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NANOPARTICLE INTERACTIONS IN ELECTROLYTE SOLUTIONS: A CLASSICAL DENSITY FUNCTIONAL THEORY AND MOLECULAR DYNAMICS STUDY

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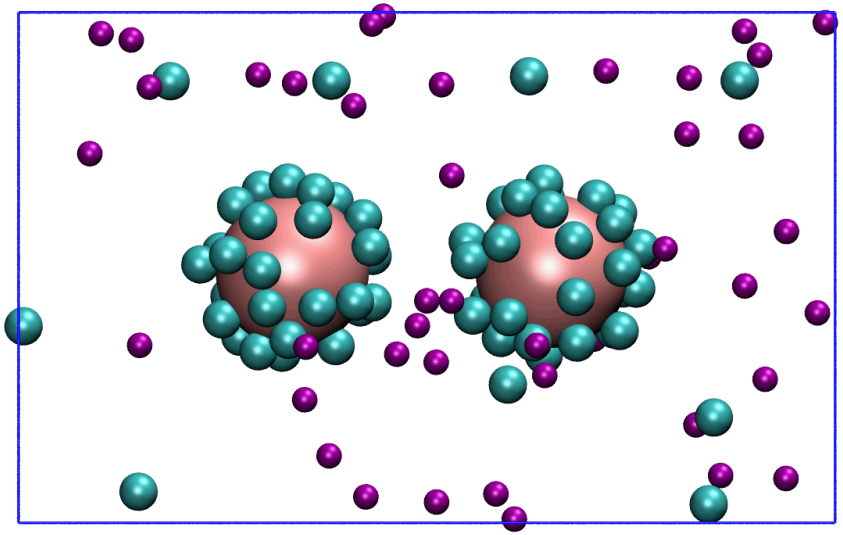

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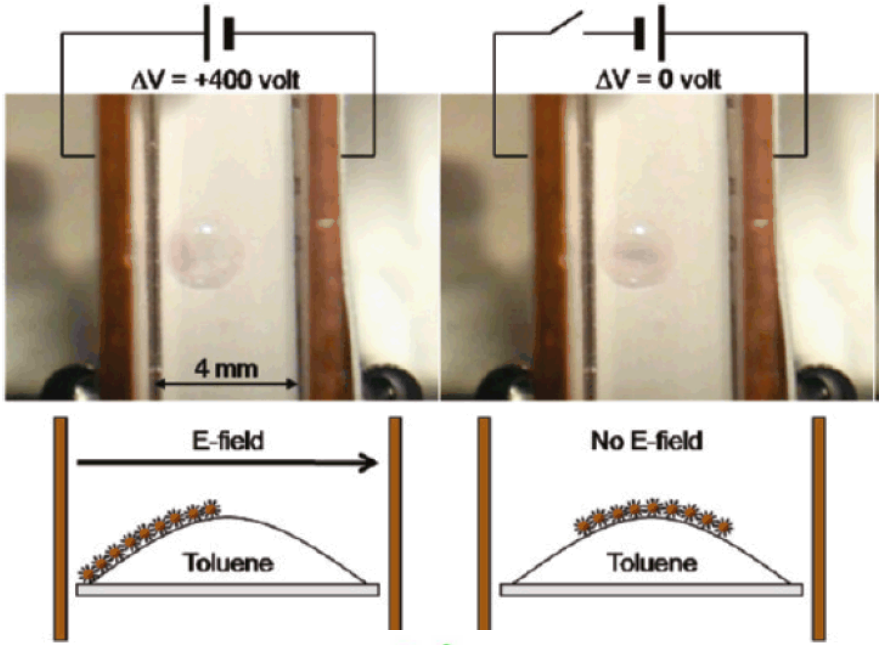
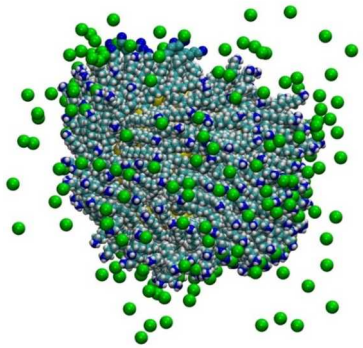
Why study charged macroions?

- Control over assembly
  - Manipulate individual NPs and assembled structures
- Dispersal / solution properties
  - Uncharged chains cluster => NPs insoluble in water
  - Charged end groups, chains are dispersed=> NPs water soluble
- Biomolecules (DNA)
  - Large charge + polyvalent salt = condensation or attraction



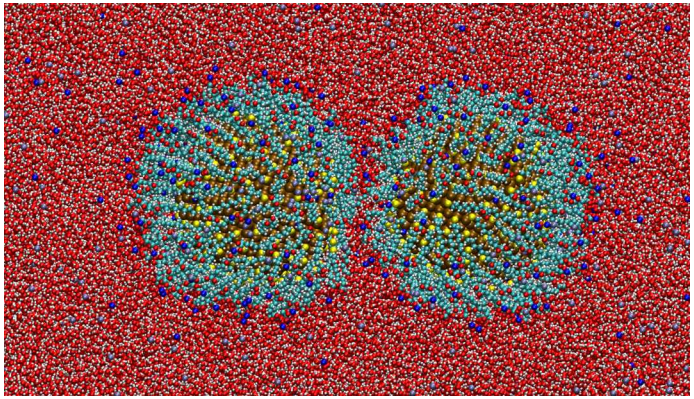


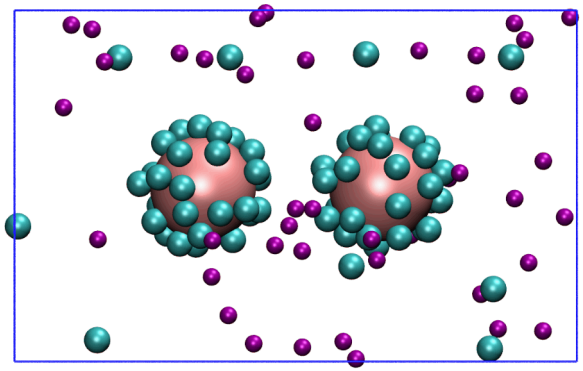
$C18\text{-}NH_3^+Cl^-$
Neutral pH=7

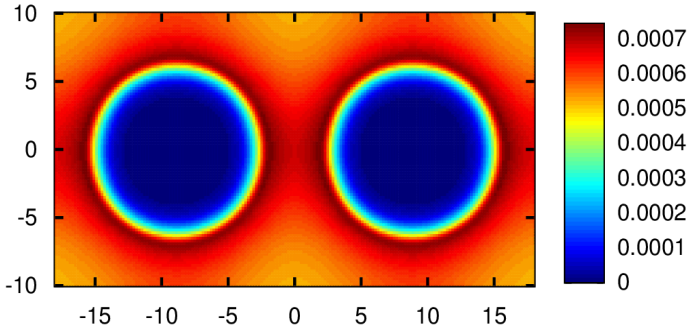
Bolintineanu, Lane, Grest.
Langmuir (2014)

Why use a DFT approach?

- Atomistic molecular dynamics
  - 4nm decanethiol coated in water ⇒ $7x10^5$ atoms
  - Can simulate ~10 realizations
- Coarse-grained molecular dynamics (CGMD)
  - Charged 4nm "NPs" with counterions and coions in neutral fluid⇒$2x10^4$ particles
- Classical fluids DFT
  - 10X faster
  - Efficiently use 10X more cores
  - Free energy (FE) functional $F[\rho(r)]$

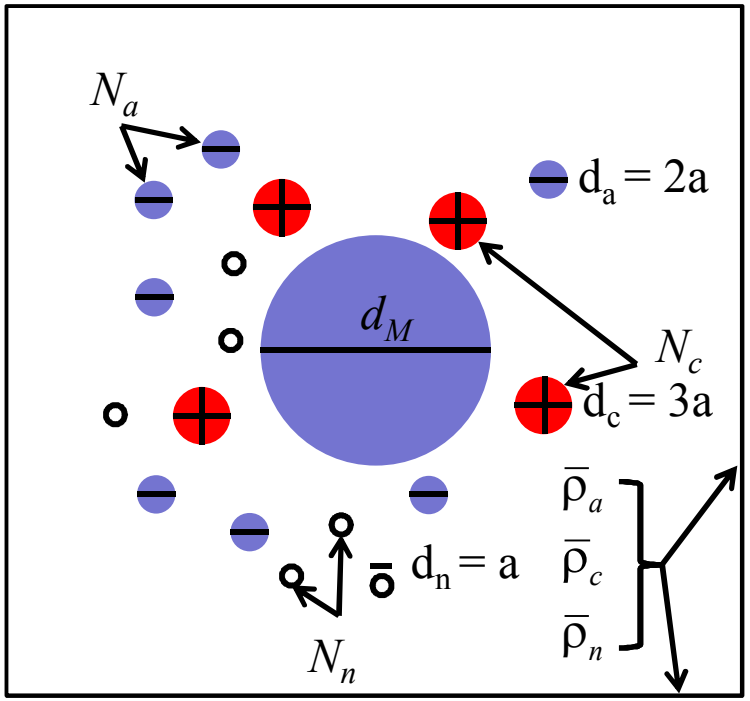






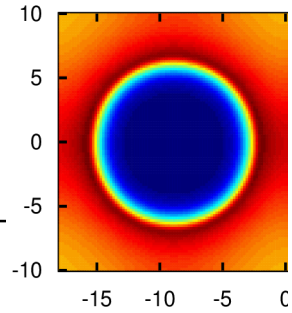
Model

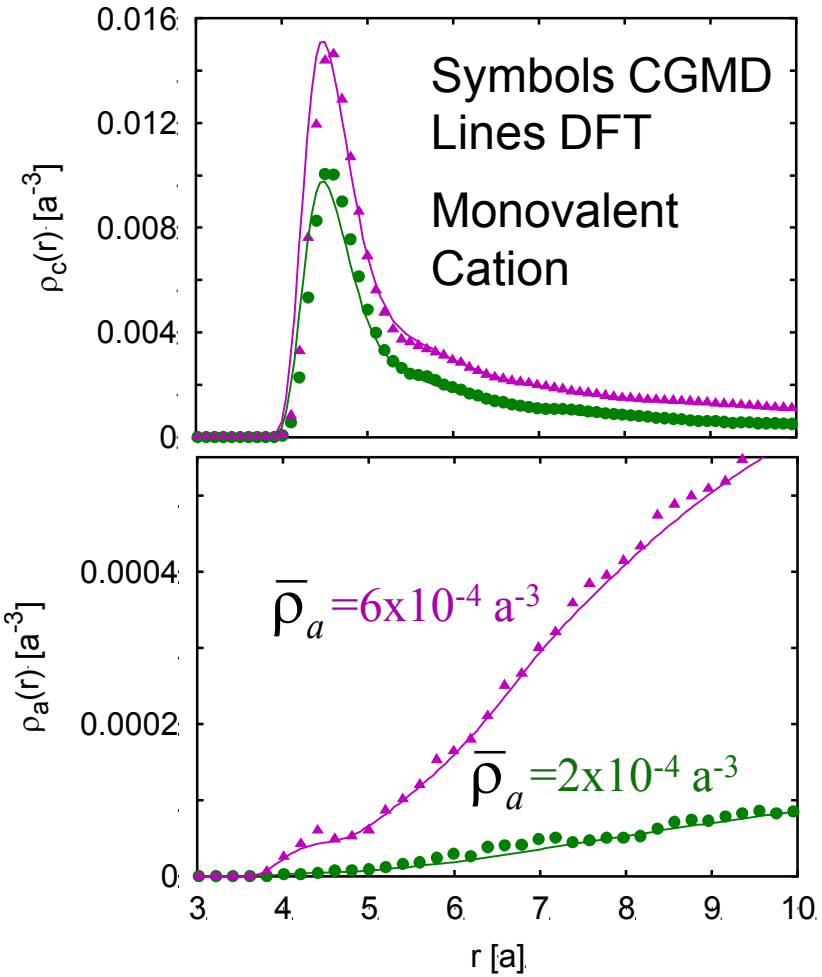
- Nanoparticle diameter d_M, negative charge $q_M = \pi d_M^2 \sigma_M$
- N_c (ρ_c) cations $d_c = 3a$, charge $q_c = 1e, 2e, 3e$
- N_a (ρ_a) anions $d_a = 2a$, charge $q_a = -1e$
- N_n (ρ_n) neutral particles $d_n = a$ (=0.285nm)
- Bjerrum length
  $\ell_B = 2.5a = 0.71$ nm
- Moderate Coupling $3 < g < 300$
  $g = 2q_c^3 \ell_B^2 q_M / (e^4 d_M^2)$
- Interactions
  - Repulsive (cut & shifted) 12-6
    $\varepsilon = k_B T$

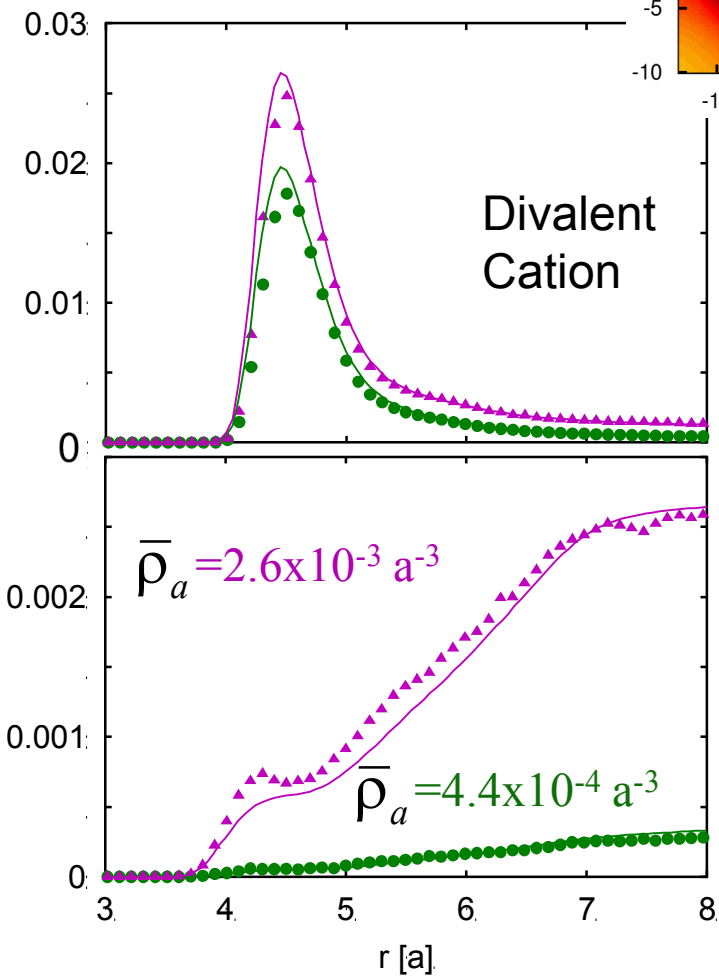


How good is a DFT approach?

- Ion density $\rho_a(r)$, $\rho_c(r)$ around $d_M=6a$ ($\approx$1.7nm) $\sigma_M=0.1e/a^2$ macroion
  - Quantitative agreement







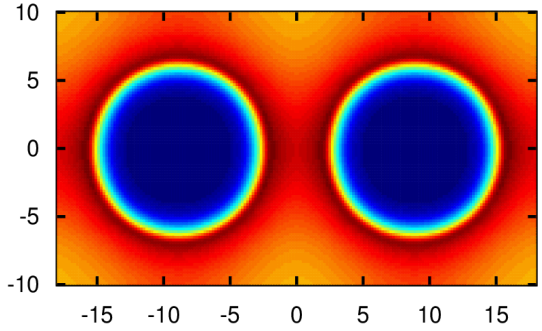
15-
190 mM

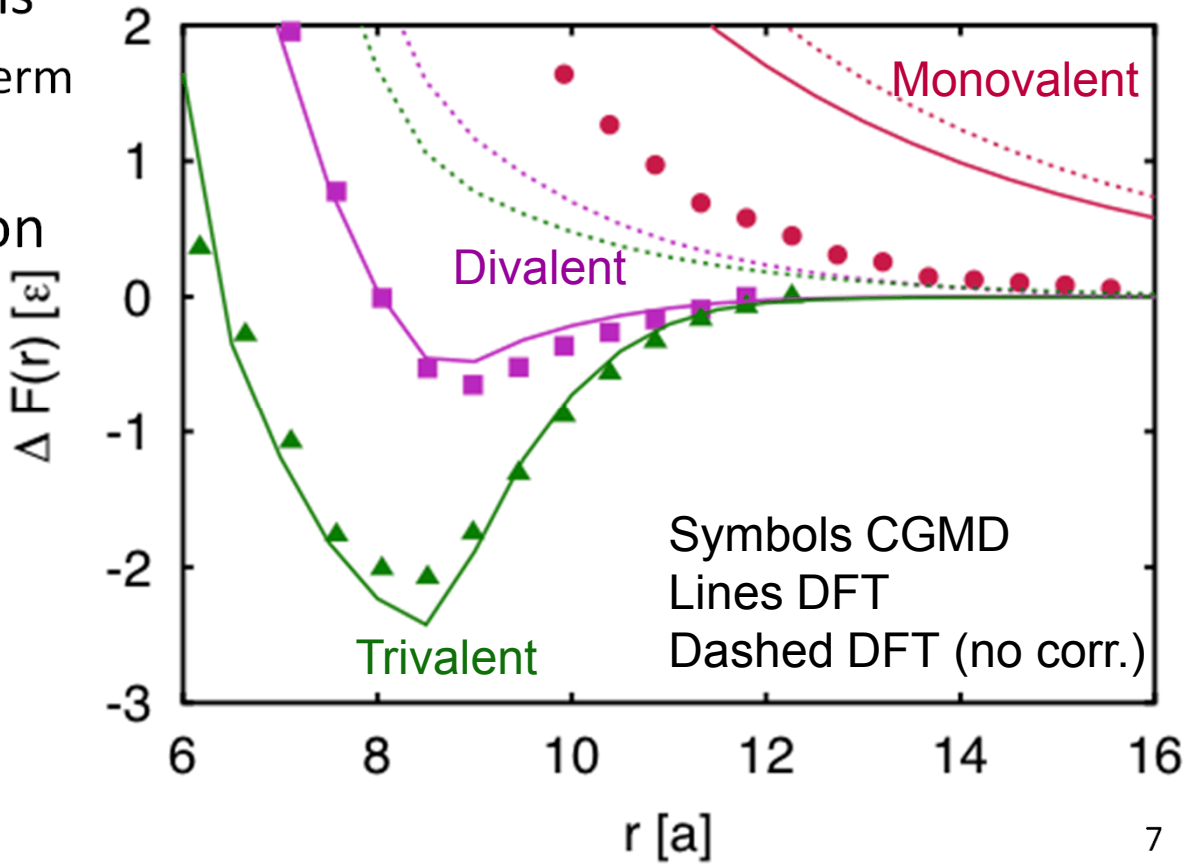
Macroion Interactions

- Ion valence increases coupling g, correlation importance
- Ion correlations drive attractive interactions
  - DFT ion correlation term produces attraction
- Qualitative Interaction agreement

$\sigma_M = 0.1 e/a^2$

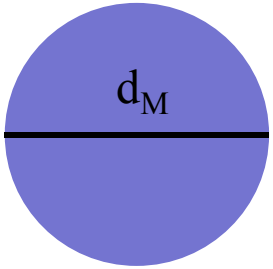
$d_M = 6a$





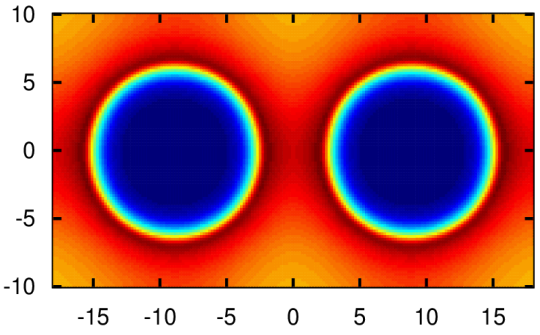
Macroion Diameter

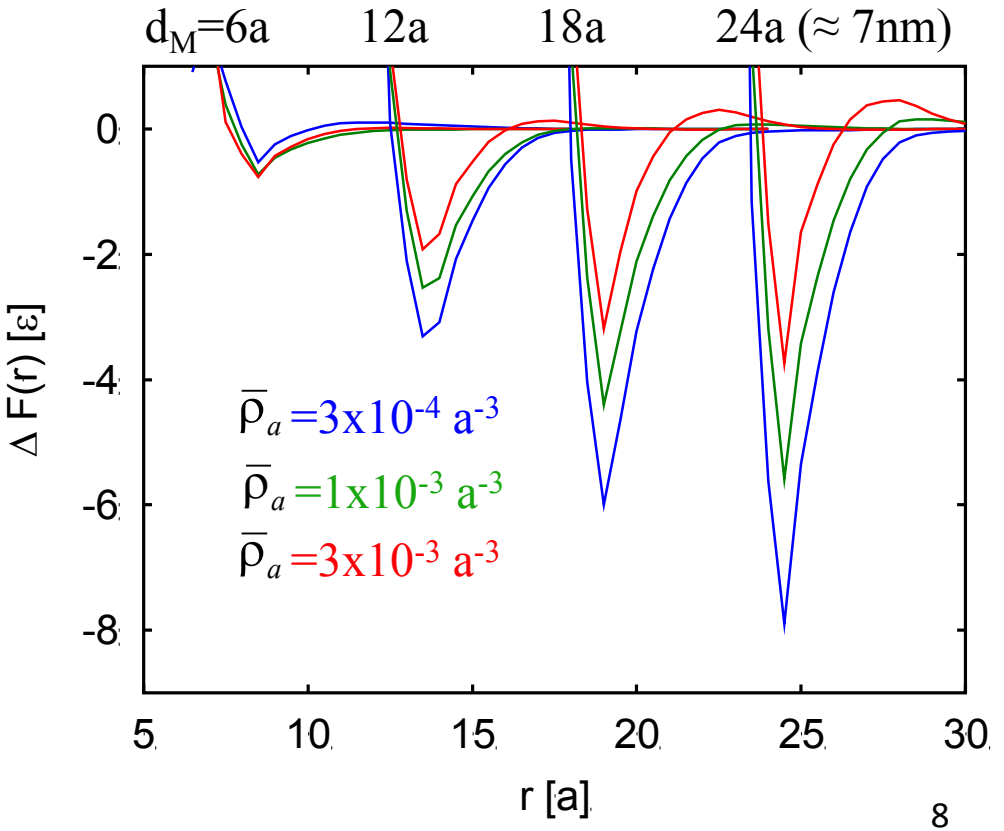
- Depth of minimum increases with d_M
- But variation depends on ion density
- $8\ kT$ minimum leads to aggregation
- Costly for CGMD, enabled by DFT model



$\sigma_M = 0.1e/a^2$

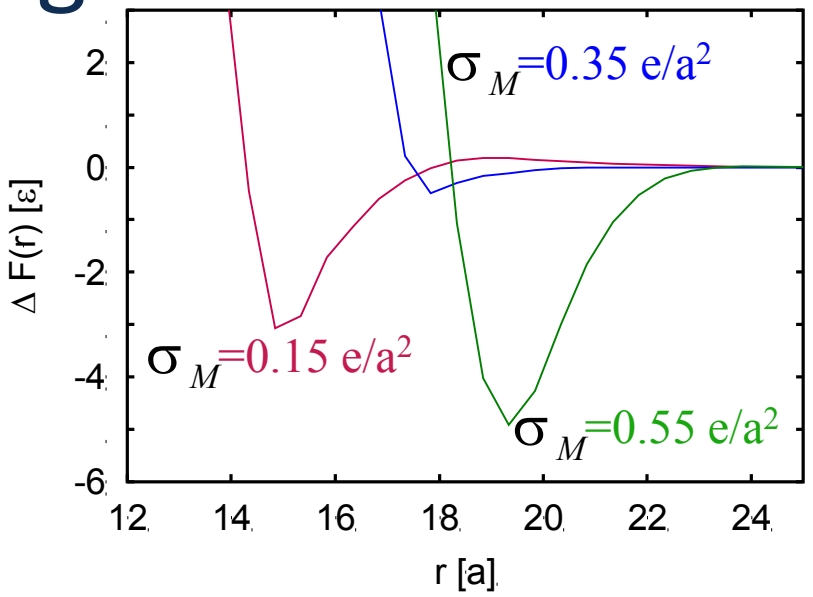
$q_c = 2e$

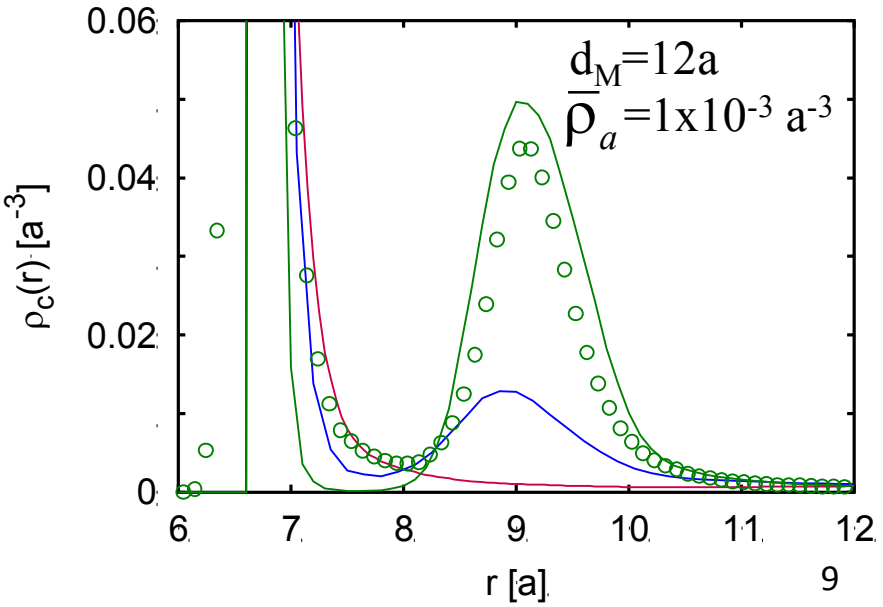




Macroion Surface Charge

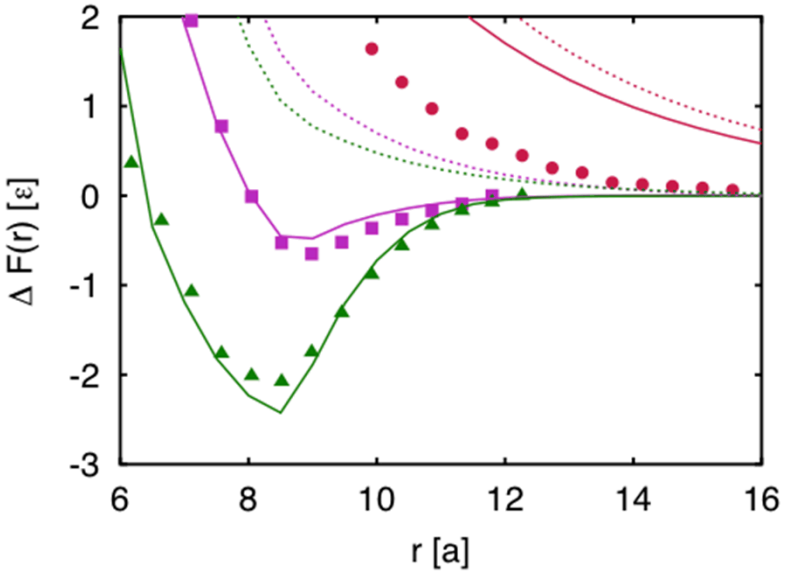
- Both minimum depth and location vary
  - Larger equilibrium separation with increasing σ_M
- Counterion layering
  - Second peak develops as interaction minimum shifts
  - Weak interaction from small secondary peak
  - Deep minimum from large secondary peak
  - Secondary peak occurs in both CGMD & DFT

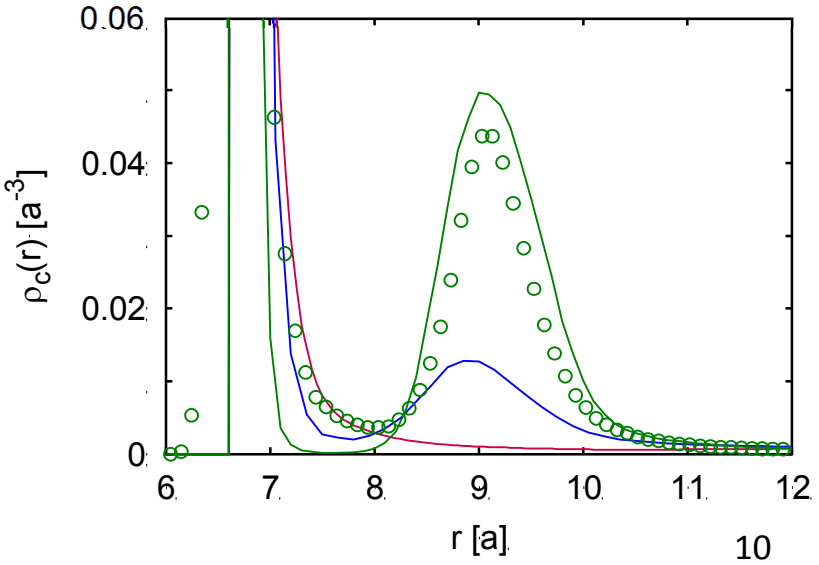




Charged Nanoparticles

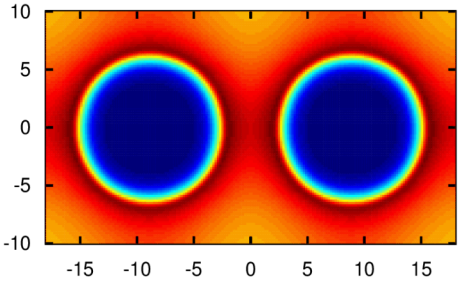
- Classical Fluids DFT & CGMD agreement
  - Quantitative density
  - Qualitative interaction FE
- Counterion valence / correlations -> attraction
- Ion concentration, macroion diameter, and macroion charge all influence interaction FE
- Counterion layering at high surface charge
  - Nonmonotonic attractive well depth
  - Equilibrium separation changes





How good is a DFT approach?

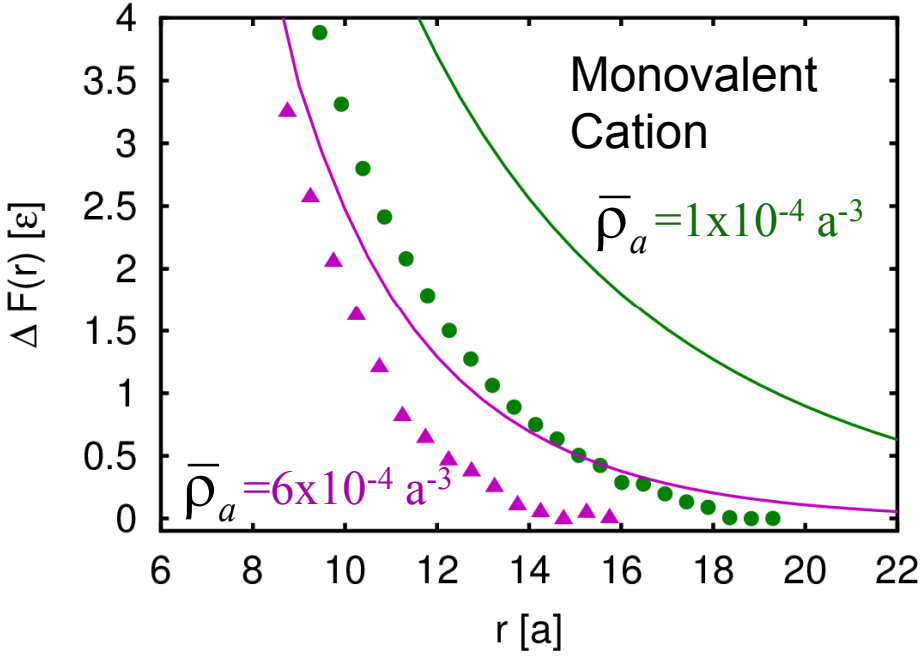
- Macroion-macroion interaction free energy
  - Qualitative agreement
  - Correct trends and order of magnitude for well depth

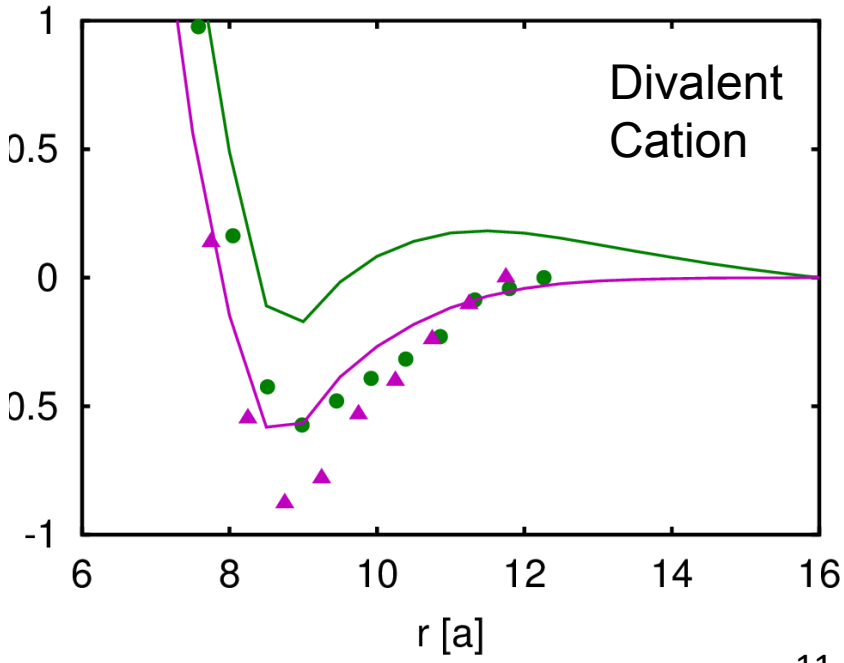


$\sigma_M = 0.1 e/a^2$

$d_M = 6a$

Symbols CGMD
Lines DFT





Macroion Surface Charge

- Interaction minimum ΔF_{min} depends on surface charge σ_M
  - NP full coverage $4.7\ e/nm^2 \approx 0.35\ e/a^2$
  - Nonmonotonic in σ_M
  - Varies widely