



# A new approach of Density functional theory (DFT) on the study of clay stability for the non-restricted primitive model

Reporter: Guomin Yang

13<sup>th</sup> Oct 2015

Email: [guomin@kth.se](mailto:guomin@kth.se)

Phone: +46 7 290 67818

# Outline

- **Introduction**
- **Applications of DFT model**
- **Validations**
  - Planar Electrical Double Layer (EDL) containing one electrolyte
  - Planar Electrical Double Layer (EDL) containing two electrolytes

# Introduction

- Overview of published work

**Comparison of 6 different DFT approaches**

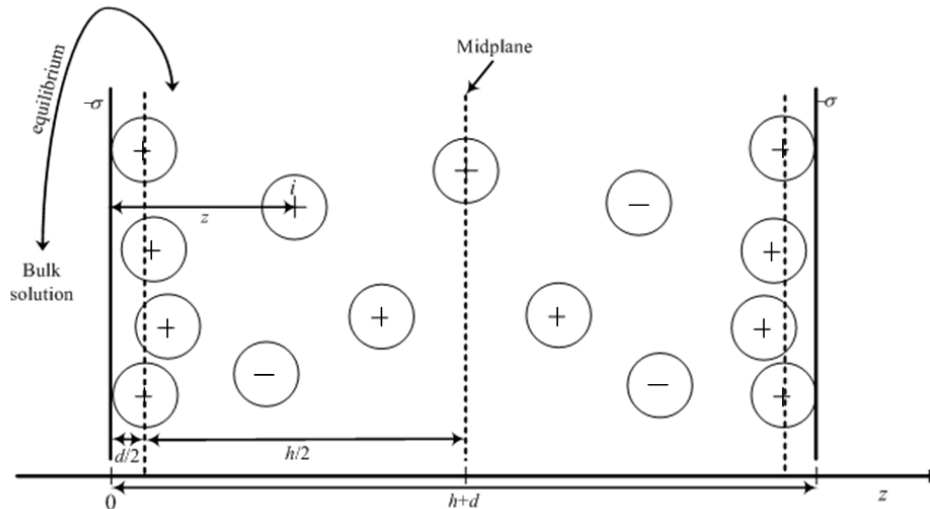
**EDL systems**

**A novel DFT approach (RWCA)<sup>1</sup>**

<sup>1</sup> From Guomin Yang 2015

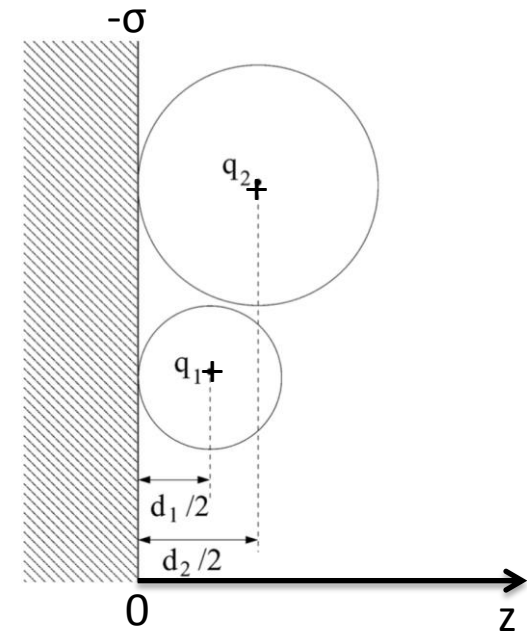
# Introduction

- Primitive model



a)

**Fig 1. a)** Restricted primitive model



b)

**Fig 1. b)** Non-restricted primitive model

# Outline

- Introduction
- Applications of DFT model
- Validations
  - Planar Electrical Double Layer (EDL) containing one electrolyte
  - Planar Electrical Double Layer (EDL) containing two electrolytes

## applied on clay systems

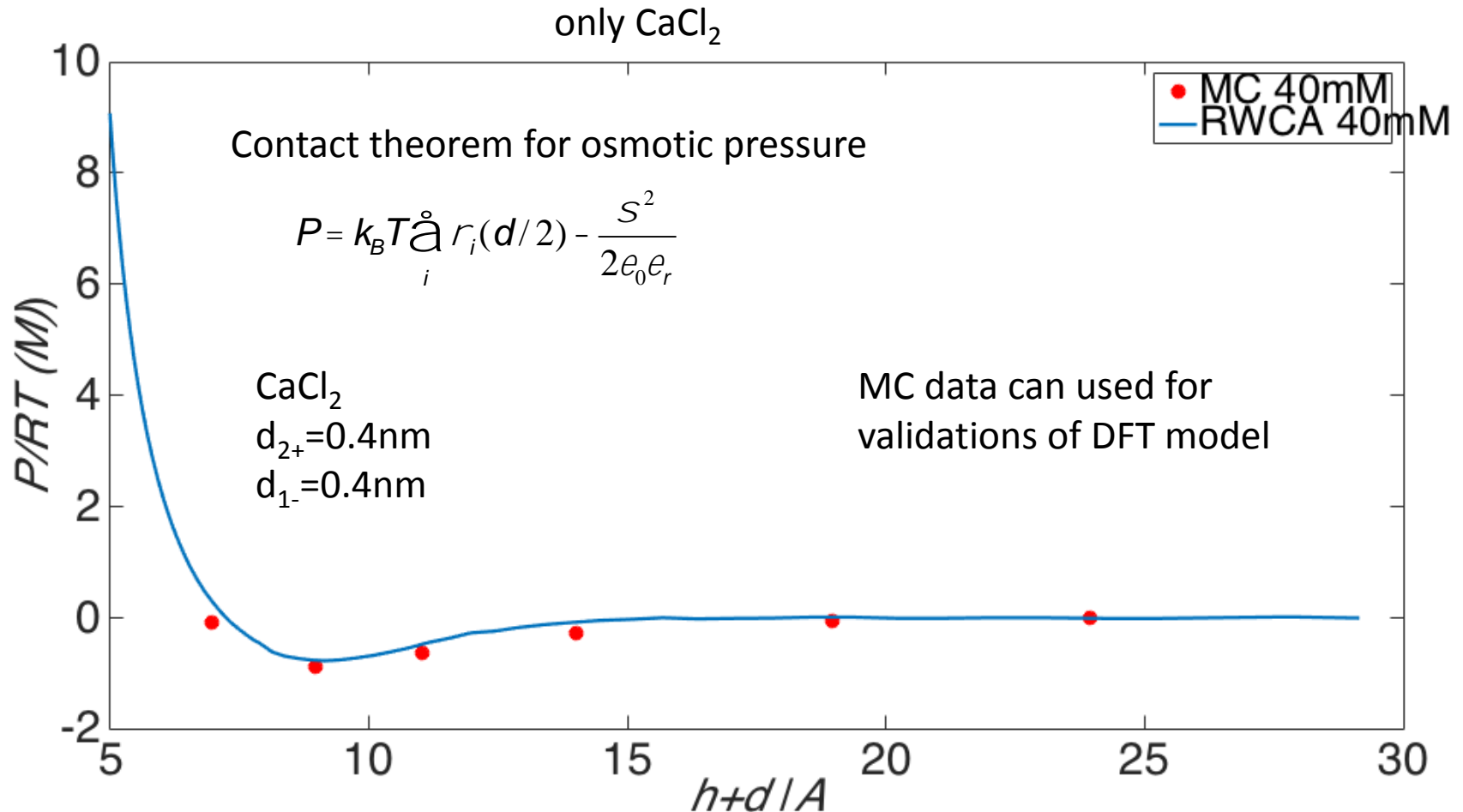


Fig 2. The net osmotic pressure with  $\sigma = -0.14$  C/m<sup>2</sup> in equilibrium with a bulk solution contain a 2:1 salt ( $\text{CaCl}_2$ ). MC data From M. Sega 2010

# only $\text{CaCl}_2$

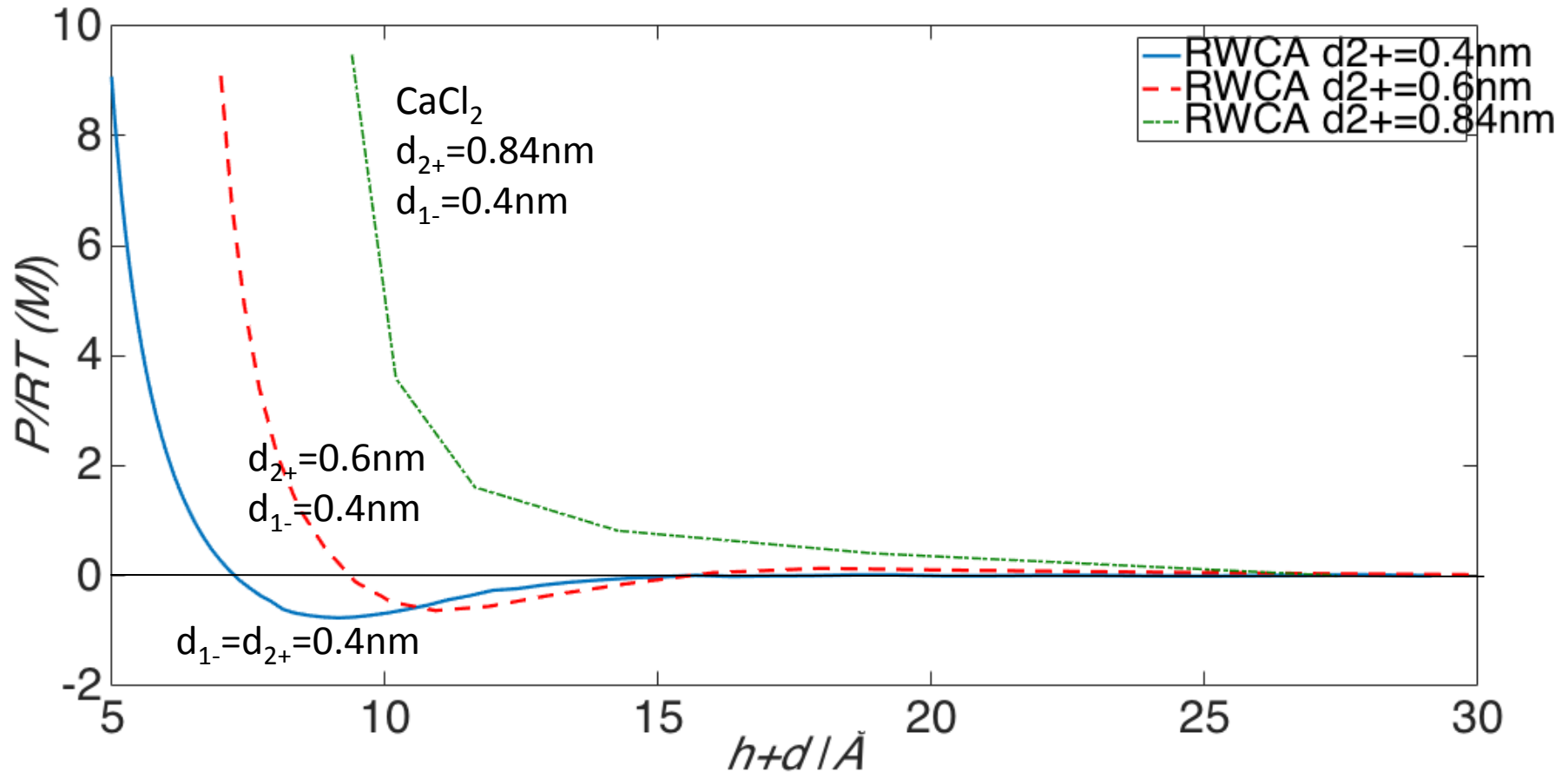


Fig 3. The same as Fig 2 but with different ion size

# NaCl and $\text{CaCl}_2$

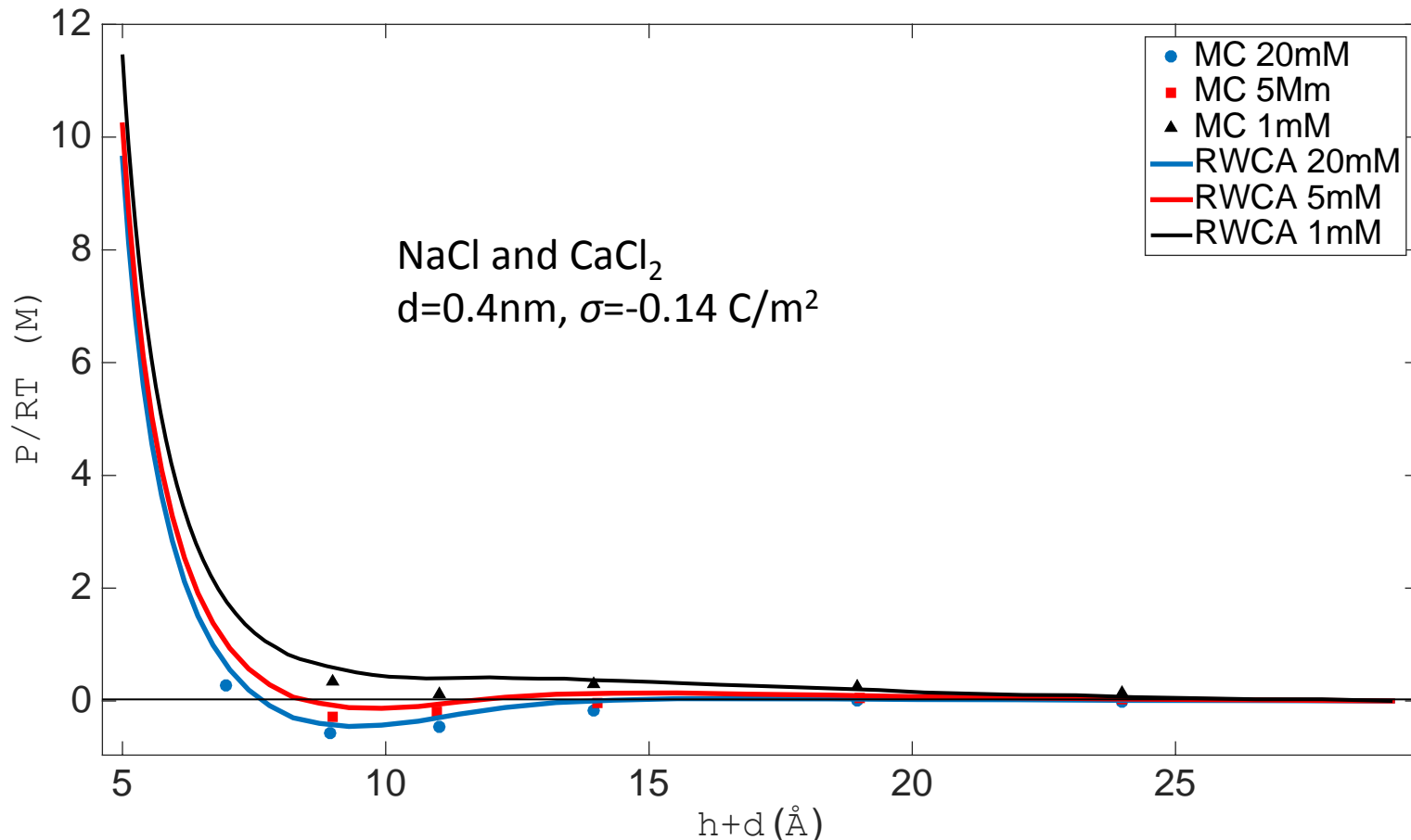


Fig 4. The NaCl is kept constant 100mM, the  $\text{CaCl}_2$  concentration is varied as indicated in the graph. MC data From M. Sega 2010



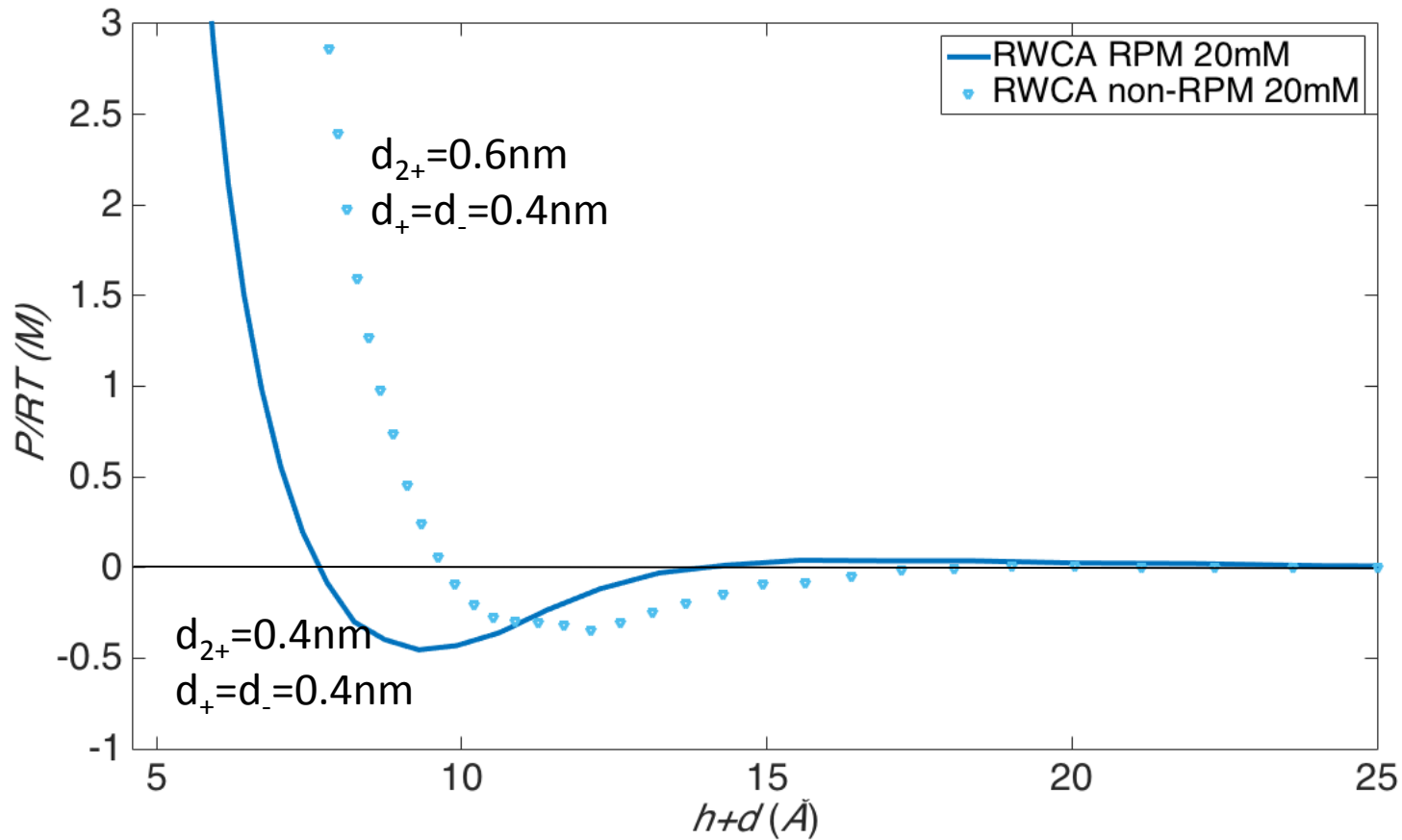


Fig 5. The same as the Fig 4 but only for the case containing 20mM CaCl<sub>2</sub> and 100 NaCl solutions

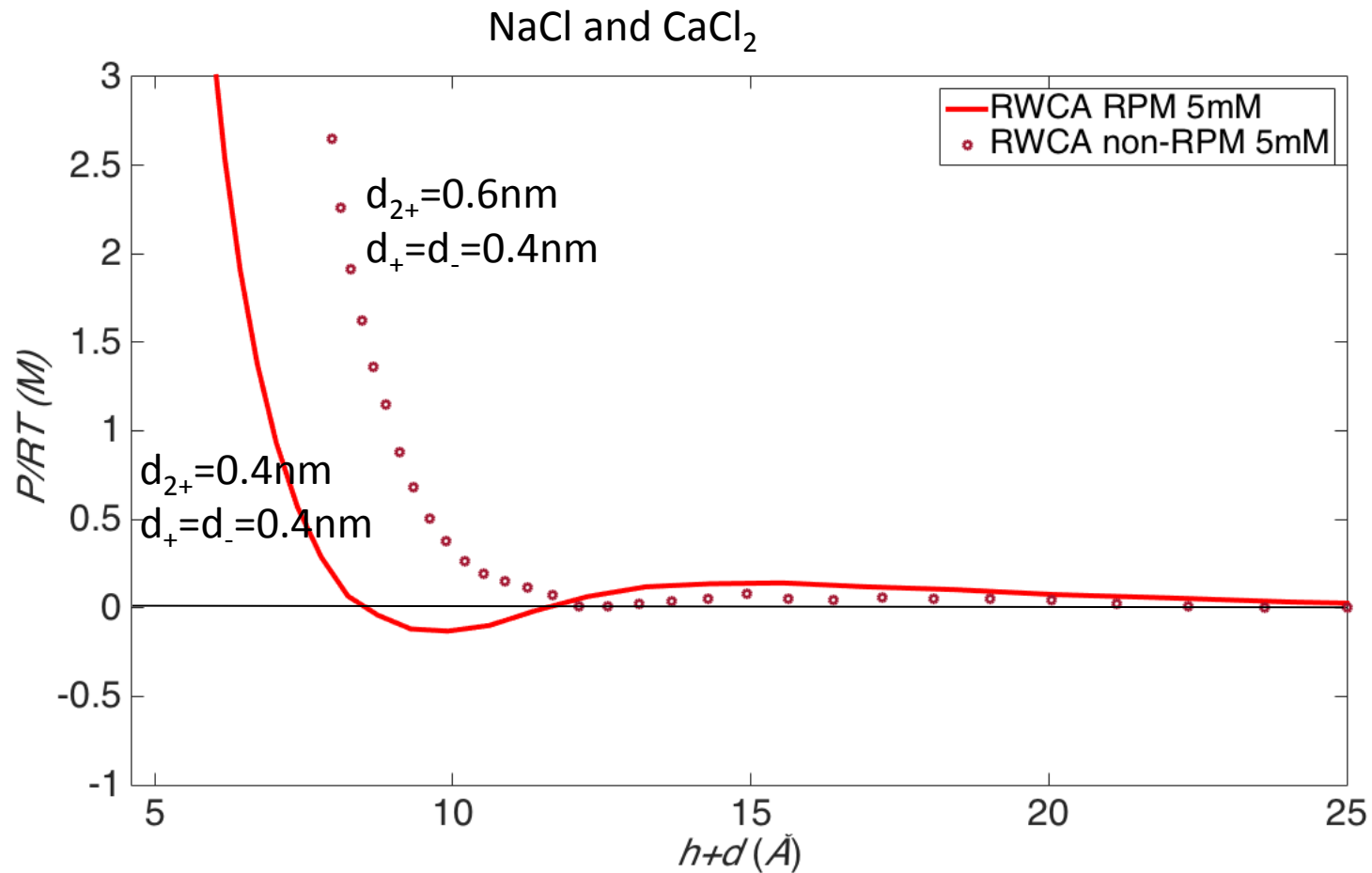
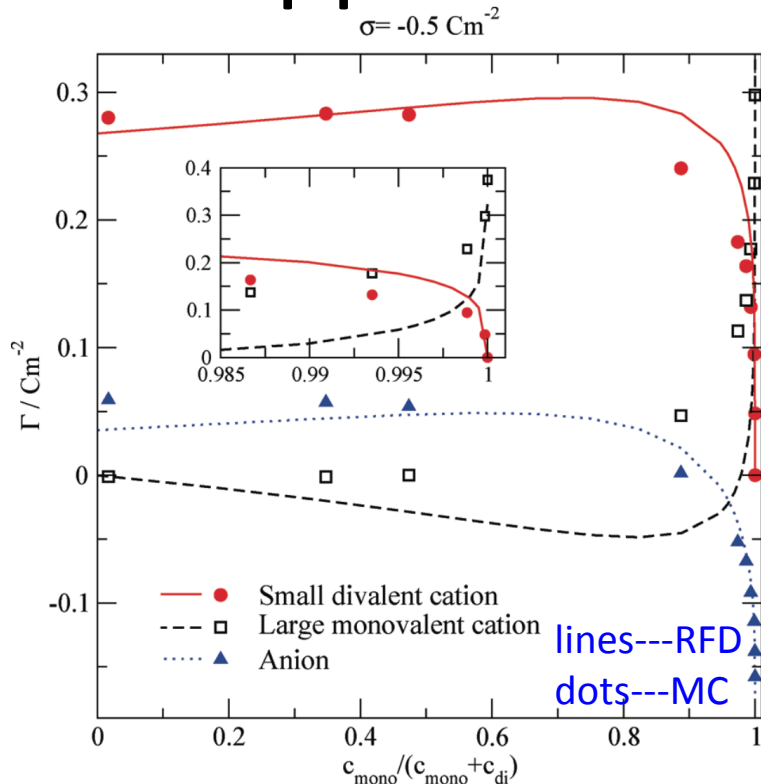


Fig 6. The same as the Fig 4 but only for the case containing 5mM CaCl<sub>2</sub> and 100 NaCl solutions

## applied on selective adsorption

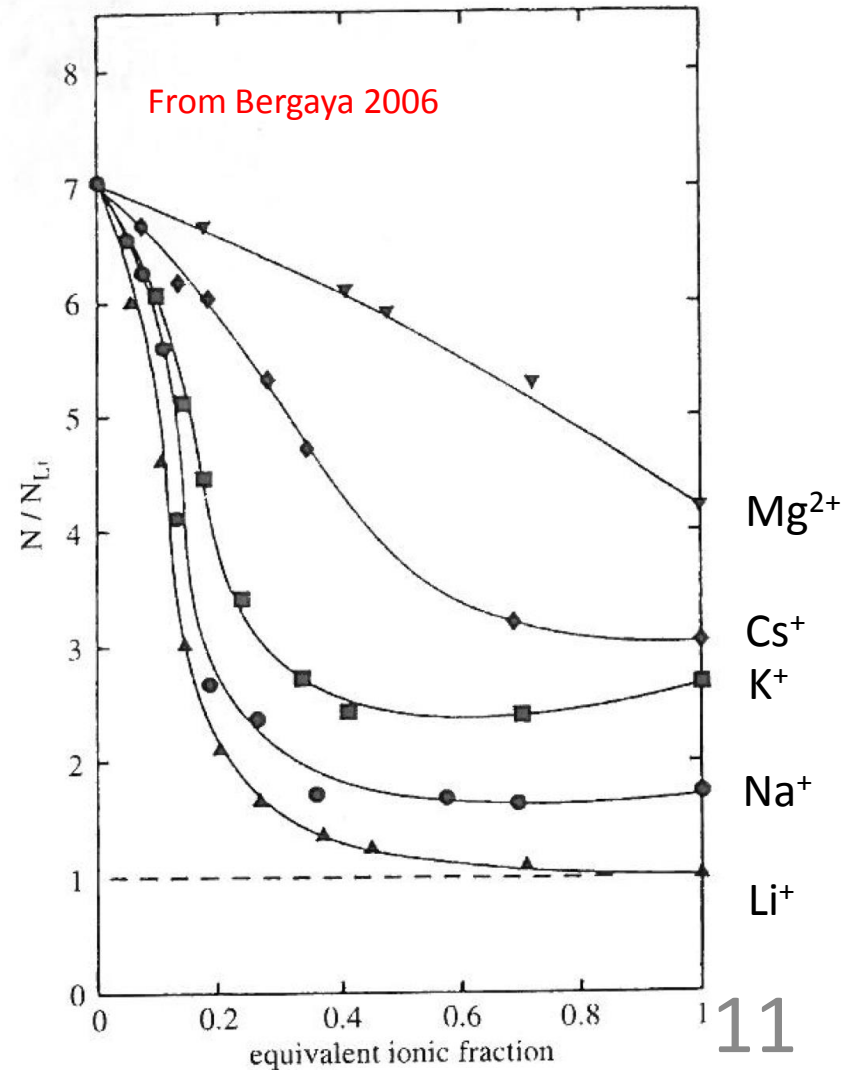


**Figure 7.** Excess adsorption of small divalent cations, large monovalent cations, and anions (3 M concentration, fixed) as a function of the cation mole fraction for electrode charge  $\sigma = -0.5 \text{ Cm}^{-2}$  (the *selective* case). The lines and symbols represent DFT and MC results, respectively. The inset magnifies the region close to the pure monovalent case.

From Valisko 2007

### Excess adsorption

$$G_i = e \int_0^\infty (r_i(x) - r_i^b) dx; \quad \sum_i z_i G_i = -s$$



# Outline

- Introduction
- Applications of DFT model
- Validations
  - Planar Electrical Double Layer (EDL) containing one electrolyte
  - Planar Electrical Double Layer (EDL) containing two electrolytes

# Validations: one electrolyte case

- RWCA vs Gillespie's RFD: **Cation profiles**

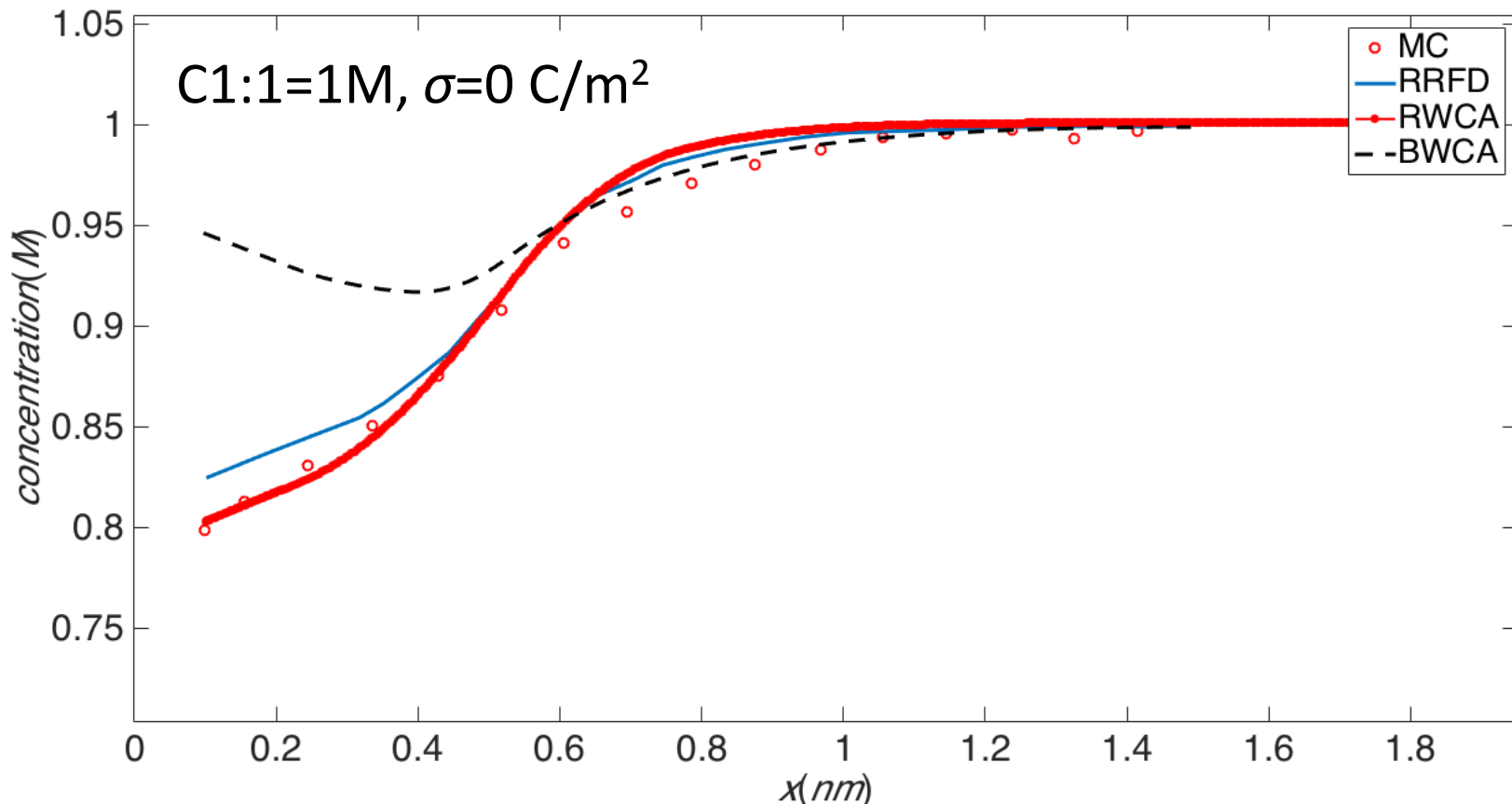


Fig 8. Cation density profiles.  $d+=0.2nm$ ,  $d-=0.425nm$ .  
MC simulations from Gillespie 2005

# Validations: one electrolyte case

- RWCA vs Gillespie's RFD: **Anion profiles**

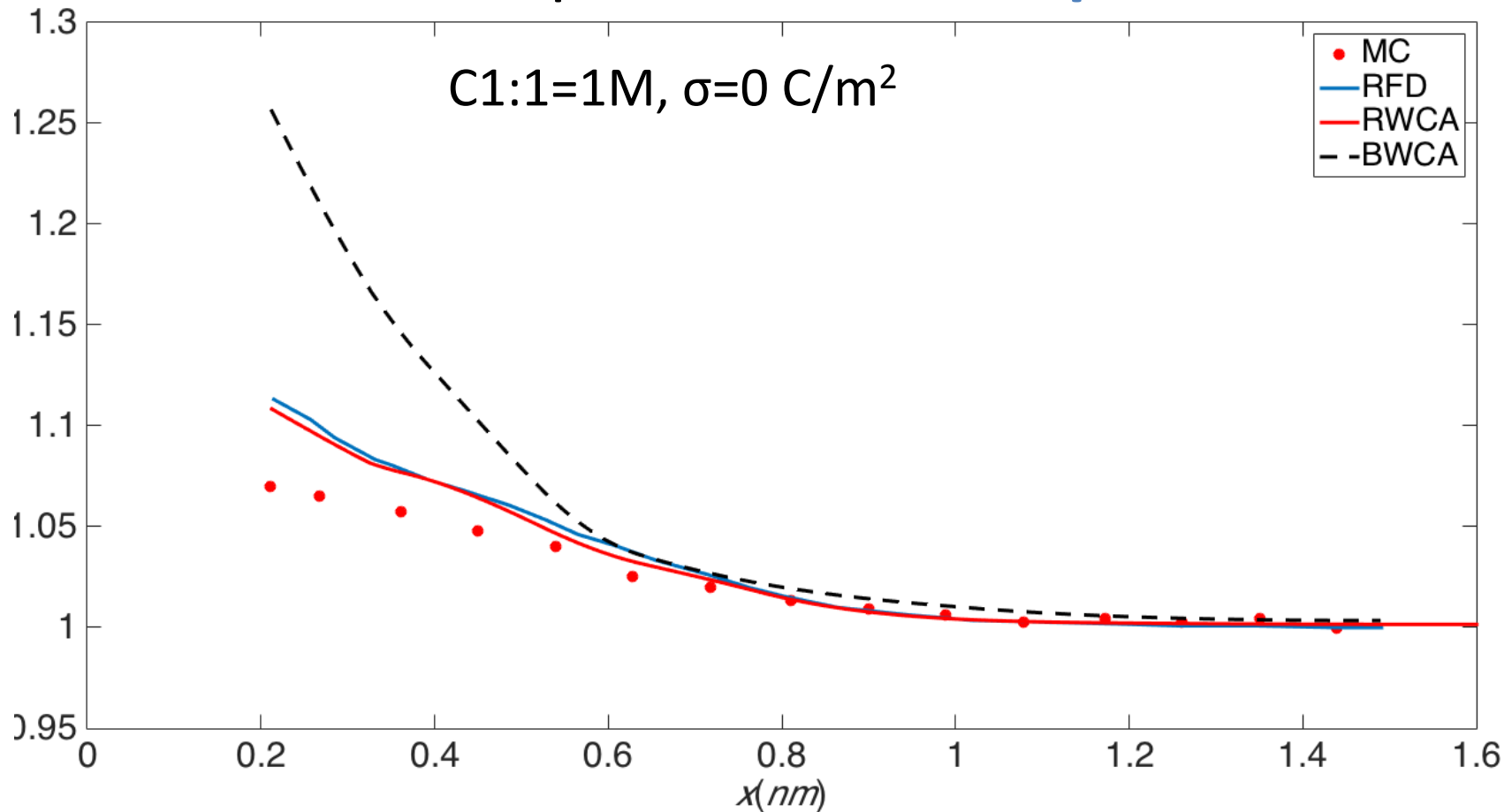


Fig 9. Anion concentration profiles.  $d+=0.2nm$ ,  $d-=0.425nm$

# Outline

- **Introduction**
- **Validations**
  - Planar Electrical Double Layer (EDL) containing one electrolyte
  - Planar Electrical Double Layer (EDL) containing two electrolytes
- **Applications of DFT model**

## two electrolytes case

- **Case 1:**  $C3:1=10\text{mM}$ ,  $C1:1=50\text{mM}$ ,  $\sigma=-0.04\text{C/m}^2$
- **Case 2:**  $C3:1=100\text{mM}$ ,  $C1:1=100\text{mM}$ ,  $\sigma=-0.16\text{C/m}^2$



# Validations: two electrolytes case

- Case 1: **Trivalent counter-ion** profiles

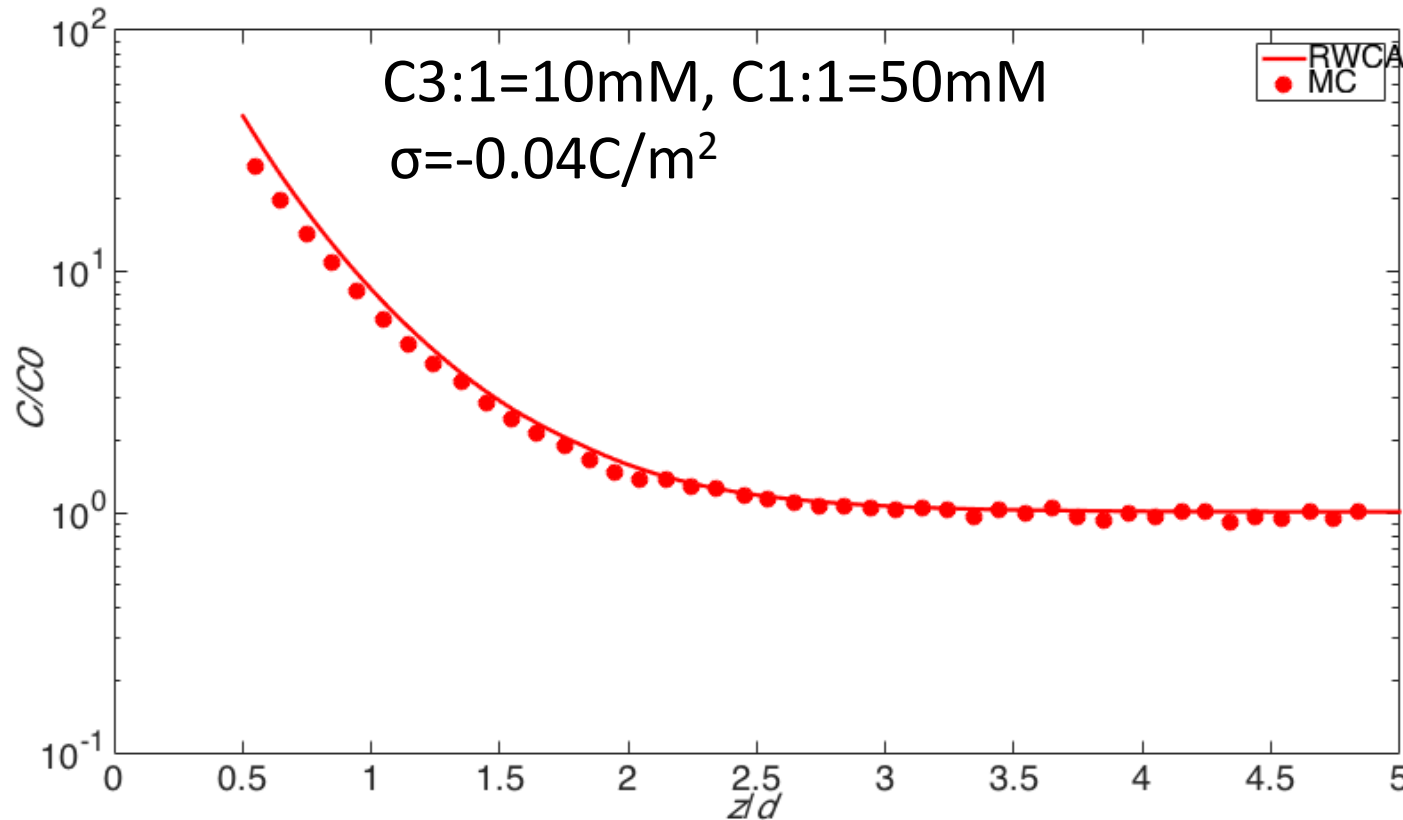


Fig 10. Trivalent counter-ion distribution function as a function the distance from the charged surface (normalized by the trivalent counter-ion diameter  $d_{3+}=0.9\text{nm}$ ).  
MC simulations from M.Q-Perez 2005



# Validations: two electrolytes case

- Case 1: Monovalent co-ion profiles

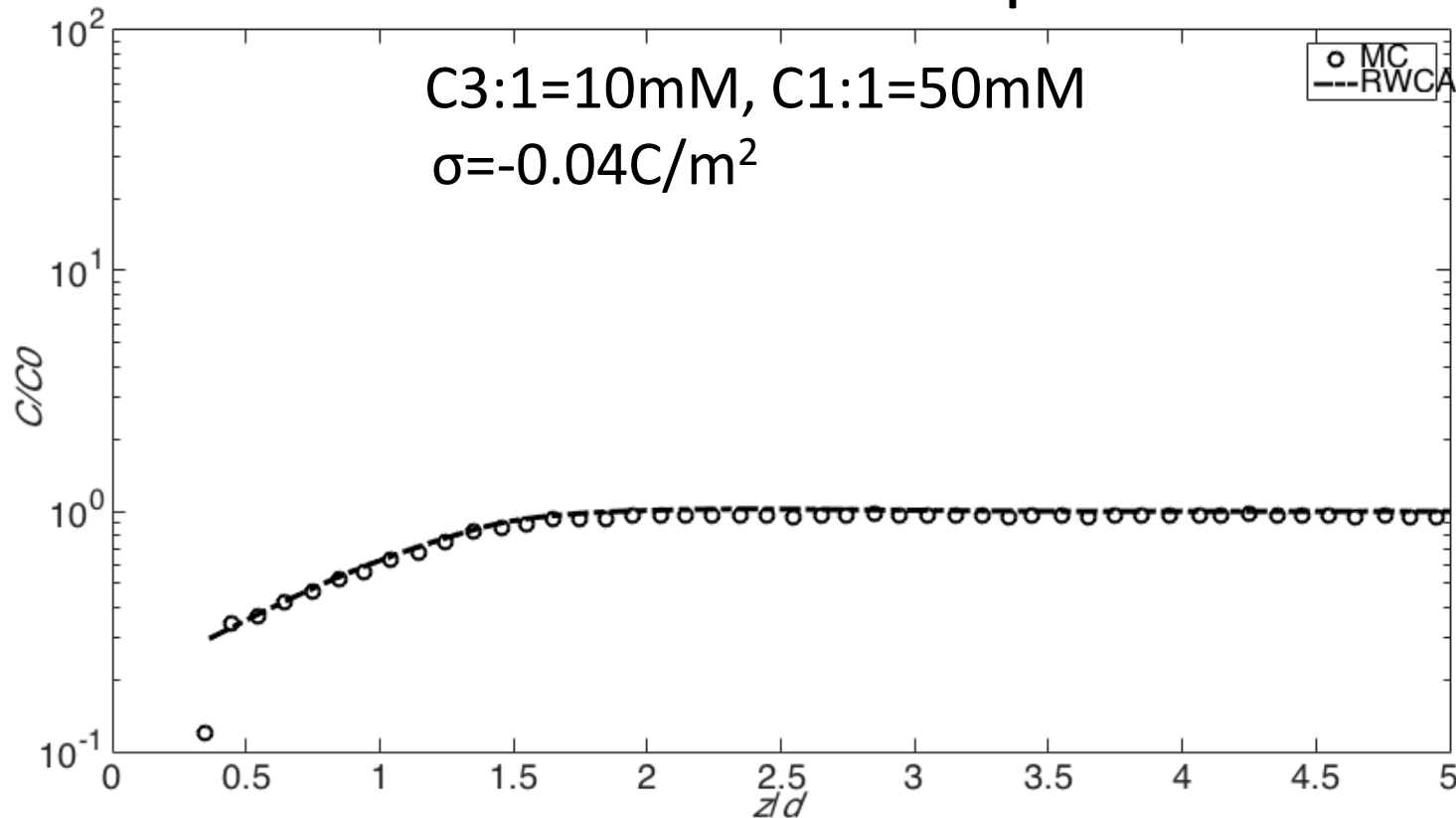


Fig 12. Monovalent co-ion function as a function the distance from the charged surface (normalized by the trivalent counterion diameter).

# Validations: two electrolytes case

- Case 1: Mixtures of Mon- and Multivalent ions

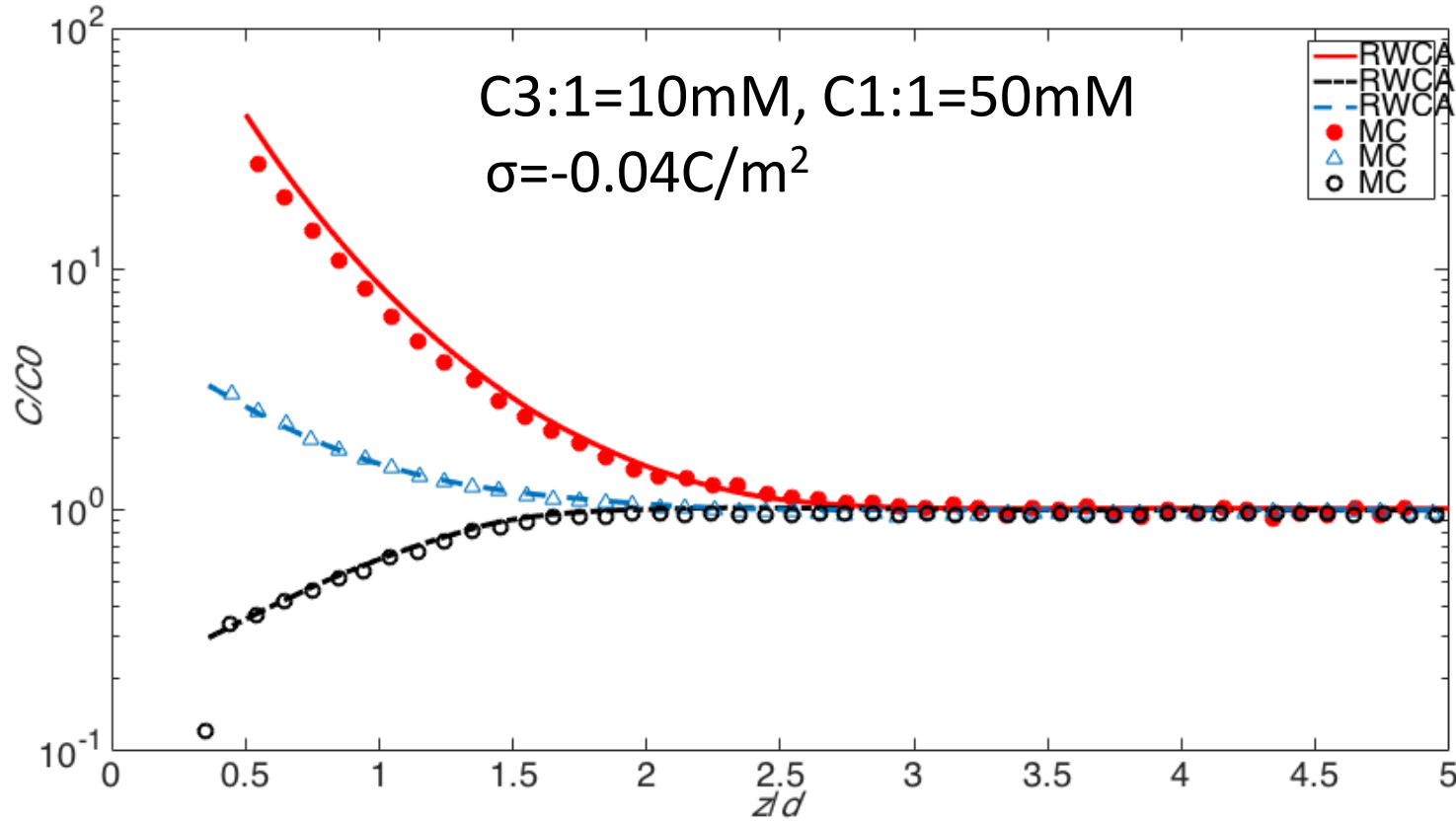


Fig 13. Ion distribution function as a function the distance from the charged surface (normalized by the trivalent counterion diameter).

## two electrolytes case

- **Case 1:**  $C3:1=10\text{mM}$ ,  $C1:1=50\text{mM}$ ,  $\sigma=-0.04\text{C/m}^2$
- **Case 2:**  $C3:1=100\text{mM}$ ,  $C1:1=100\text{mM}$ ,  $\sigma=-0.16\text{C/m}^2$

# Validations: two electrolytes case

- Case 2: **Trivalent counter-ions** profiles

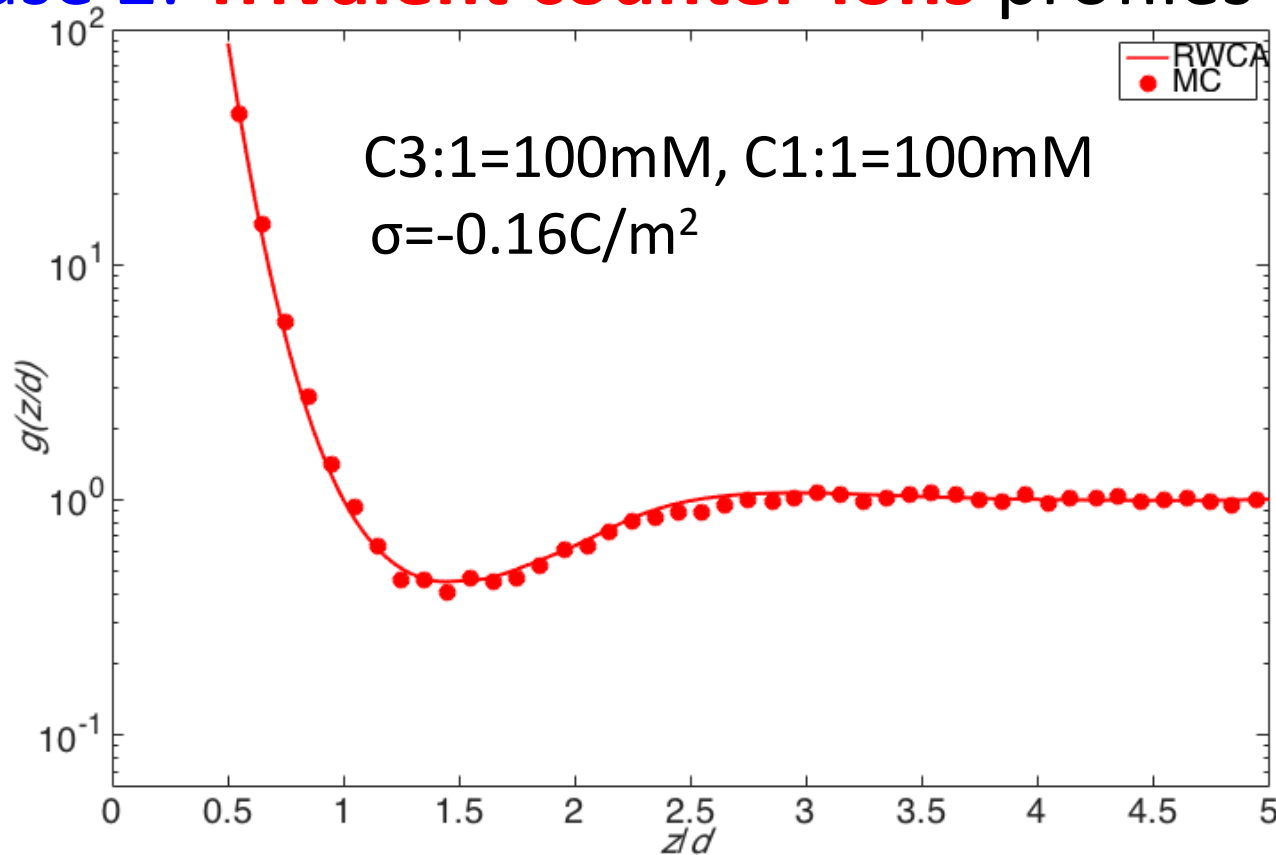


Fig 14. Trivalent counter-ion distribution function as a function the distance from the charged surface (normalized by the trivalent counterion diameter)

MC simulations from M.Q-Perez 2005

# Validations: two electrolytes case

- Case 2: Monovalent counter-ions profiles

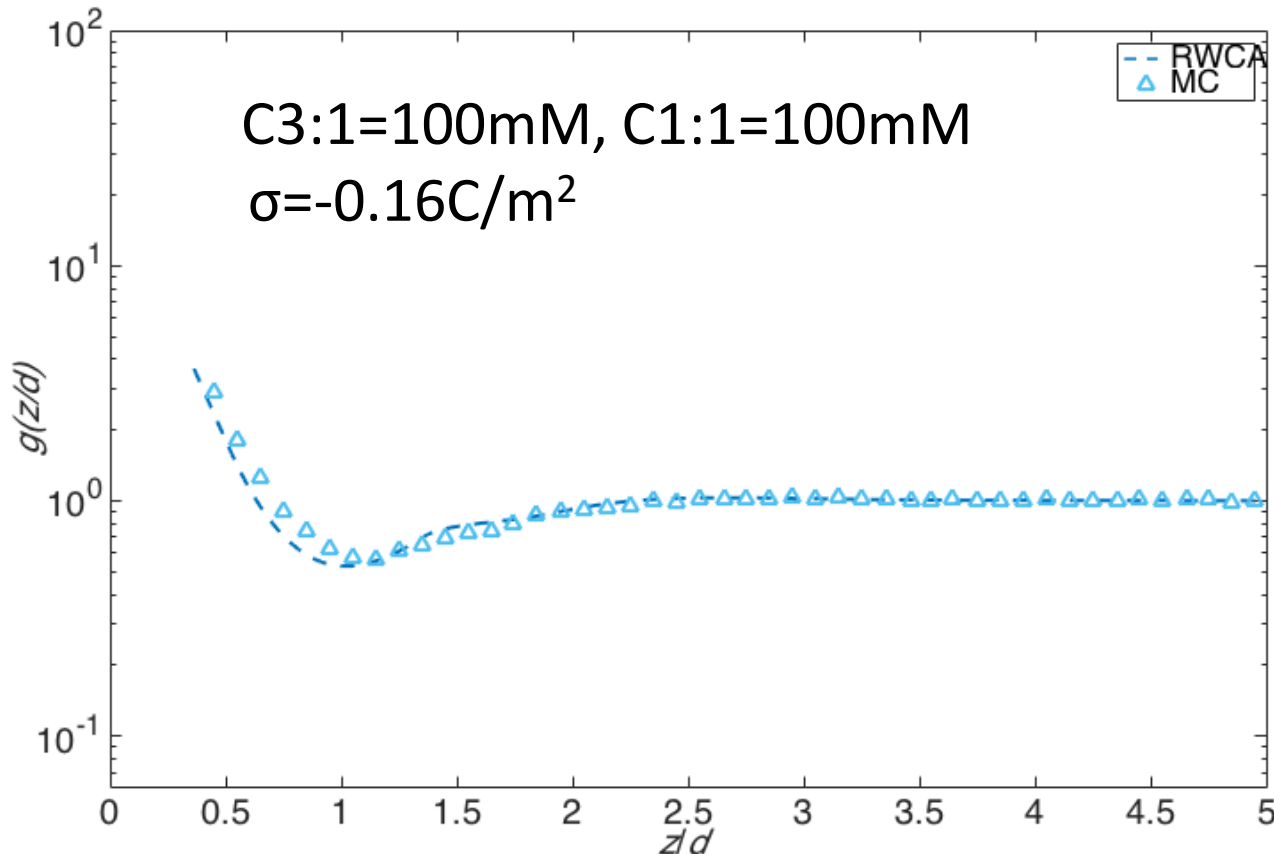


Fig 15. Monovalent counter-ion distribution function as a function the distance from the charged surface (normalized by the trivalent counterion diameter)

# Validations: two electrolytes case

- Case 2: **Monovalent co-ions** profiles

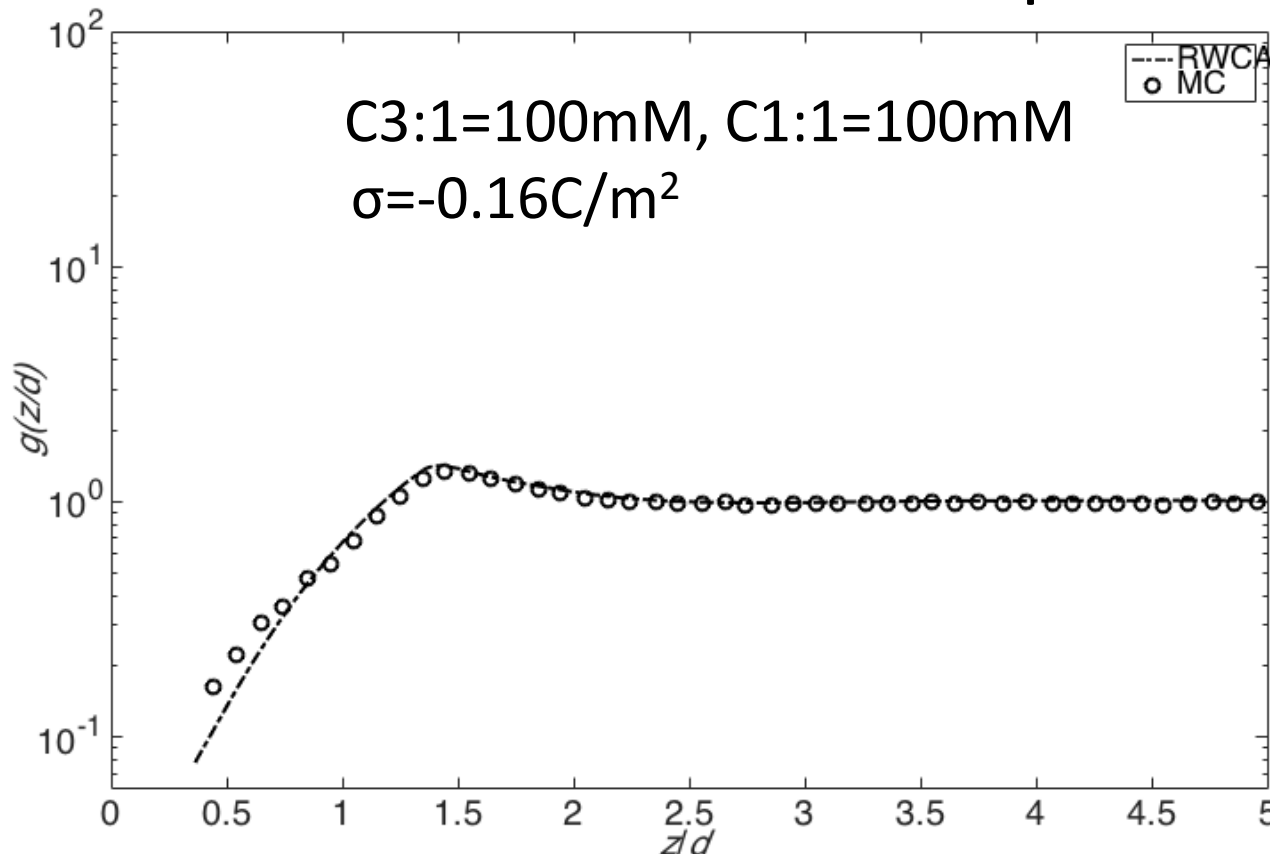


Fig 16. Monovalent co-ion distribution function as a function the distance from the charged surface (normalized by the trivalent counterion diameter)



## two electrolytes case

- Case 2: Mixtures of Mon- and Multivalent ions

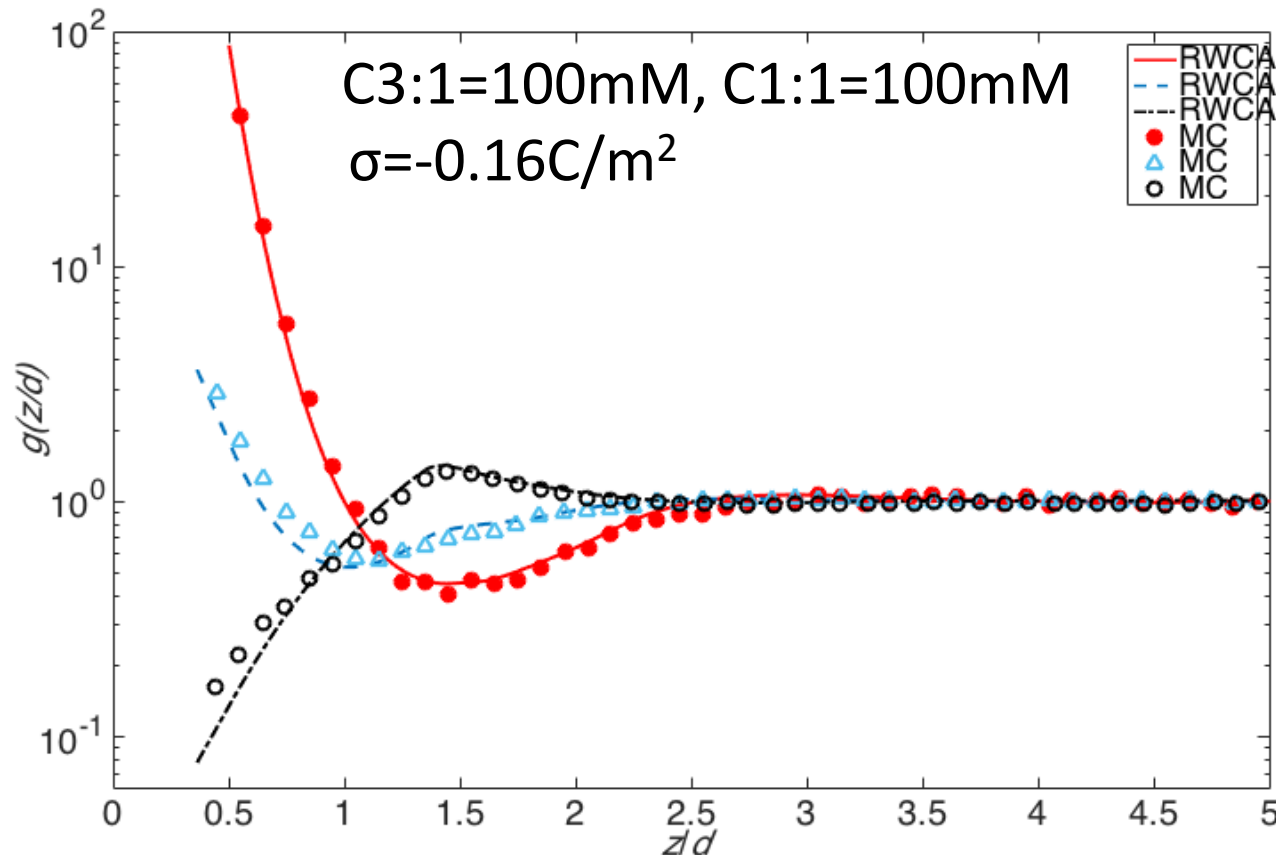


Fig 17. Ion distribution function as a function the distance from the charged surface (normalized by the trivalent counterion diameter)

# Acknowledgments

- Acknowledgements to the encouragement and financial support of the Swedish Nuclear Fuel and Waste Management Company (SKB).
- The work was also partly funded by the European Union through the BELBaR project.
- Expressions of sincere gratitude are given to Ivars Neretneiks and Patrik Sellin for discussions.

***Thanks for you attention***