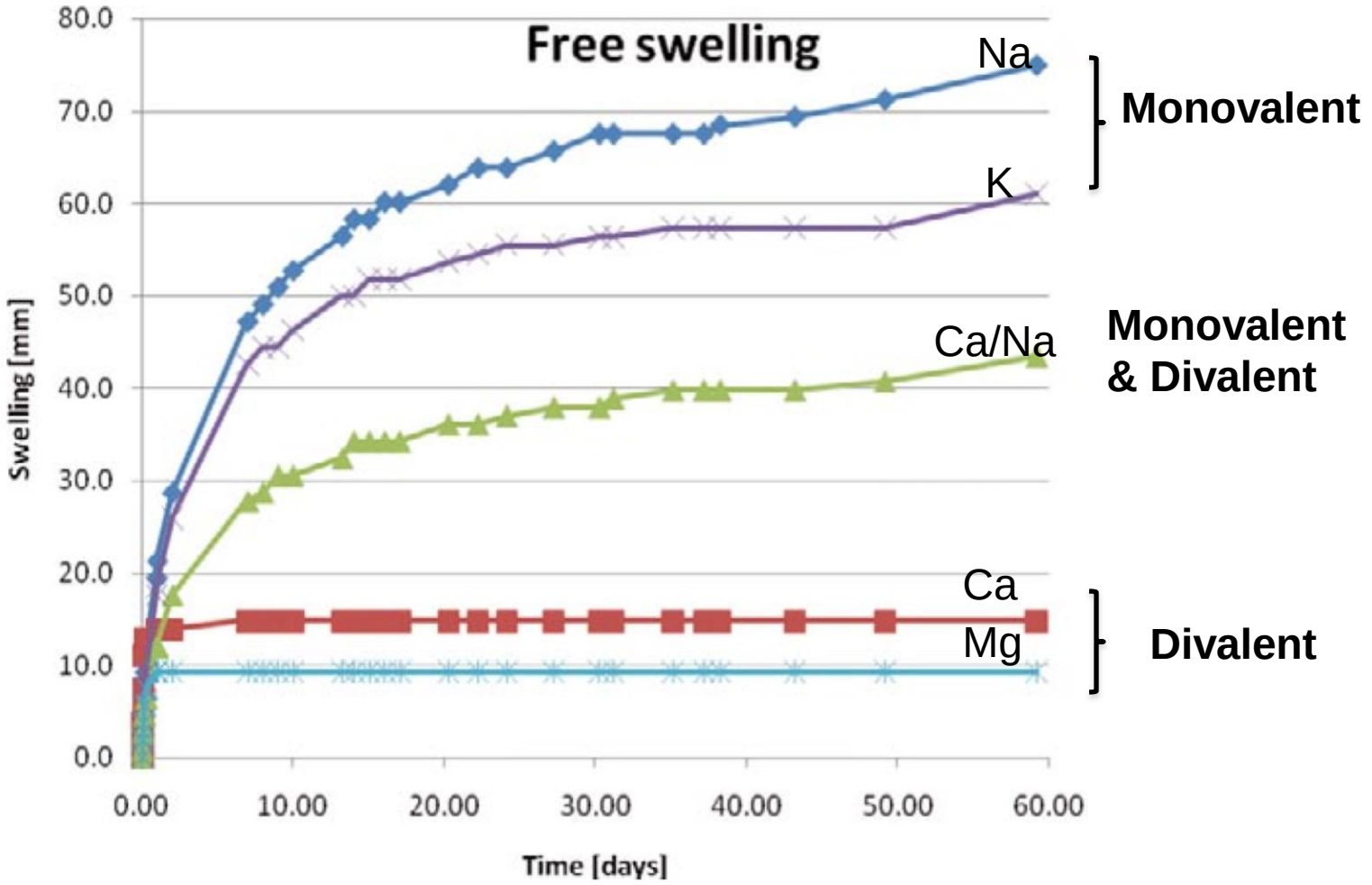


Fig 5. Height of test samples versus time measured for free swelling in deionised water. ***Birgersson et al. 2009***

Methods

Theories

➢ Most popular methods:

- Hypernetted Chain Approximation (HNC)
- Modified Gouy-Chapman Theory (MGC)
- Density Functional Theory (DFT)

DFT → Why ?

Methods

- **HNC---Integral Equation Method**
- **MGC---Poisson-Boltzmann Theory (PB)**
- **PB and DFT**

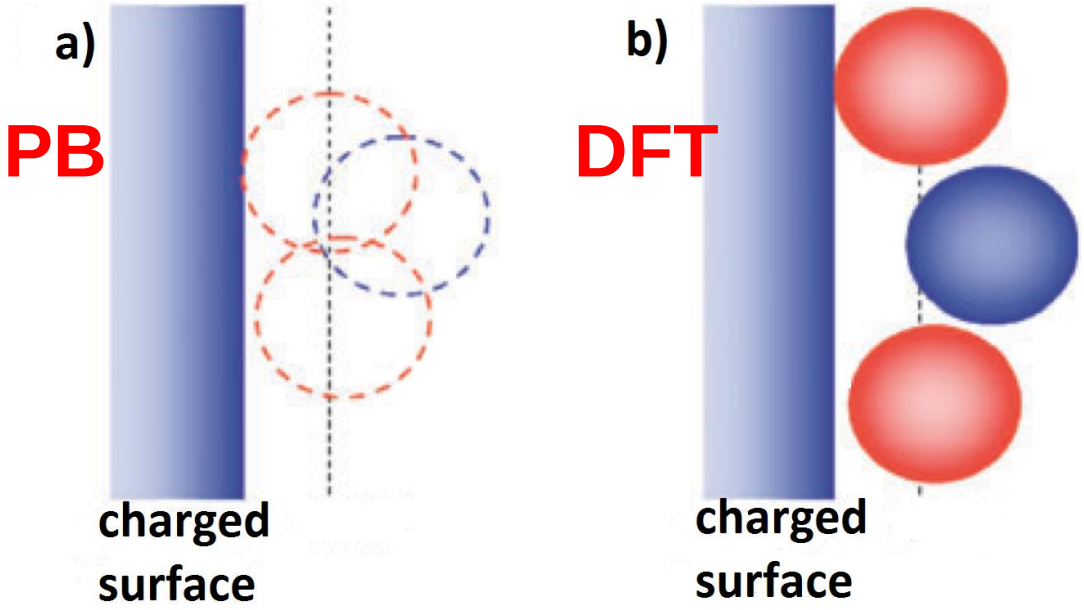


Fig 6. (a) PB picture. (b) DFT picture

PB

$$r_i(\mathbf{r}) = r_i^b \exp\{-bz_i ey(\mathbf{r})\}$$

the missing part

DFT

$$r_i(\mathbf{r}) = r_i^b \exp\{-bz_i ey(\mathbf{r}) + Dc_i^{(1),hs} + Dc_i^{(1),el}\}$$

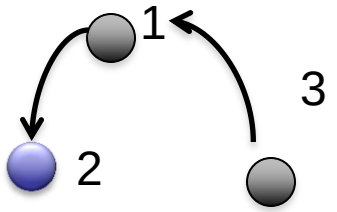
the change of the first order direct correlation function (DCF)

Ornestion-Zernick (O.Z.) equation

DCF

$$h(\mathbf{r}_{1,2}) = c(\mathbf{r}_{1,2}) + r \int h(\mathbf{r}_{2,3}) c(\mathbf{r}_{1,3}) d\mathbf{r}_3$$

Total Direct Indirect



1-2: direct effect
3-2: indirect effect

Methods

- **Restricted Primitive Model (RPM)**

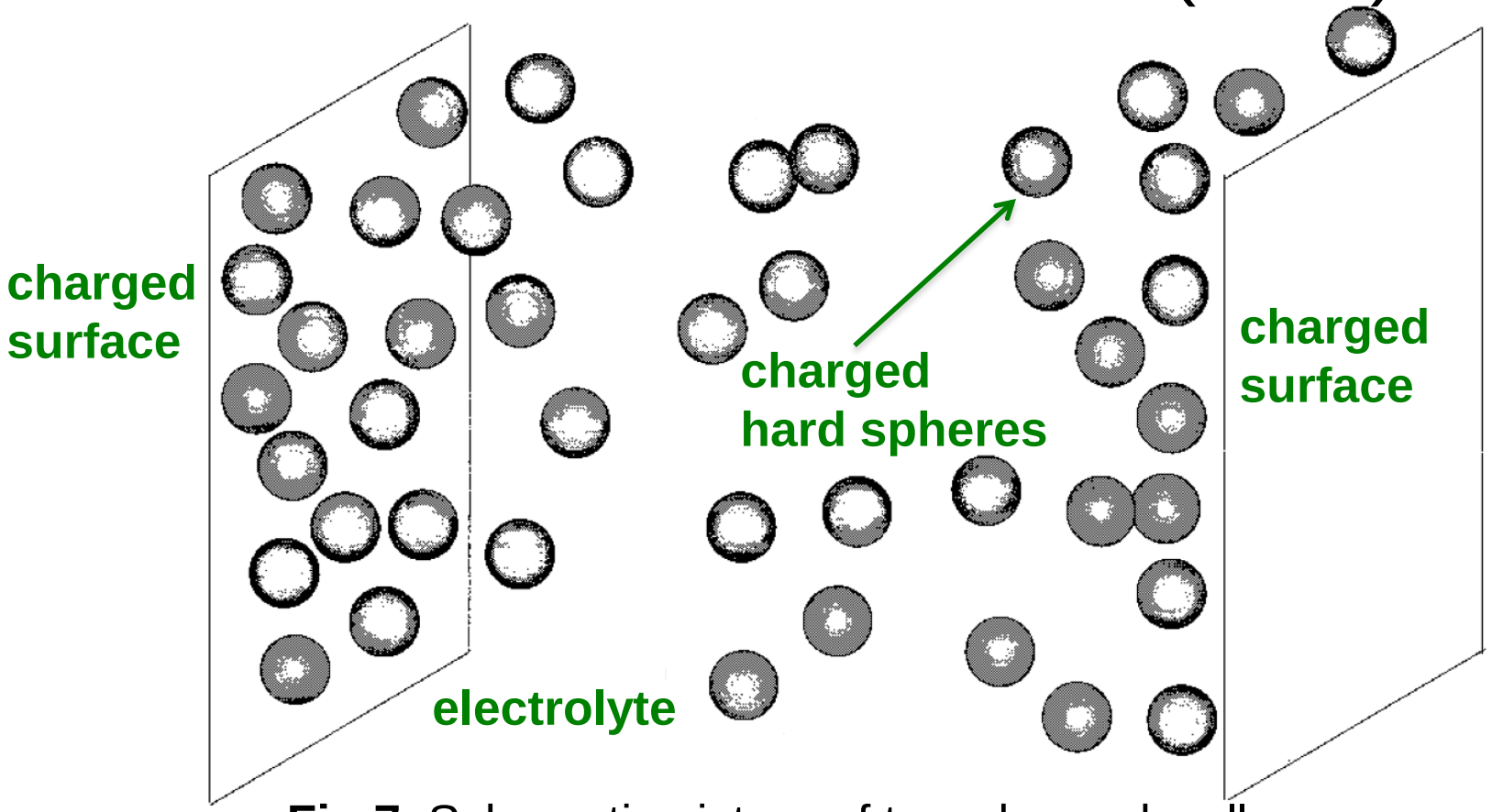


Fig 7. Schematic picture of two charged walls immersed in a bulk solution

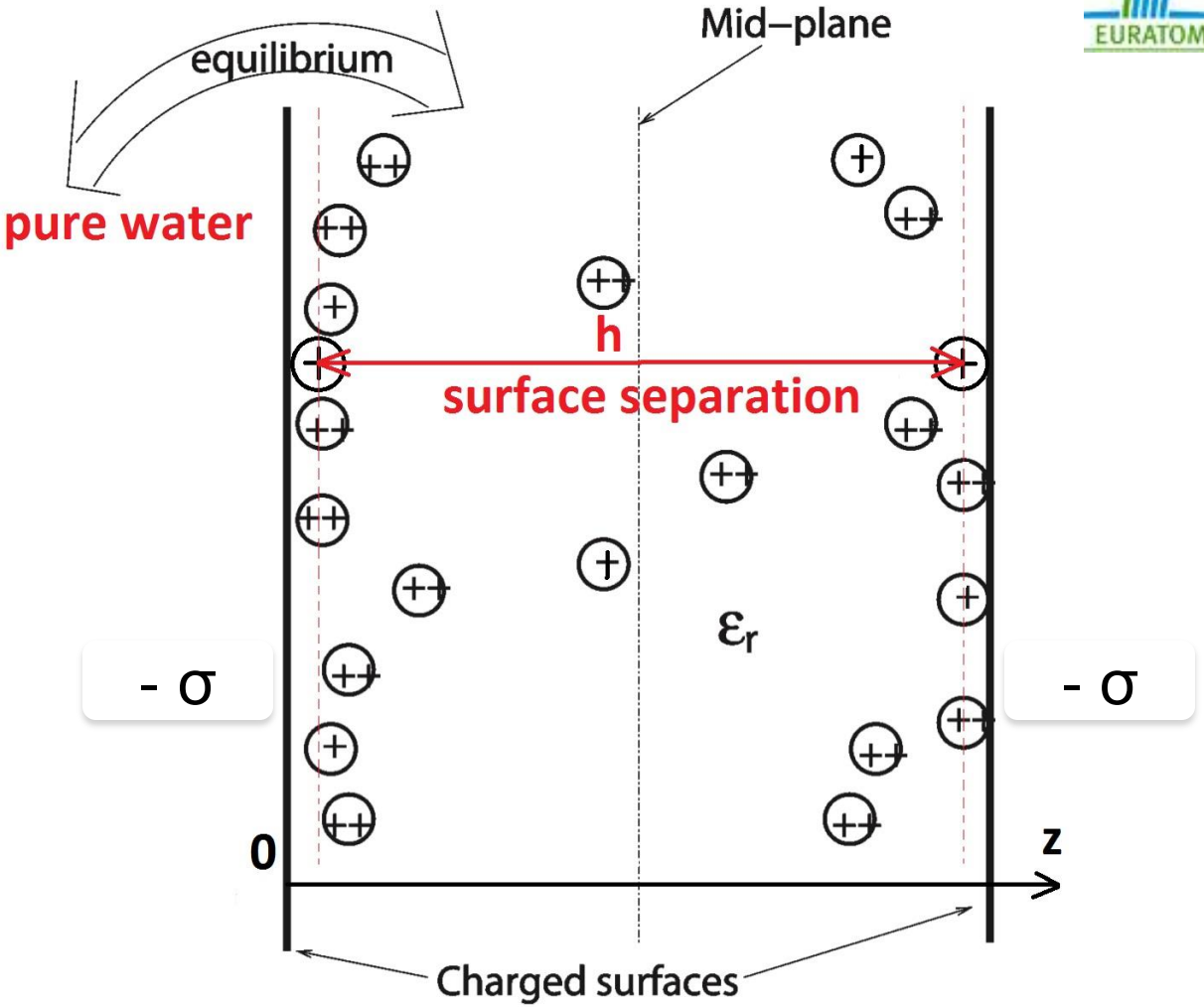


Fig 8. Schematic picture of two clay platelets system being in equilibrium with pure water

Model Validation ⟺  **Monte Carlo simulations**

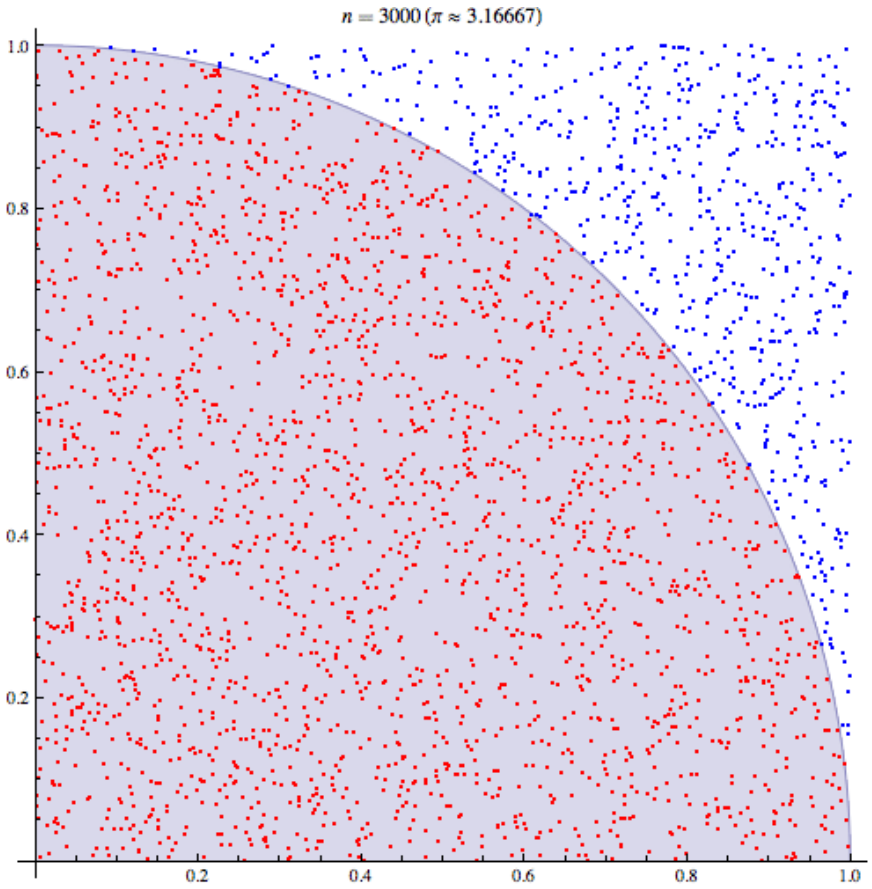


Fig 9. Monte Carlo method for calculating pi (π)

Results: Structures

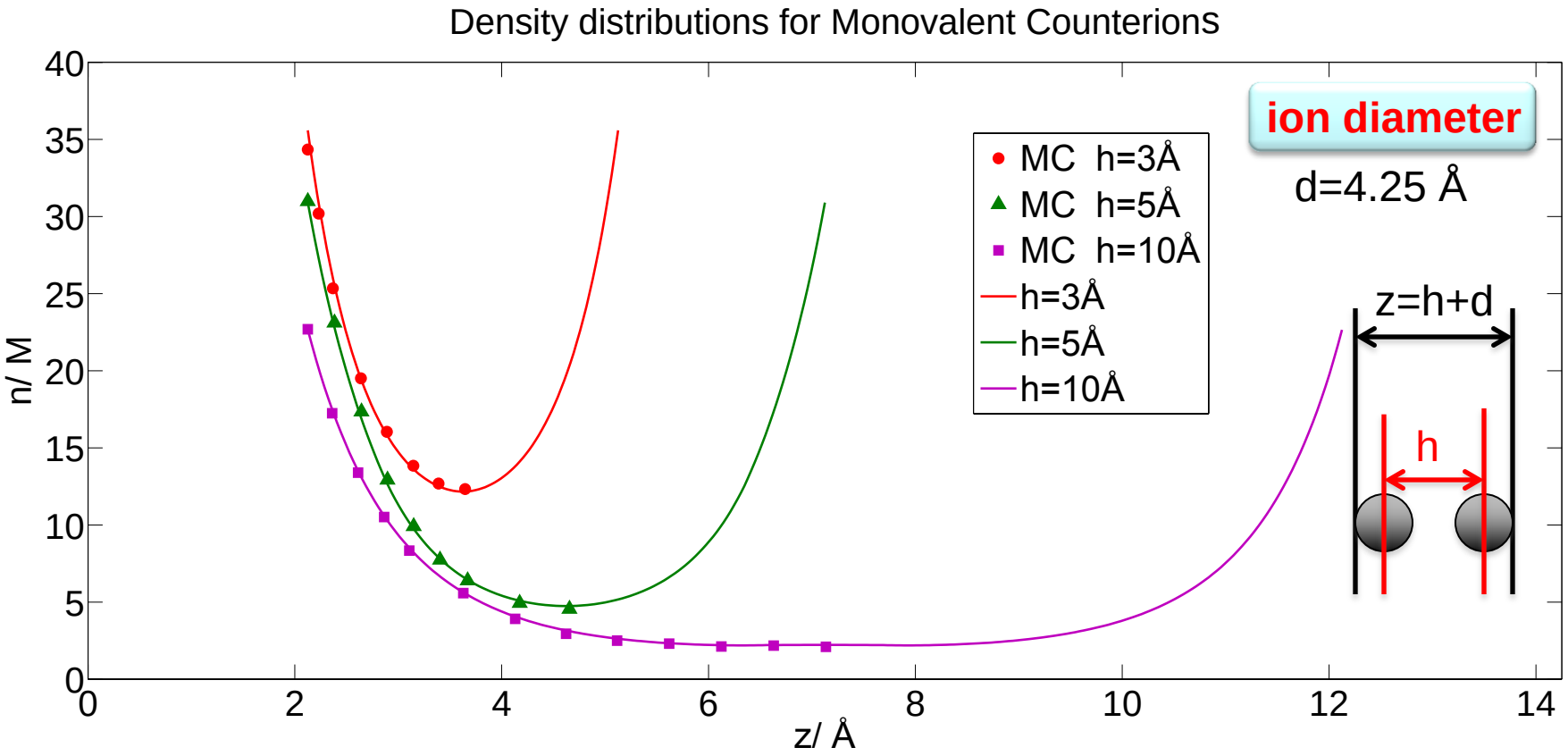


Fig 10. Density profiles n(z) in mol dm^{-3} for a system with two planar, charged walls in equilibrium with pure water and with only monovalent counterions between surfaces. The surface charge density is 0.267 C m^{-2}, ion size d=4.25Å, surface separations h=3, 5, 10 Å.

Results: Forces

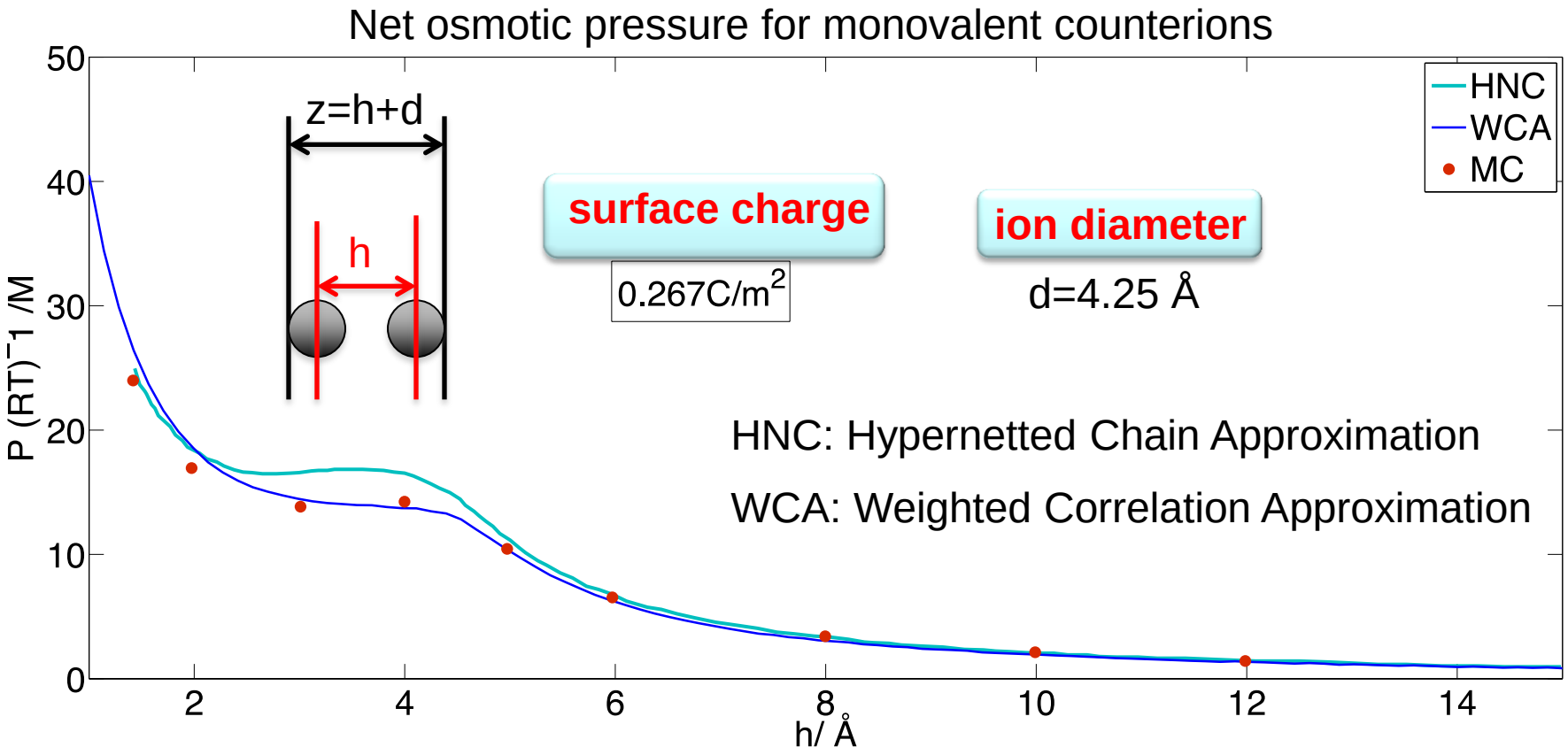


Fig 11. As Fig 10. Double layer net osmotic pressure.

Results: Forces

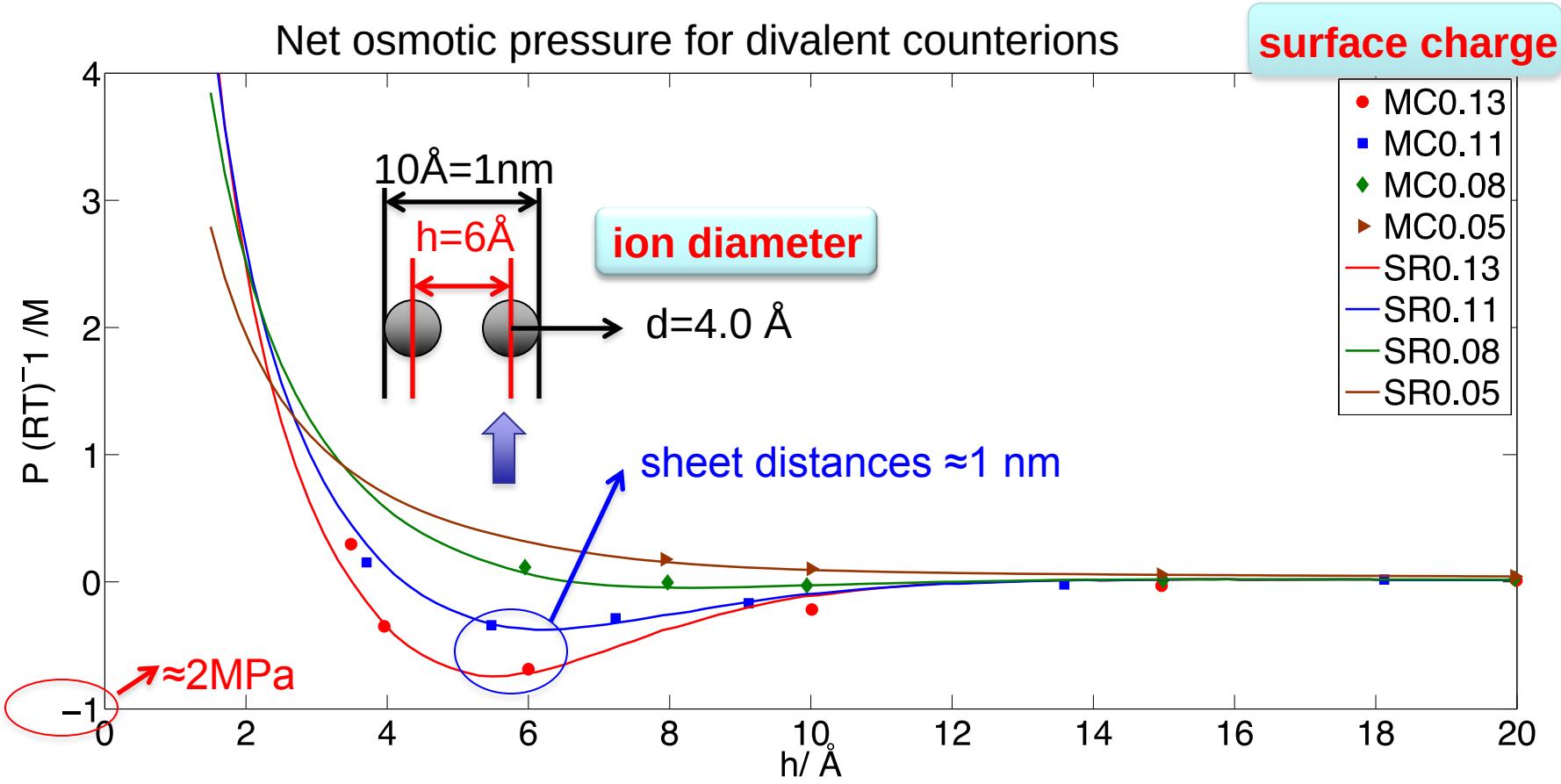


Fig 12. but for the system with only divalent counterions, the surface charge density is varied from 0.13 to 0.05 C m^{-2}, d=4.0Å

Results: Forces

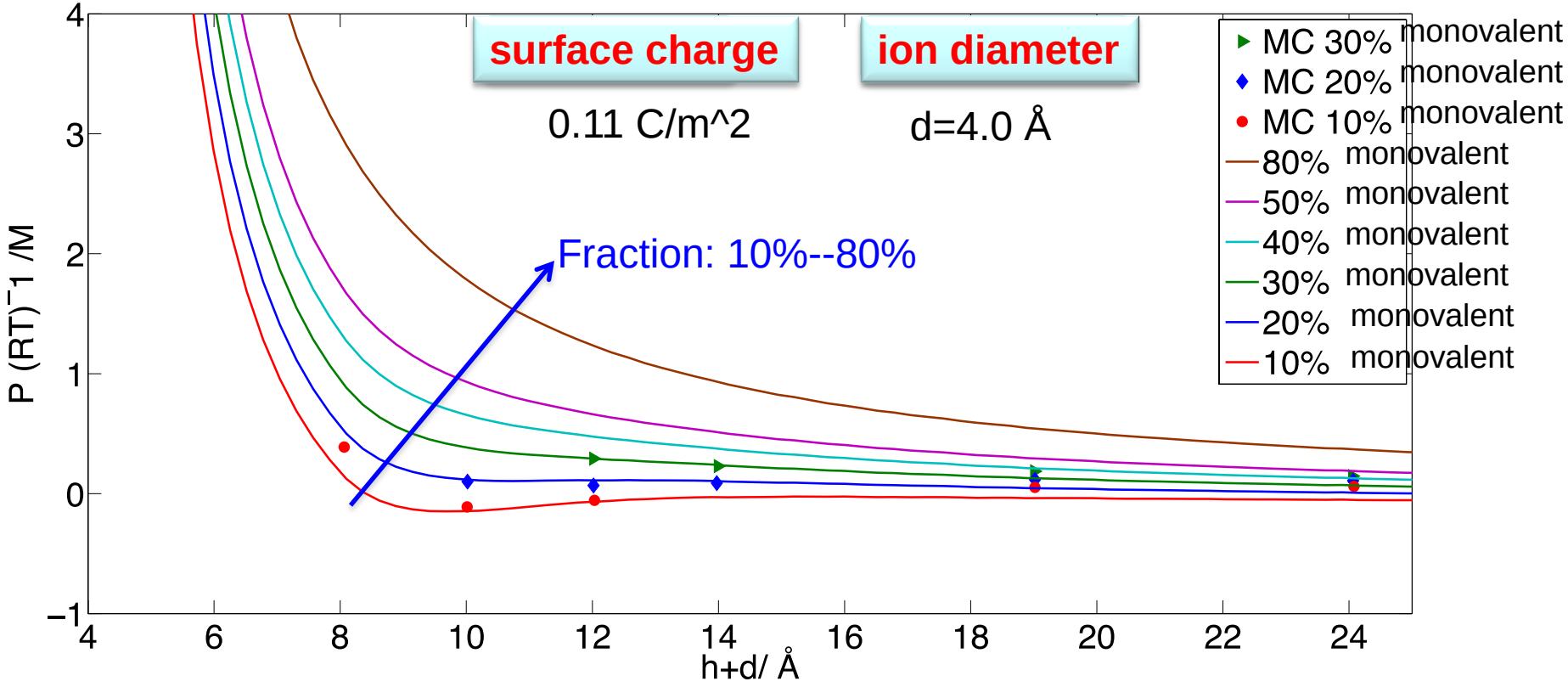


Fig 12. As Fig11. but the fraction of surface charge neutralized by monovalent counterions is indicated in figure. The surface charge density is 0.11 C/m^2

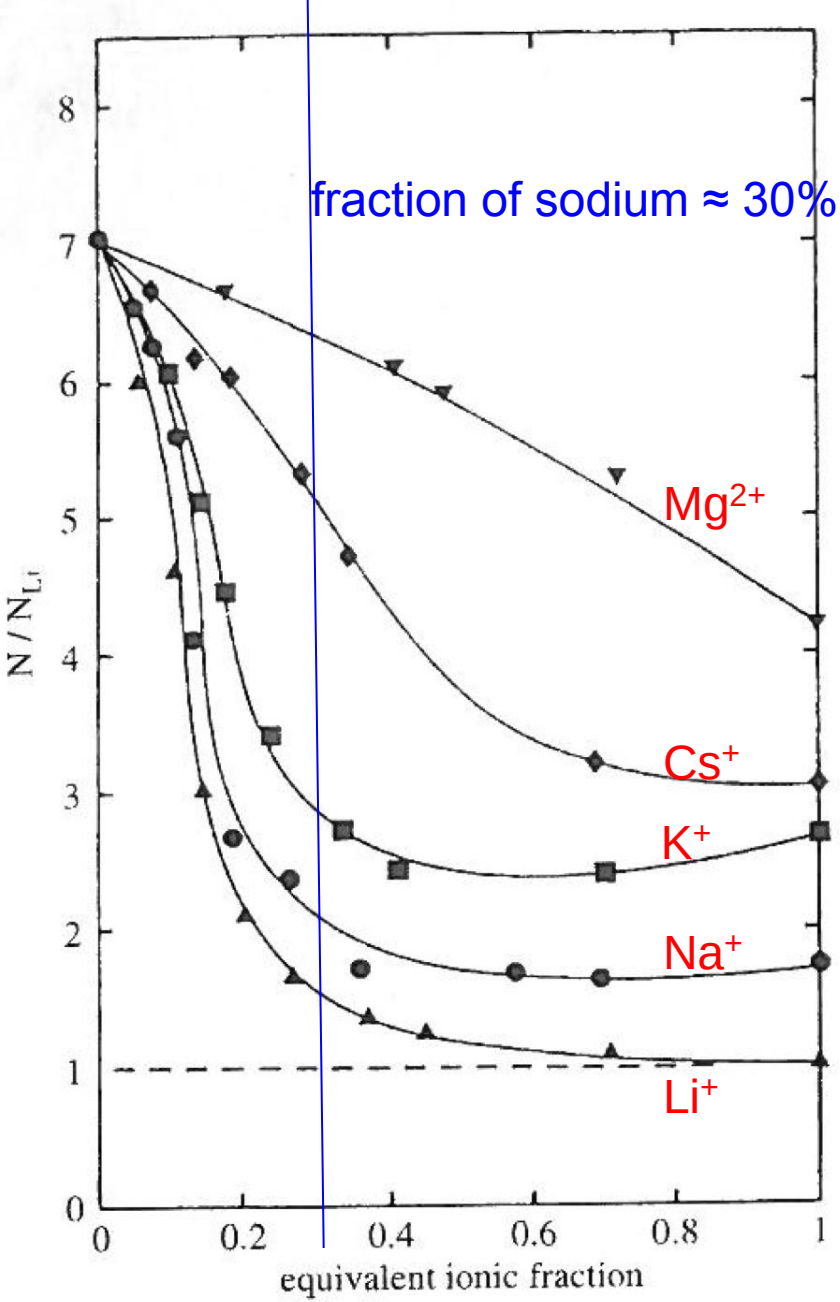
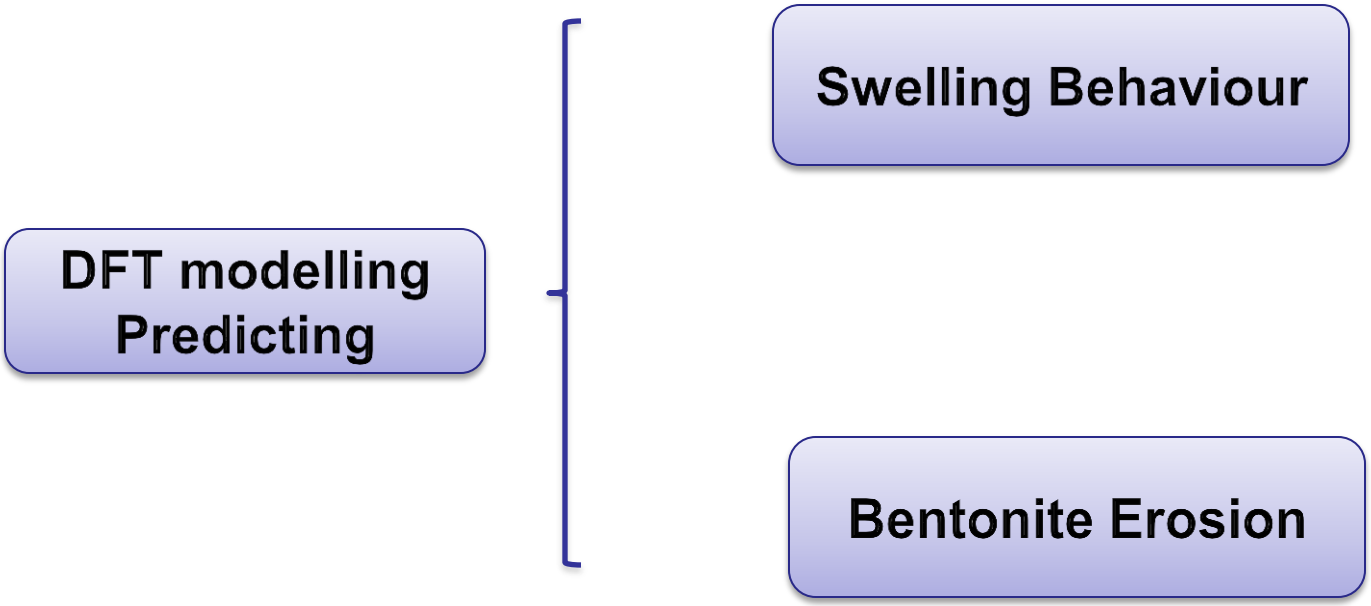


Fig 13. Relative number of layers per particle as a function of surface coverage when the Ca^{2+} ions exchanged by Li^{+}, Na^{+}, K^{+}, Cs^{+} and Mg^{2+} ions **(Schramm and Kwak, 1982a).**

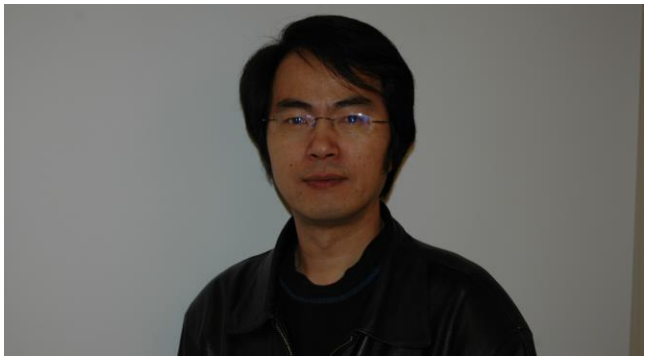
From (Jasmund and Lagaly, 1993)

Conclusions and applications

- Simulations agree quite well with the MC data



Acknowledgements



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Thank you

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