

ENERGETICS OF ION SELECTIVITY IN SLIT LIKE PORES

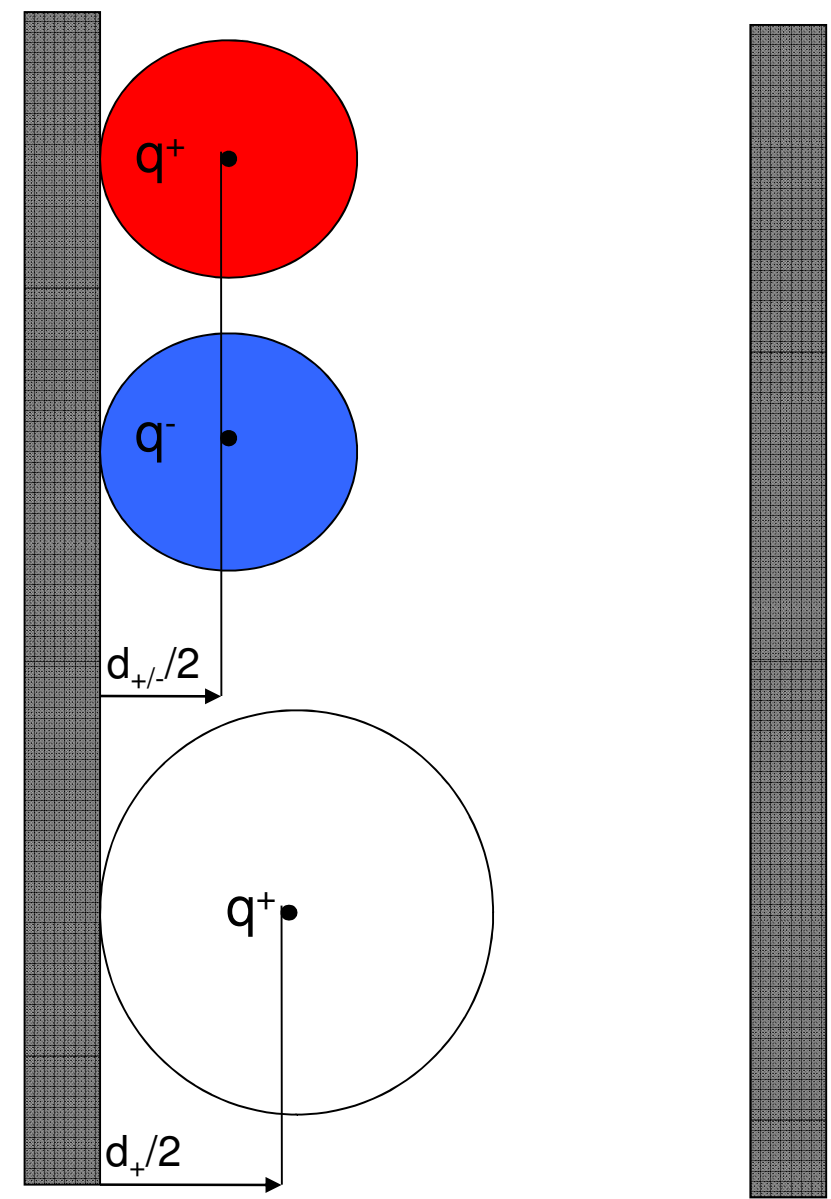
Mónika Valiskó¹, Tímea Nagy¹, Dezsdő Boda¹, Dirk Gillespie²

¹Department of Physical Chemistry, University of Pannonia, Veszprém, Hungary, ²Department of Molecular Biophysics and Physiology, Rush University Medical Center, Chicago, USA

INTRODUCTION

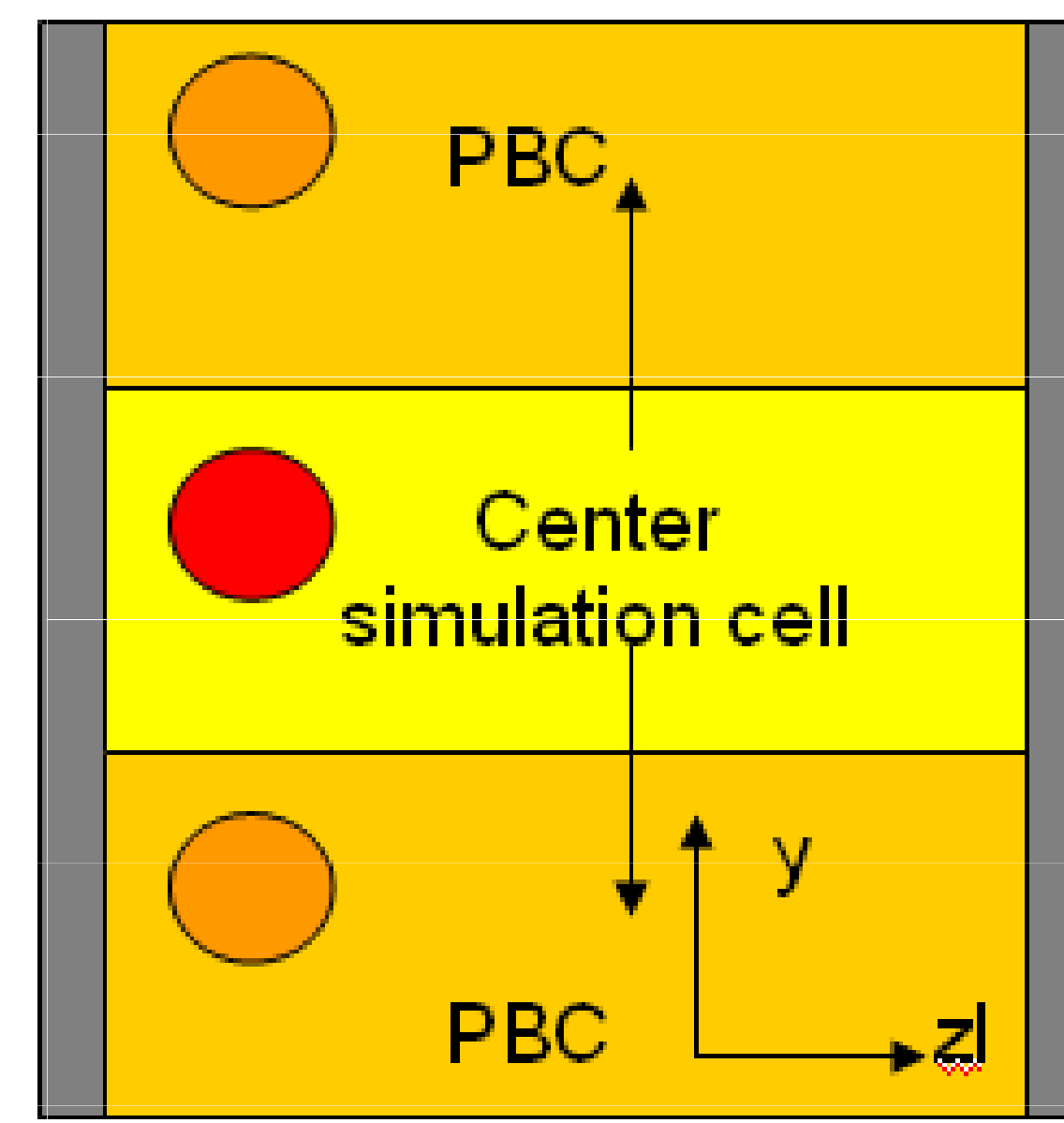
The electrical double layer is formed at the interface of the solid phase (electrode) and the electrolyte. We study the effect of the charge and/or size asymmetry, we show results for a wide range of electrode charge and we study the effect of charge and size asymmetry on the electrode potential, and the competition of two cations of different size and valence near a highly charged electrode. If the ions have different diameters and/or valences, the electrode potential is nonzero even if the electrode charge is zero (PZC potential) [1]. Size and valence asymmetries are two competing effects regarding the sign and magnitude of the PZC potential [2,3]. Grand canonical simulations are used to study the ion selectivity of electrolyte mixtures into slit-like pores.

MODEL



- We consider the primitive model of electrolytes between hard, planar, charged surfaces.
- The solvent is described by a uniform dielectric constant
- The ions are modeled as charged, hard spheres with a point charge in their center
- Diameter of the anion: $d_+ = 0.425$ nm
- Valence of the anion: $z = -1$
- Diameter of the small and large cations are 0.2 and 0.425 nm
- Monovalent and divalent cations are considered
- The distance between the charged walls was varied

MONTE CARLO SIMULATION



MC: Molecular computer simulation method. Its results are accepted as exact for a well-defined model within statistical accuracy. We used the grand canonical (μVT) ensemble.

The chemical potentials corresponding to prescribed concentrations were determined with the method of Malasics et al. [4] The process converges fast, needed just a few iterations.

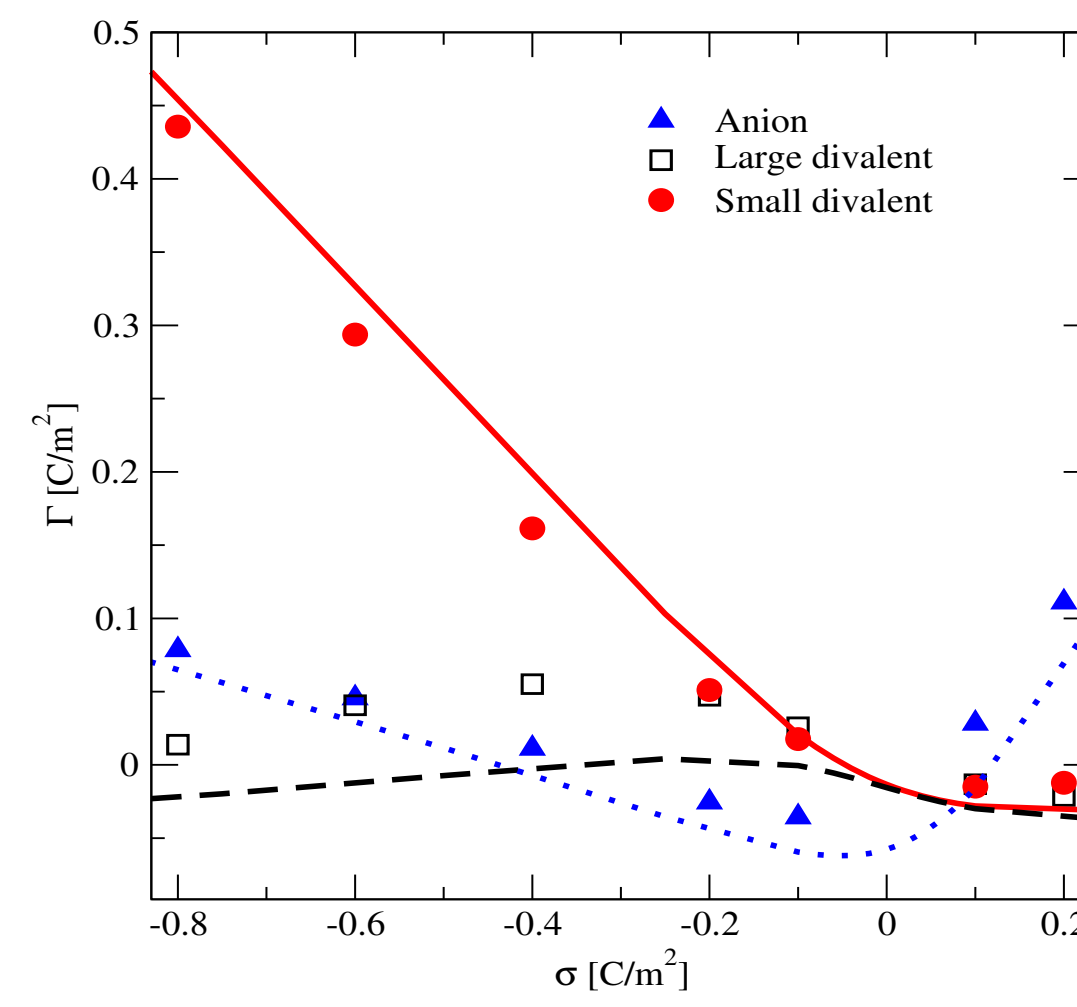
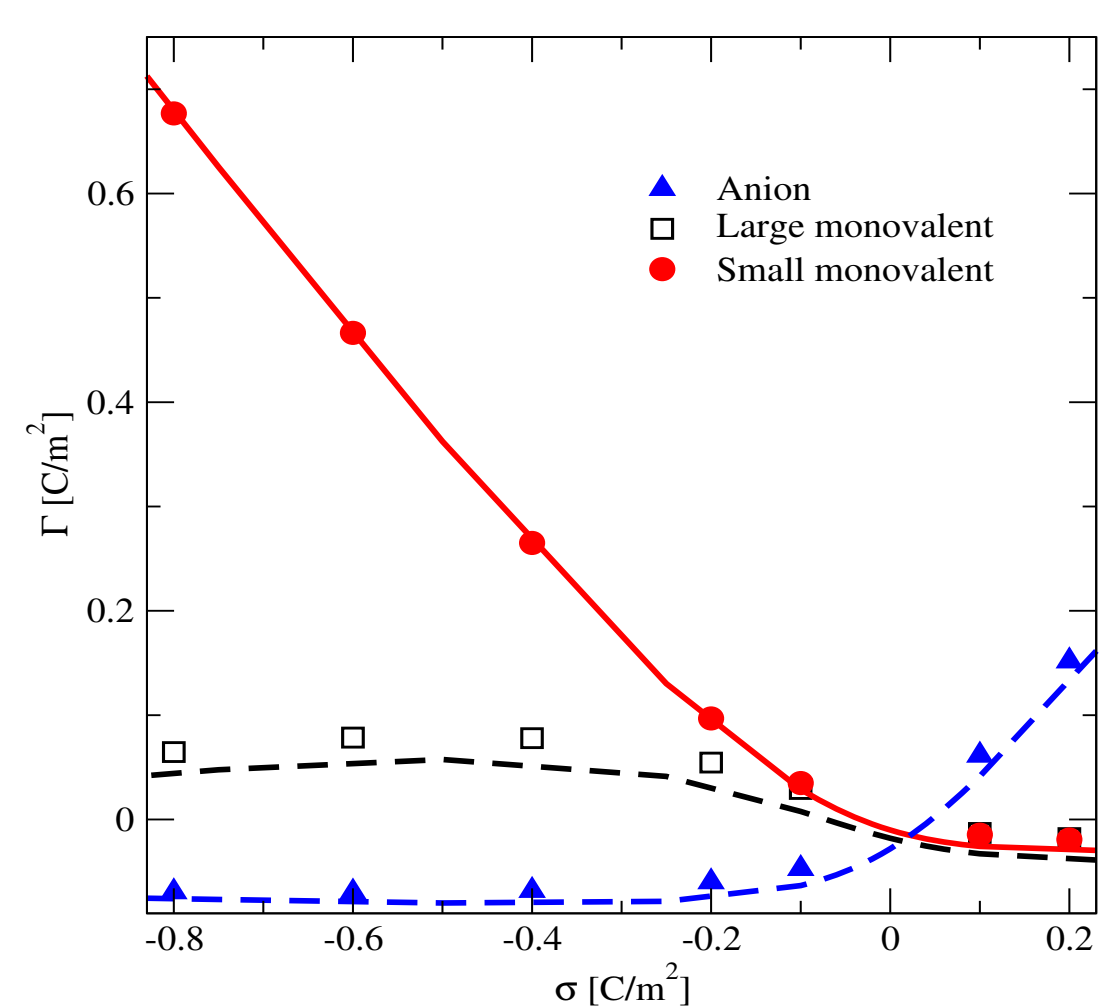
We computed the terms of the chemical potential profiles using Widom's particle insertion method.

STUDY OF THE SELECTIVE ADSORBANCE OF DIFFERENT TYPE OF CATIONS ON THE SURFACE OF THE ELECTRODE

COMPETITION BETWEEN SIZE AND VALENCE

We use an integrated quantity, the excess adsorption, to characterize the different ability of the various ions to be adsorbed at the electrode. It is the integral of the difference of the concentration profile and the bulk concentration:

$$\Gamma = \int_{x=0}^{\infty} [c_i(x) - c_{bulk,i}] dx$$

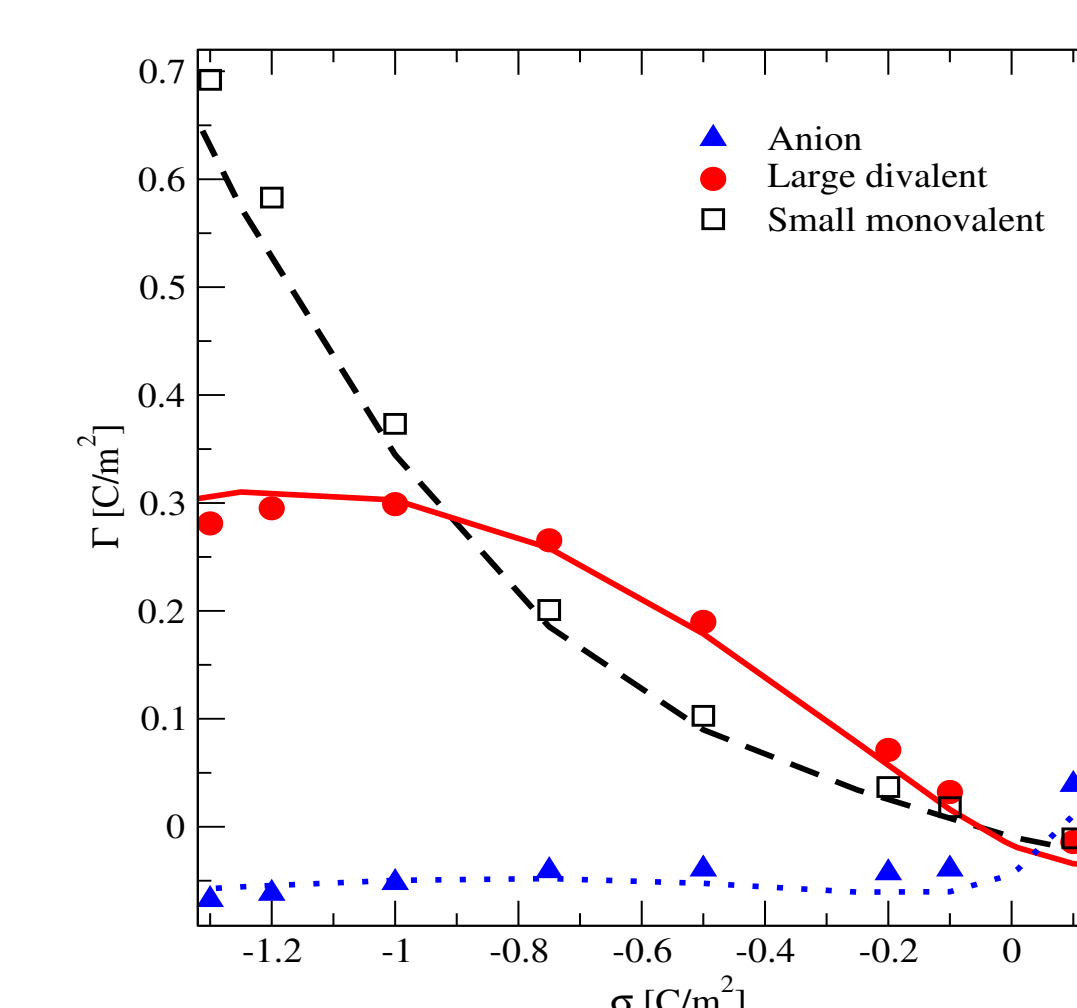
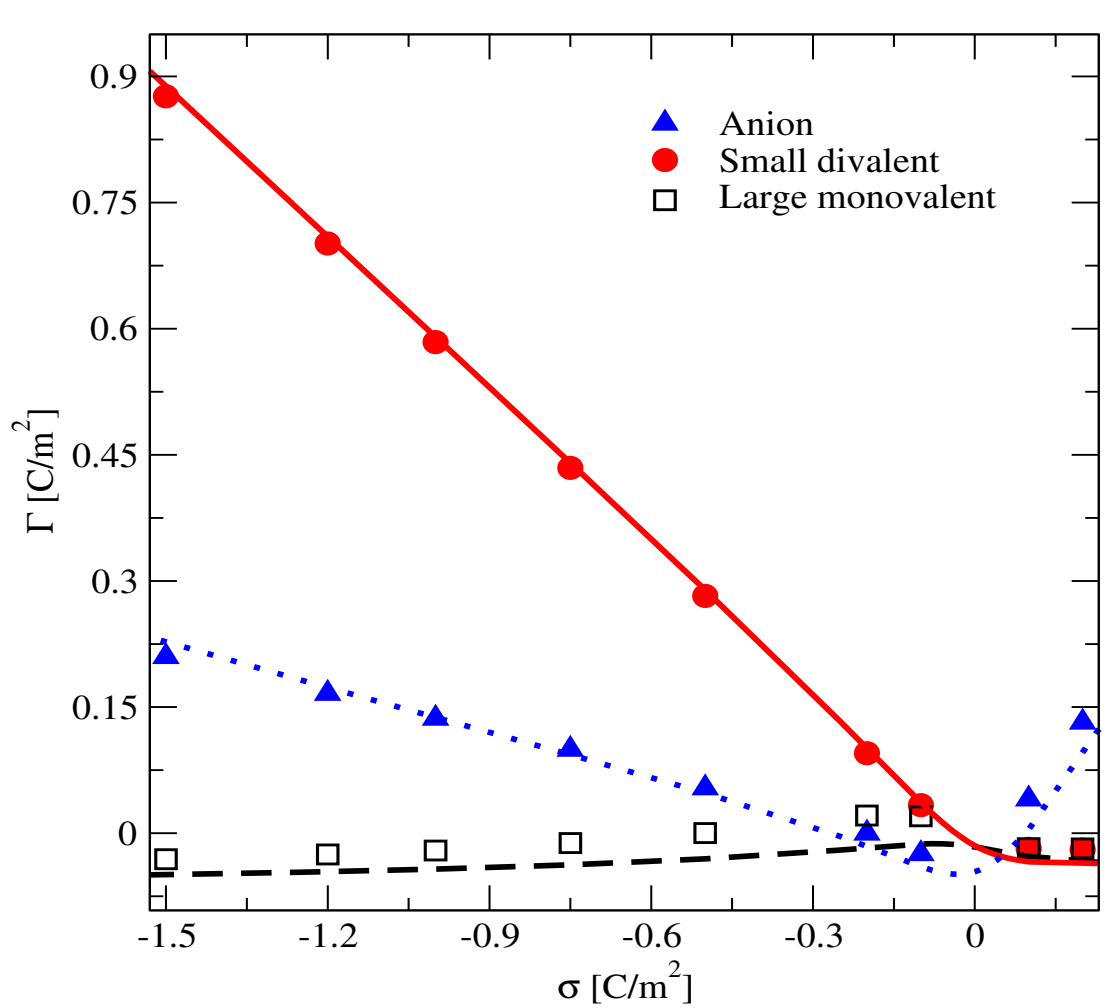


The adsorption as a function of the electrode charge for small and large monovalent cations. The concentration of either cations is 1 M, the concentration of the anion is 2 M.

The adsorption as a function of the electrode charge for small and large divalent cations. The concentration of either cations is 1 M, the concentration of the anion is 4 M.

At positive surface charges anions are preferred at the electrode, while at negative surface charges the two cations compete for space near the interface. No wonder that the smaller ions come out of the competition as a winner. Their preference is more pronounced at higher surface charges.

For mixtures of small and large divalent ions this preference is even more obvious. At large negative surface charges the large cations even surpassed by the anions. Its explanation is that the association of a divalent cation with two anions have a higher probability. This association is more probable in the case of small ions. At high surface charges, the small cations tend to bring the anions with themselves to the interface to maintain electroneutrality and minimum free energy just to the degree entropy allows. A layering structure is formed at the electrode (charge inversion).



The adsorption as a function of the electrode charge for small divalent and large monovalent cations. Cation concentrations are 1 M, anion concentration is 3 M.

The adsorption as a function of the electrode charge for large divalent and small monovalent cations. Cation concentrations are 1 M, anion concentration is 3 M.

We studied the electrical double layer when the ions are allowed to have different size and/or valence. In the case of a pure salt, the electrode potential at the point of zero charge (PZC) depends on the charge and valence asymmetry.

In the case of mixtures of two salts, cations of different size and charge compete for space at the negatively charged electrode. The competition is won by the small and/or divalent cations, because they provide more charge to balance the electrode charge using less space.

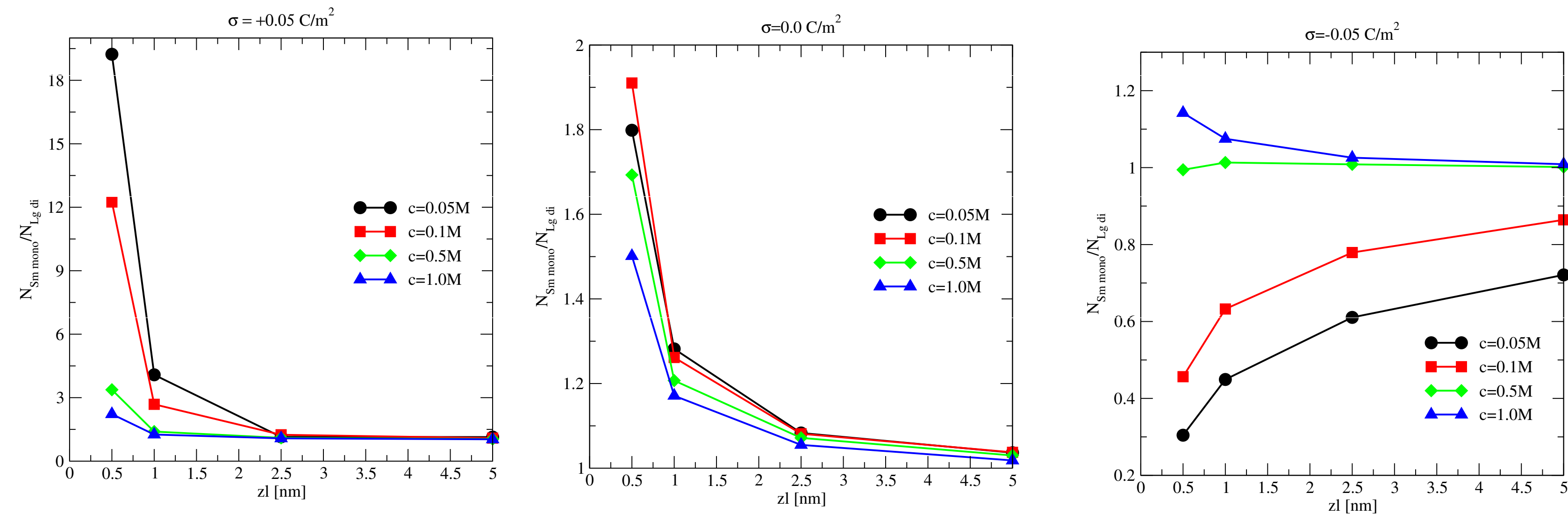
REFERENCES AND ACKNOWLEDGEMENT

- [1] Valiskó, M., Henderson, D., Boda, D.: The competition between the effects of differences in ion diameters and charges in an electrical double layer studied by Monte Carlo simulations: *J. Phys. Chem. B*, 108 (42): 16548-16555, 2004.
- [2] Gillespie, D; Valiskó, M; Boda, D: Density functional theory of the electrical double layer: the RFD functional, *J. Phys.-Condens. Mat.*, 17 (42): 6609-6626, 2005.
- [3] Valiskó, M; Boda, D; Gillespie, D: Selective adsorption of ions with different diameter and valence at highly charged interfaces, *J. Phys. Chem. C* 111: 15575-15585, 2007.
- [4] Malasics, A; Gillespie, D; Boda D: Simulating prescribed particle densities in the grand canonical ensemble using iterative algorithms, *J. Chem. Phys.* 128: 124012, 2008.

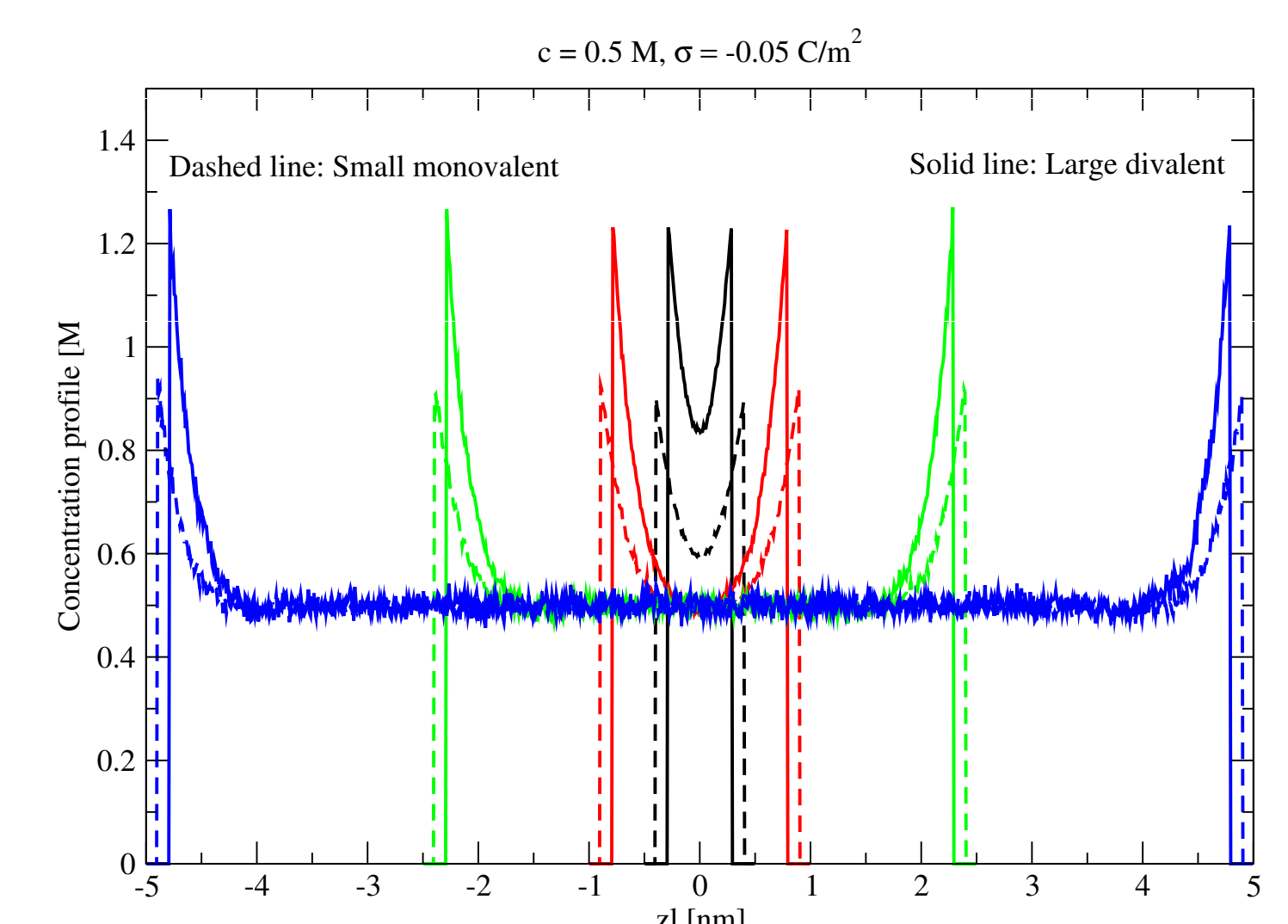
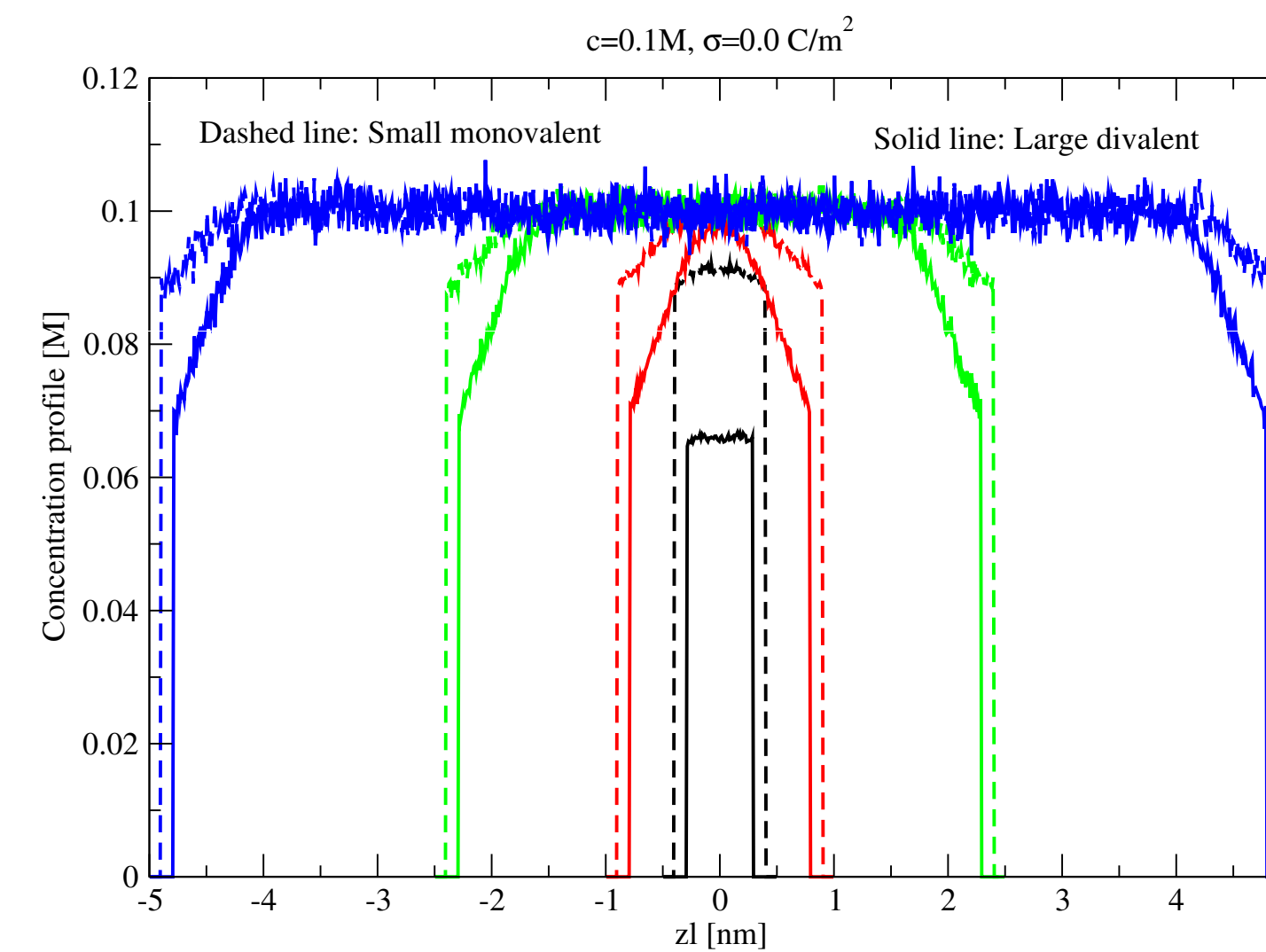
This work was supported by the Hungarian National Research Fund (OTKA 68641) and János Bolyai Research Fellowship.

ION SELECTIVITY IN A SLIT

Here we studied the competitive case, where the small monovalent cation compete with the large divalent cation in case of different electrode charge and width of the slit. The concentrations of the two cations are the same. We studied 4 different cases: 0.05, 0.1, 0.5 and 1M cation concentrations. Ion selectivity is defined as the ratio of the number of the small monovalent and large divalent cations in the slit.



Ion selectivity as a function of the width of the slit for different cation concentrations. The figures refer to different electrode charges.



Cationic concentration profiles as functions of the width of the slit. The figures refer to different electrode charges and cation concentrations. At moderate electrode charges the large divalent cations are preferred because of their larger valence. At high electrode charges the small monovalent cations are more preferable because their smaller size is more advantageous in the crowded slit. Decreasing the width of the slit the bulk phase disappears, the double layers overlap.

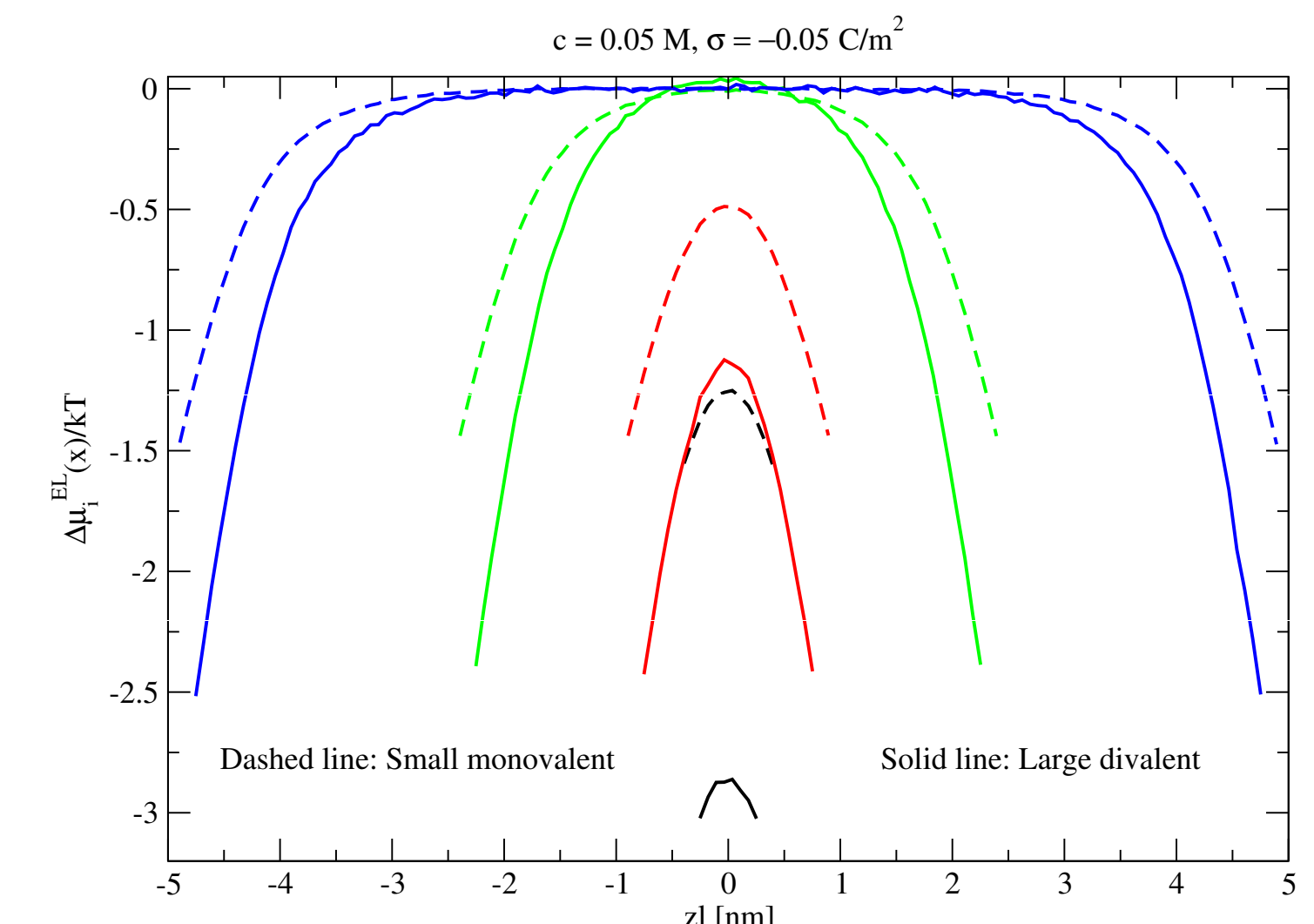
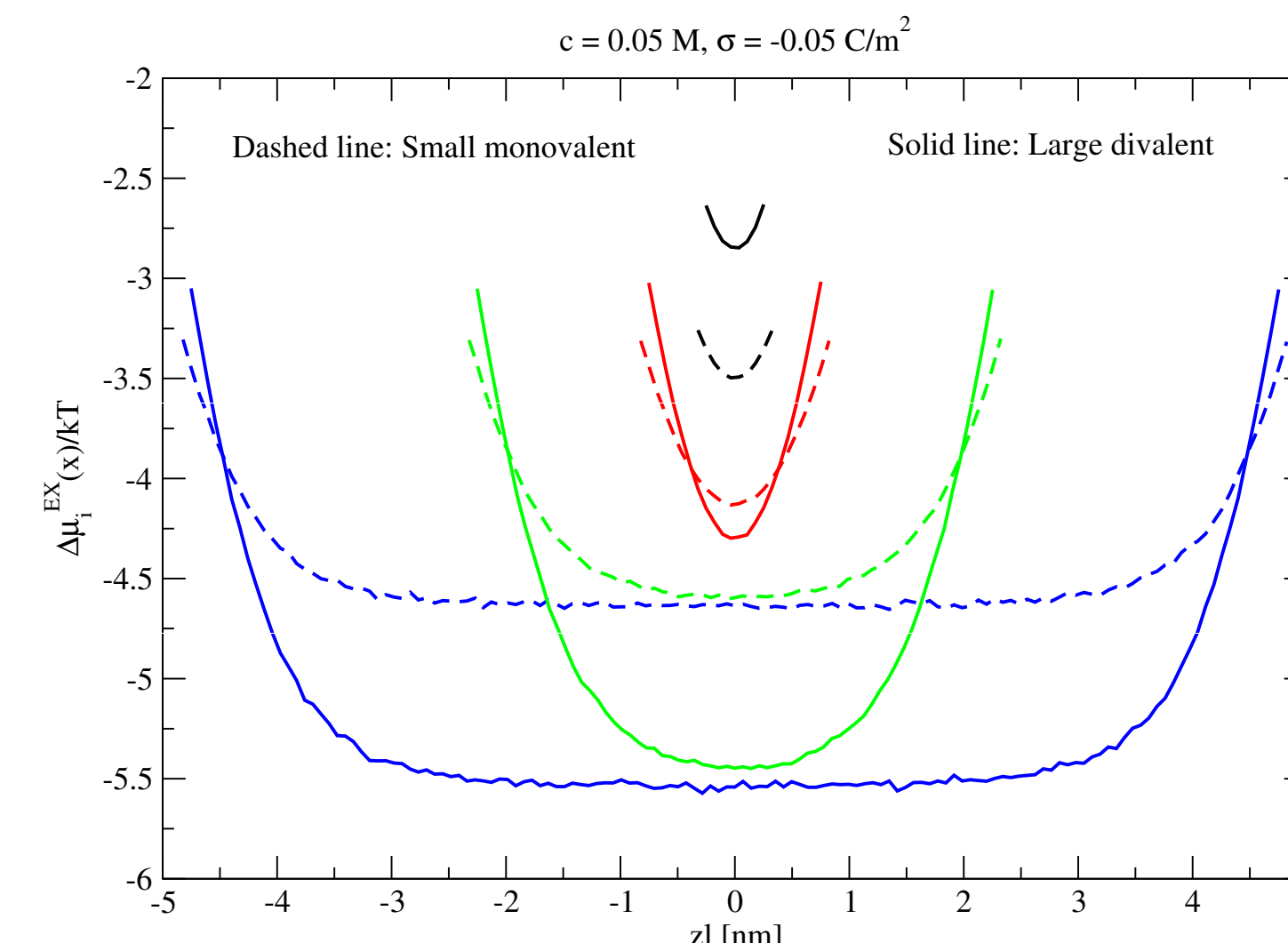
ENERGETICS IN THE SLIT

The competition of the repulsive entropic (hard spheres exclusion) and the attractive electrostatic forces can be demonstrated by the separation of the total chemical potential in profiles in the following way:

$$\mu_i^{TOT} = kT \log c_i(x) + \mu_i^{EX}(x) = kT \log c_i(x) + \mu_i^{HS}(x) + \mu_i^{EL}(x)$$

The total chemical potential was calculated with an iterative method of Malasics et al. [4]. We are interested in the accumulation of the ions at the interface or in the slit from an electrolyte of fixed concentrations. So, we related our terms of the chemical potential to the bulk values:

$$\Delta \mu_i^{HS}(x) = \mu_i^{HS}(x) + \mu_i^{HS,bulk}$$



The excess (EX), the electrostatic (EL) and the hard spheres (HS) terms of the chemical potential referred to the bulk as a function of the width of the slit. The concentration of the cations is 0.05M, the surface charge is -0.05Cm⁻².

If a chemical potential term is more negative for ion A than for ion B, than this term favours ion A. For example, the EL term favours the divalent ion, while the HS term favours the small ion.

