

Dependency of colloidal charge reversal on additional salt

Olaf Lenz

Tuesday 29 May 2007

System description

- charged colloid, $q = -Z$ (here: -300)
- multivalent (+3) counterions
- additional 1:1 salt

- experiments (*e.g.* electrophoresis) show *charge reversal* of the complex
- (+3) ions assemble on colloid surface
- dependency on 1:1 salt concentration?

Theory

- Poisson-Boltzmann fails: multivalent ions
- DFT theories predict charge reversal
- basic idea: (+3) ions form crystal-like lattice on colloid surface
- growing 1:1 salt concentration: theories predict an *increase* of the reversed charge (“giant overcharging”)
- basic idea: 1:1 salt screens the interaction between (+3) ions
- in contrast, experiments show a *decrease*

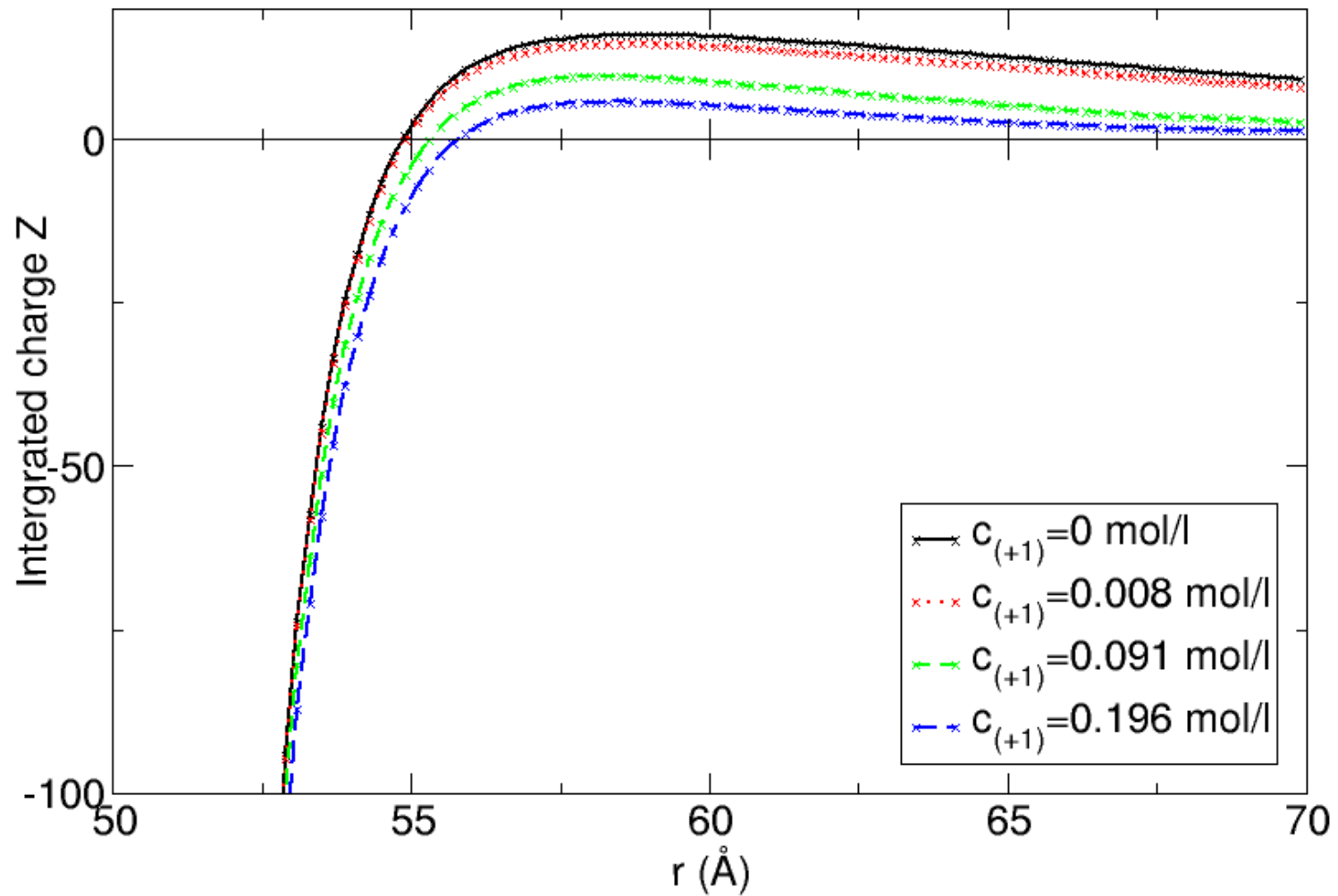
Theory 2

- Pianegonda, Barbosa, Levin 2005: DFT theory that predicts decrease
- central idea: (+3) counterions and (-1) coions form clusters in the bulk
- less counterions available for charge reversal
- screening negligible
- my job: simulations

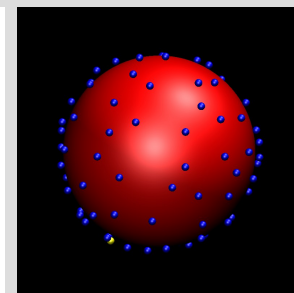
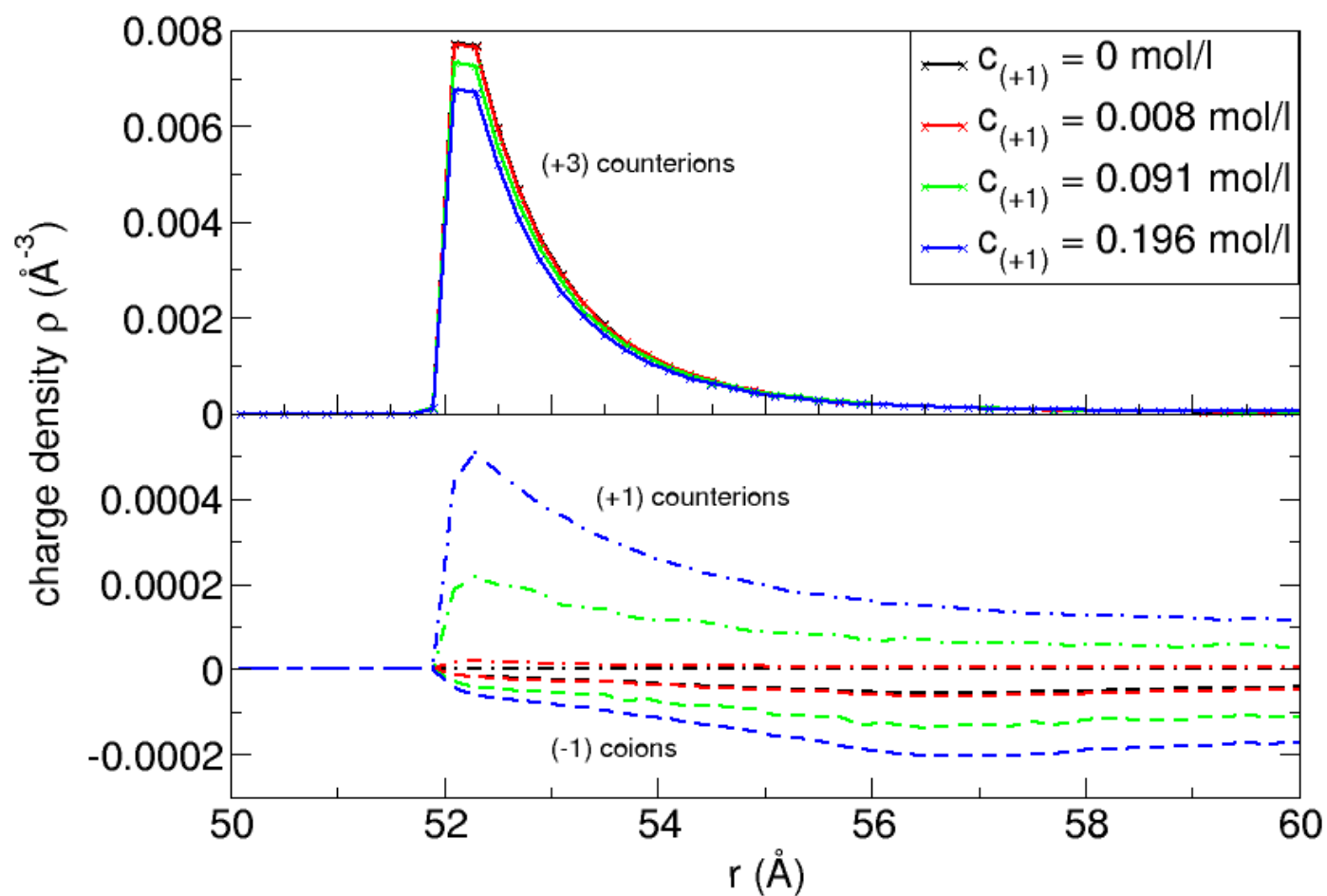
Simulation system

- 1 colloid, $Z = -300$, $R = 50 \text{ \AA}$
- 200 (+3) counterions, $q = +3$, $r = 2 \text{ \AA}$
- 300 + $N_{1:1}$ (-1) coions, $q = -1$, $r = 2 \text{ \AA}$
- $N_{1:1}$ (+1) counterions, $q = +1$, $r = 2 \text{ \AA}$
- $N_{1:1}$ between 0 and 1300
- soft-core interaction
- Bjerrum length $l_b = 7.1 \text{ \AA}$
- Langevin thermostat $T = 1.0$

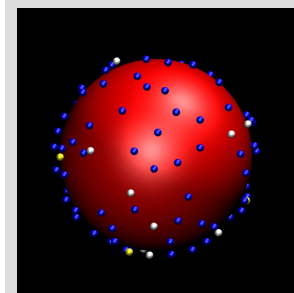
Charge reversal



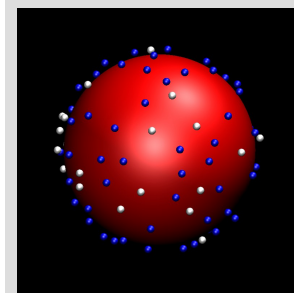
Colloidal surface



$$N_{1:1} = 0$$

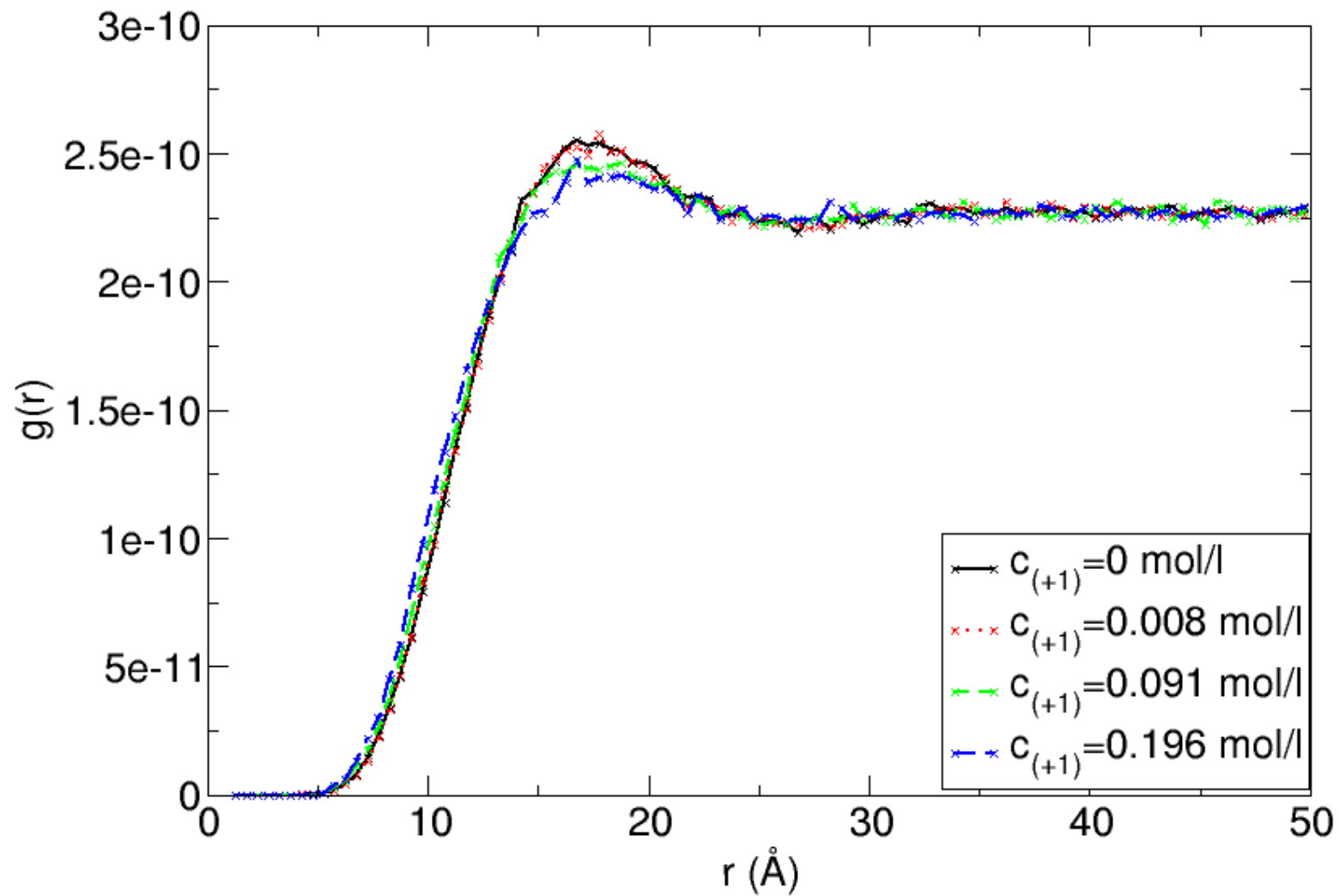


$$N_{1:1} = 600$$

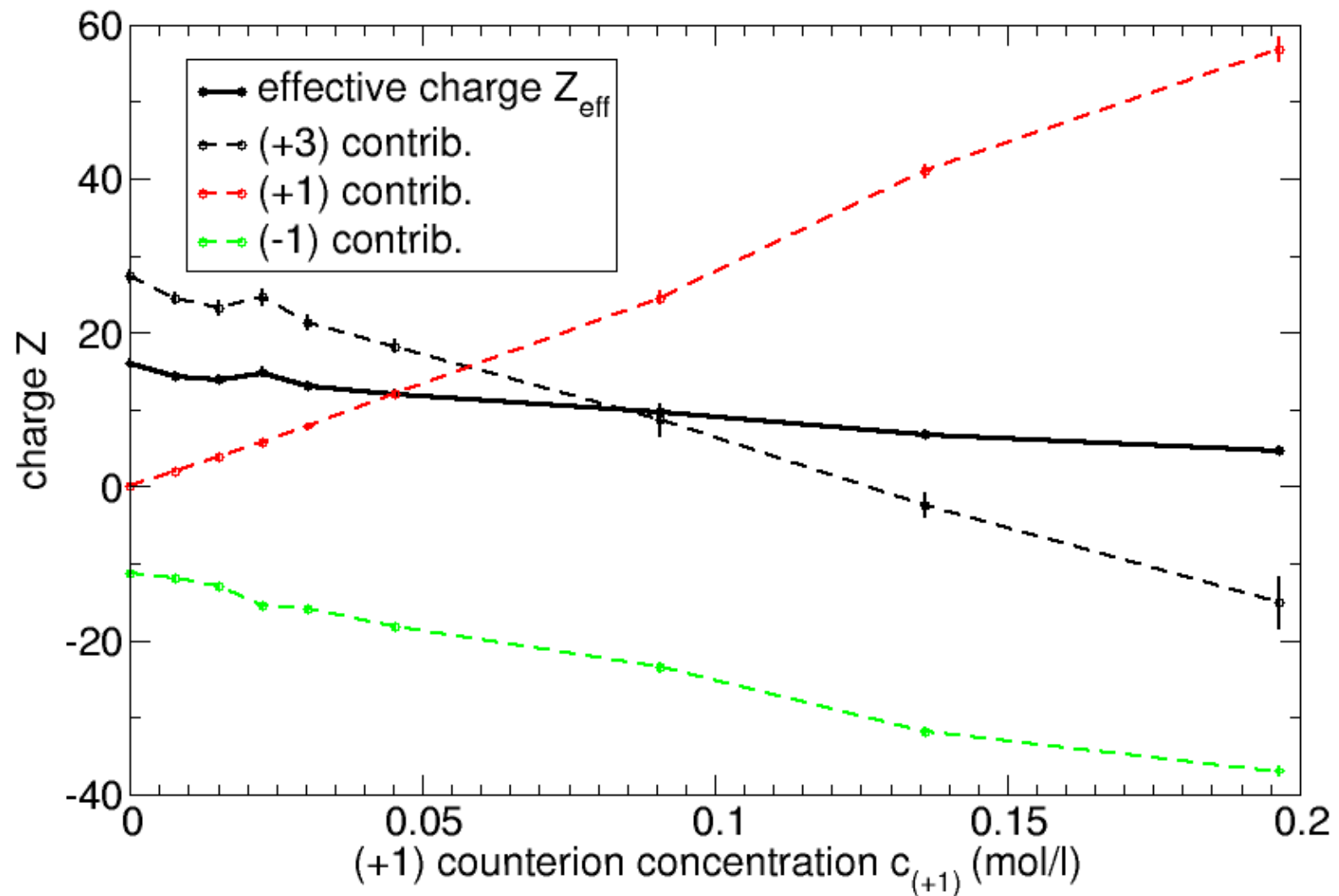


$$N_{1:1} = 1300$$

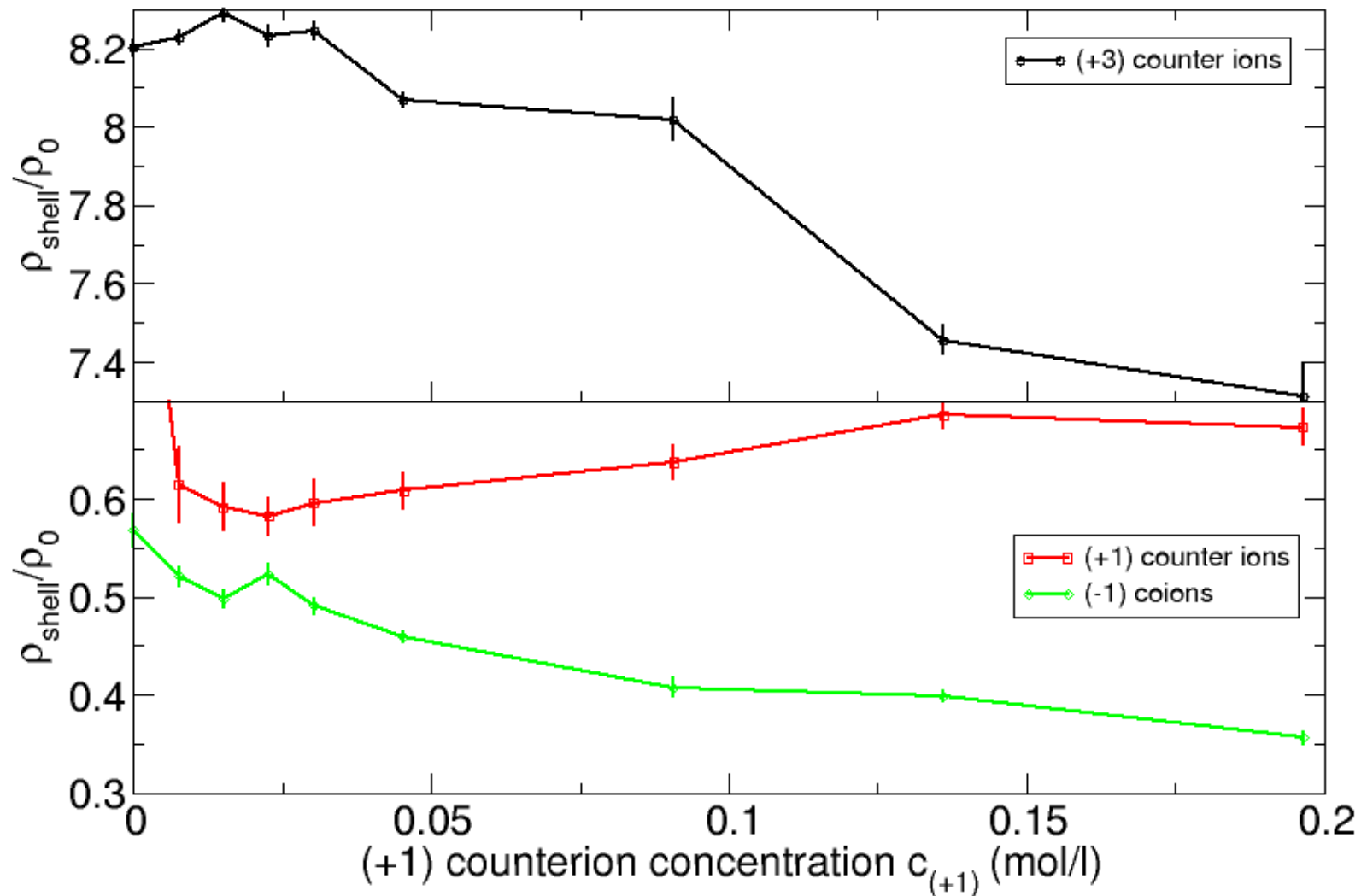
No screening on surface



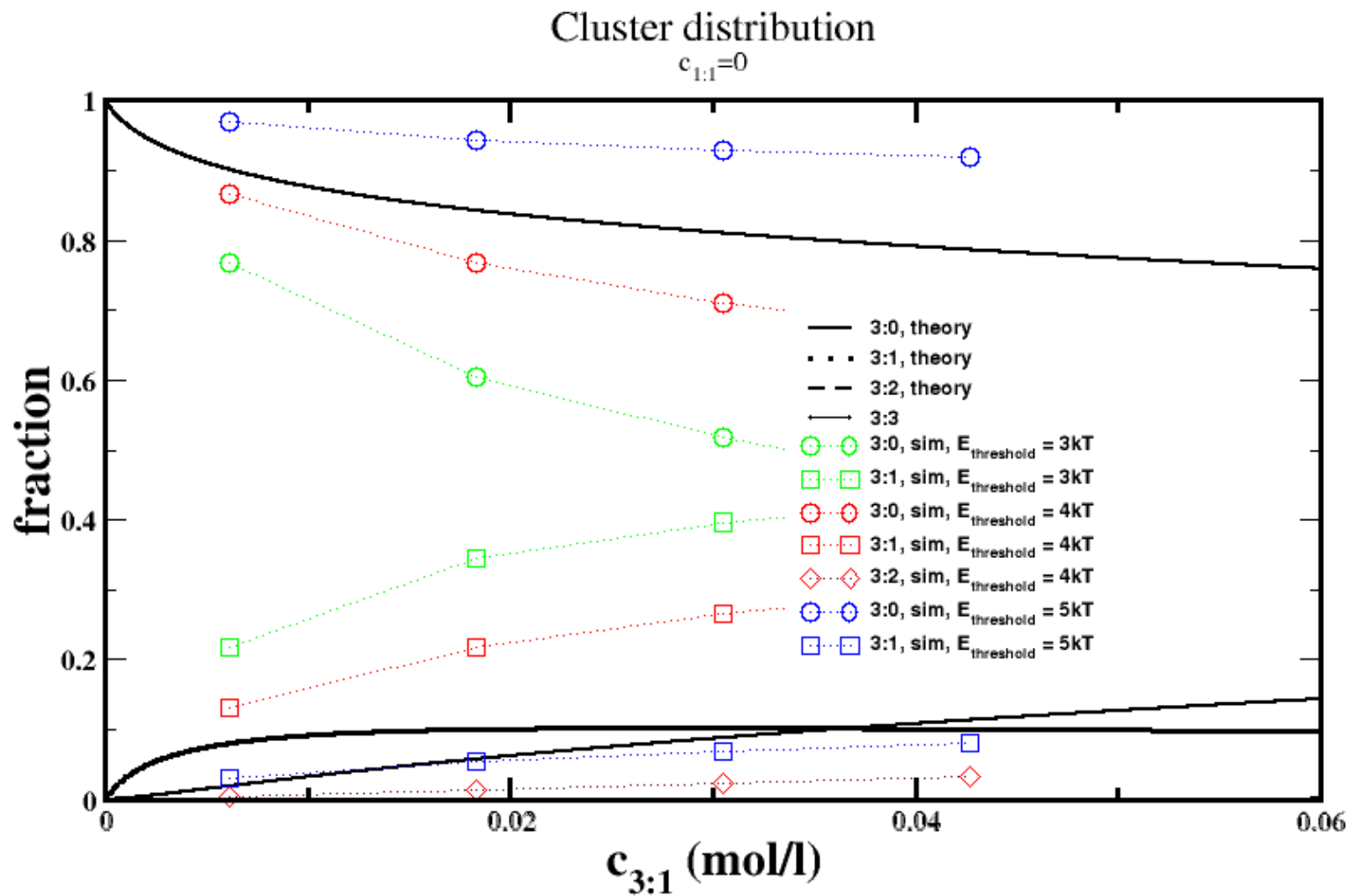
What happens?



What happens 2?



Cluster formation



Cluster formation 2

