SUPPLEMENTARY MATERIAL

Electrostatic correlations in electrolytes: Contribution of screening ion interactions to the excess chemical potential

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This file contains

- further details on the comparisons of MCSA and MSA with GCMC simulations
- a table of all MCSA and MSA quantities/equations referenced in the main text
- figures of the screening component of the excess chemical potential for different electrolytes.

Details of comparisons with Grand Canonical Monte Carlo (GCMC) simulations

In the grand canonical ensemble, the chemical potentials of the species μ_i are fixed (in addition to T and V). Each ion species' chemical potential μ_i is the sum of ideal gas ($\ln(\rho_i)$), hard-sphere, and screening components. We determine the latter by subtraction, using the set of $\{\mu_i\}$ and the ideal gas and hard-sphere components computed with the GCMC simulations for a given set of desired ion concentrations $\{\rho_i\}$. These $\{\rho_i\}$ define the ideal gas component.

To find the $\{\mu_i\}$ values that produce the desired $\{\rho_i\}$, we applied the Adaptive GCMC procedure.[1] In this iteration process, the $\{\mu_i\}$ are changed in every iteration according to Eq. (19) of Ref. 1. At the end, each μ_i is determined to within an error of a few percent (with error derived from fluctuations in the iterative results). The number of ions for each species fluctuates in these GCMC simulations due to insertions and deletions of individual ions. The initial guess for the $\{\mu_i\}$ values in the iteration was from Widom test particle simulations in the canonical ensemble.[2]

The hard-sphere component is computed from the acceptance/rejection ratios of attempts to insert *uncharged* hard sphere particles of each species *i* in a Widom-like procedure.[3] Because these uncharged "ions" were never inserted (only attempted), this computes the energy needed to insert an uncharged version of each species. To mimic this in the MSA, where inserting an uncharged particle costs electrostatic energy (unlike the MCSA), we included a trace concentration (sub-nanomolar) of uncharged versions of all species. The sum of their hard-sphere and MSA screening components, then, is equivalent to the GCMC hard-sphere procedure. For comparison with the GCMC, this was the hard-sphere contribution subtracted from the μ_i of the *charged* ions.

In the simulations, extra care was taken at high packing fractions of large and multivalent ions due to difficulties with ion insertions. Above 1 M, we only report results for $\{\rho_i\}$ at which the $\{\mu_i\}$ did not change with 2–4 different simulation box sizes. Error bars are standard deviations of results from these different box sizes. In the figures, their heights are usually within the symbols.

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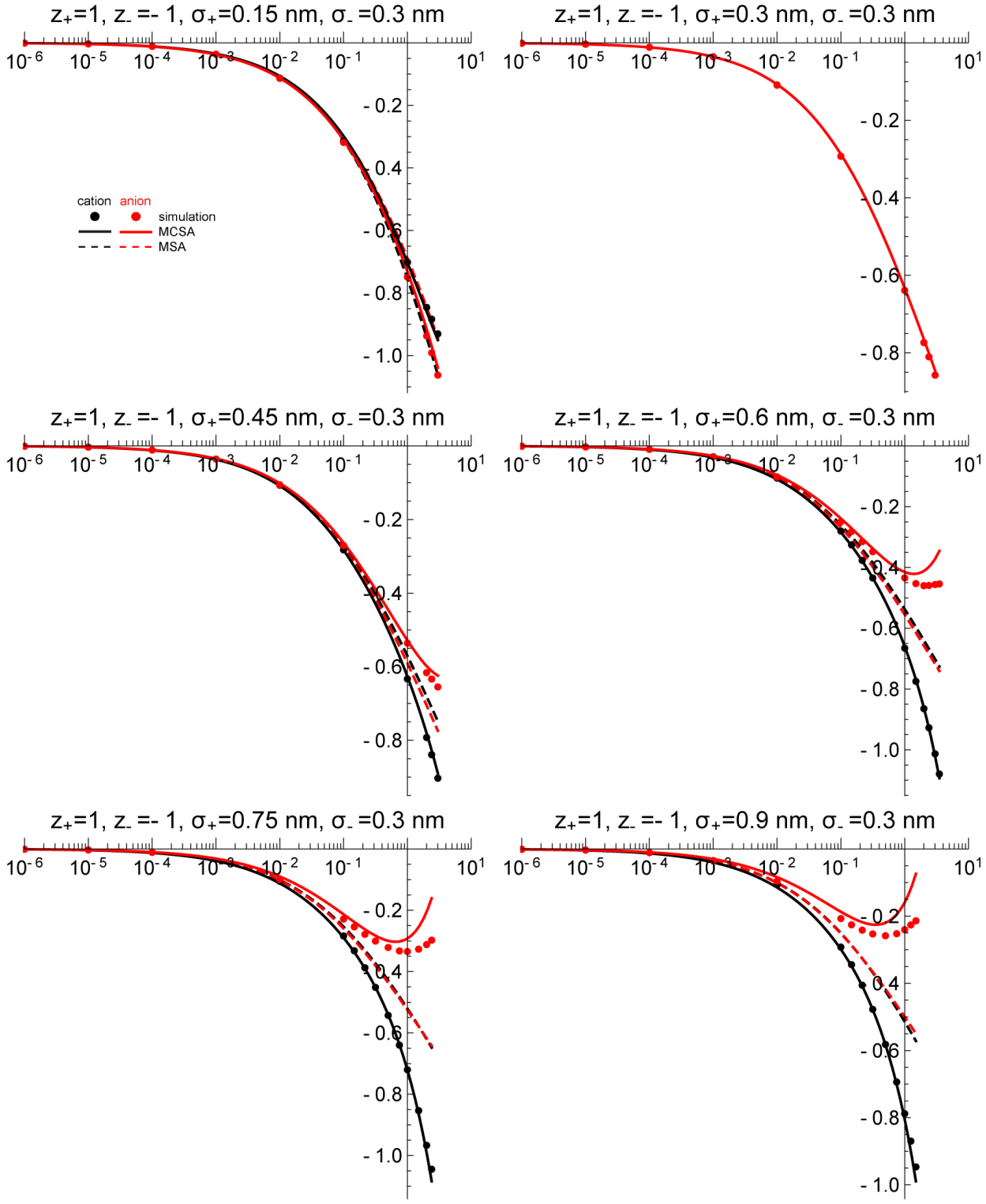
[1] A. Malasics and D. Boda, J. Chem. Phys. **132**, 244103 (2010).
[2] P. Sloth and T. S. Sørensen, Chem. Phys. Lett. **173**, 51 (1990).
[3] D. Boda, J. Giri, D. Henderson, R. S. Eisenberg, and D. Gillespie, J. Chem. Phys. **134**, 055102 (2011).

Table of MSA and MCSA quantities

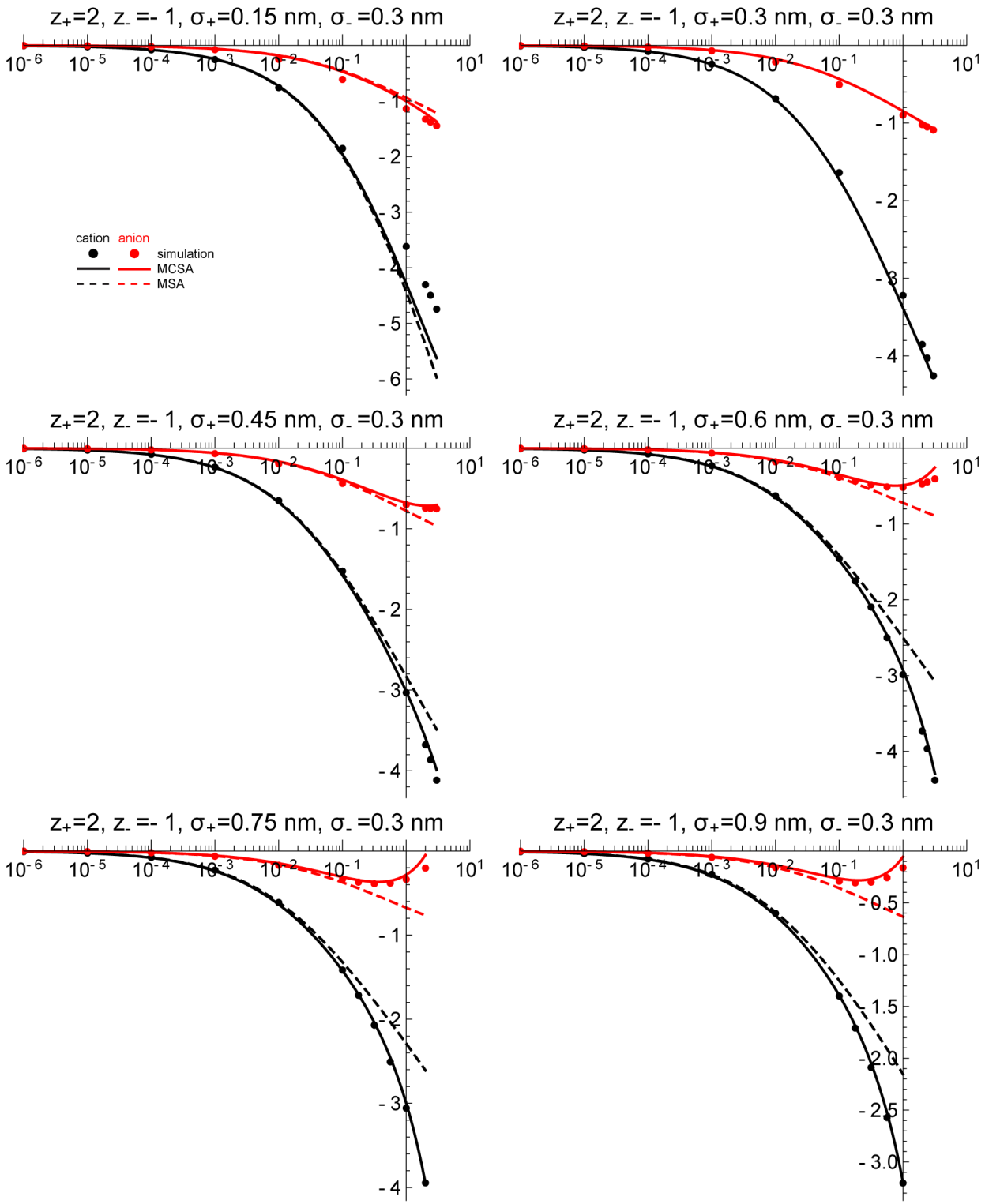
quantity	MSA	MCSA
electrostatic energy density	$\beta E^{\mathrm{MSA}} = -\frac{\lambda_B}{2}\sum_i \frac{z_i^2\rho_i}{R_i + \left(2\Gamma_{\mathrm{MSA}}\right)^{-1}} - \frac{\lambda_B}{2}\eta\sum_i \frac{z_i\rho_i\sigma_i}{\left(R_i + \left(2\Gamma_{\mathrm{MSA}}\right)^{-1}\right)\Gamma}$	$\beta E^{\mathrm{MCSA}} = -\frac{\lambda_B}{2}\sum_i \frac{z_i^2\rho_i}{R_i + \left(2\Gamma_{\mathrm{MCSA}}\right)^{-1}}$
entropy density	$S^{\mathrm{MSA}} = -\frac{k}{3\pi}\Gamma_{\mathrm{MSA}}^3$	$S^{\mathrm{MCSA}} = -\frac{k}{3\pi}\Gamma_{\mathrm{MCSA}}^3$
excess chemical potential	$\beta\mu_i^{\mathrm{MSA}} = -\frac{\lambda_B}{2}\frac{z_i^2}{R_i + \left(2\Gamma_{\mathrm{MSA}}\right)^{-1}} - \lambda_B\eta\sigma_i\left(\frac{2z_i - \eta\sigma_i^2}{1+\Gamma_{\mathrm{MSA}}\sigma_i} + \frac{\eta\sigma_i^2}{3}\right)$	$\beta\mu_i^{\mathrm{MCSA}} = -\frac{\lambda_B}{2}\frac{z_i^2}{R_i + \left(2\Gamma_{\mathrm{MCSA}}\right)^{-1}} - \frac{2\pi}{3}\lambda_B z_i\sum_j z_j\rho_j\left[R_j + \left(2\Gamma_{\mathrm{MCSA}}\right)^{-1}\right]^2$
screening length parameter	$\Gamma_{\mathrm{MSA}}^2 = \pi\lambda_B\sum_i \rho_i\left(\frac{z_i - \eta\sigma_i^2}{1+\Gamma_{\mathrm{MSA}}\sigma_i}\right)^2$	$\Gamma_{\mathrm{MCSA}}^2 = \pi\lambda_B\sum_i \frac{z_i^2\rho_i}{\left(1+\Gamma_{\mathrm{MCSA}}\sigma_i\right)^2}$
pressure	$P^{\mathrm{MSA}} = -\frac{\Gamma_{\mathrm{MSA}}^3}{3\pi} - \frac{2\lambda_B\eta^2}{\pi}$	$P^{\mathrm{MCSA}} = -\frac{\Gamma_{\mathrm{MCSA}}^3}{3\pi}$
Gibbs free energy density	$G^{\mathrm{MSA}} = \sum_i \mu_i^{\mathrm{MSA}}\rho_i$	$G^{\mathrm{MCSA}} = \sum_i \mu_i^{\mathrm{MCSA}}\rho_i$
η	$\eta = \frac{\frac{\pi}{2}\sum_i \frac{z_i\rho_i\sigma_i}{1+\Gamma_{\mathrm{MSA}}\sigma_i}}{\frac{\pi}{2}\sum_i \frac{\rho_i\sigma_i^3}{1+\Gamma_{\mathrm{MSA}}\sigma_i} + 1 - \frac{\pi}{6}\sum_i \rho_i\sigma_i^3}$	no MCSA equivalent

Table S1. List of formulas for quantities in both the MSA and MCSA. Only the screening component (if applicable) is listed. All variables and symbols are as defined in the main text.

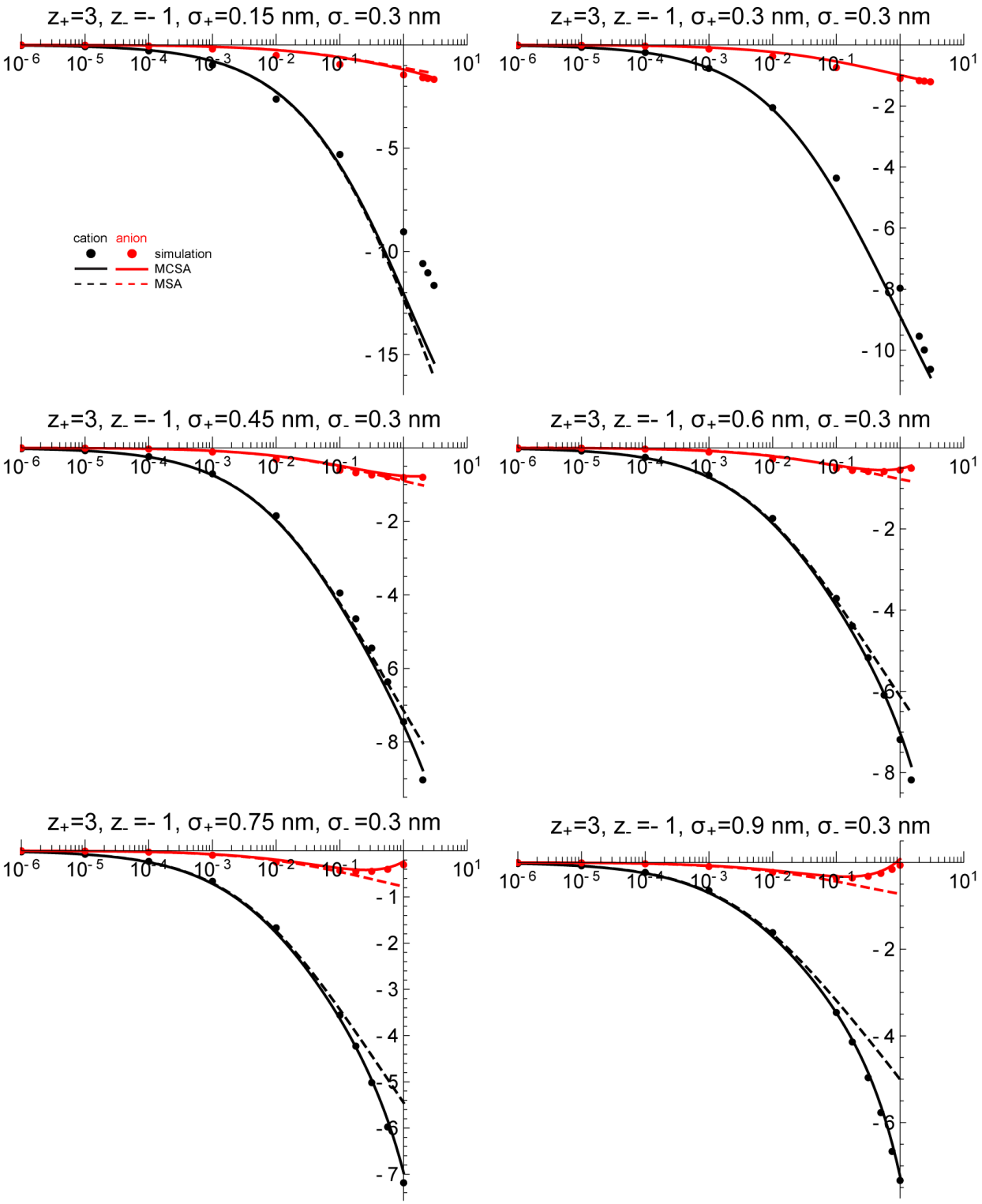
Further comparisons of MCSA and MSA with GCMC simulations



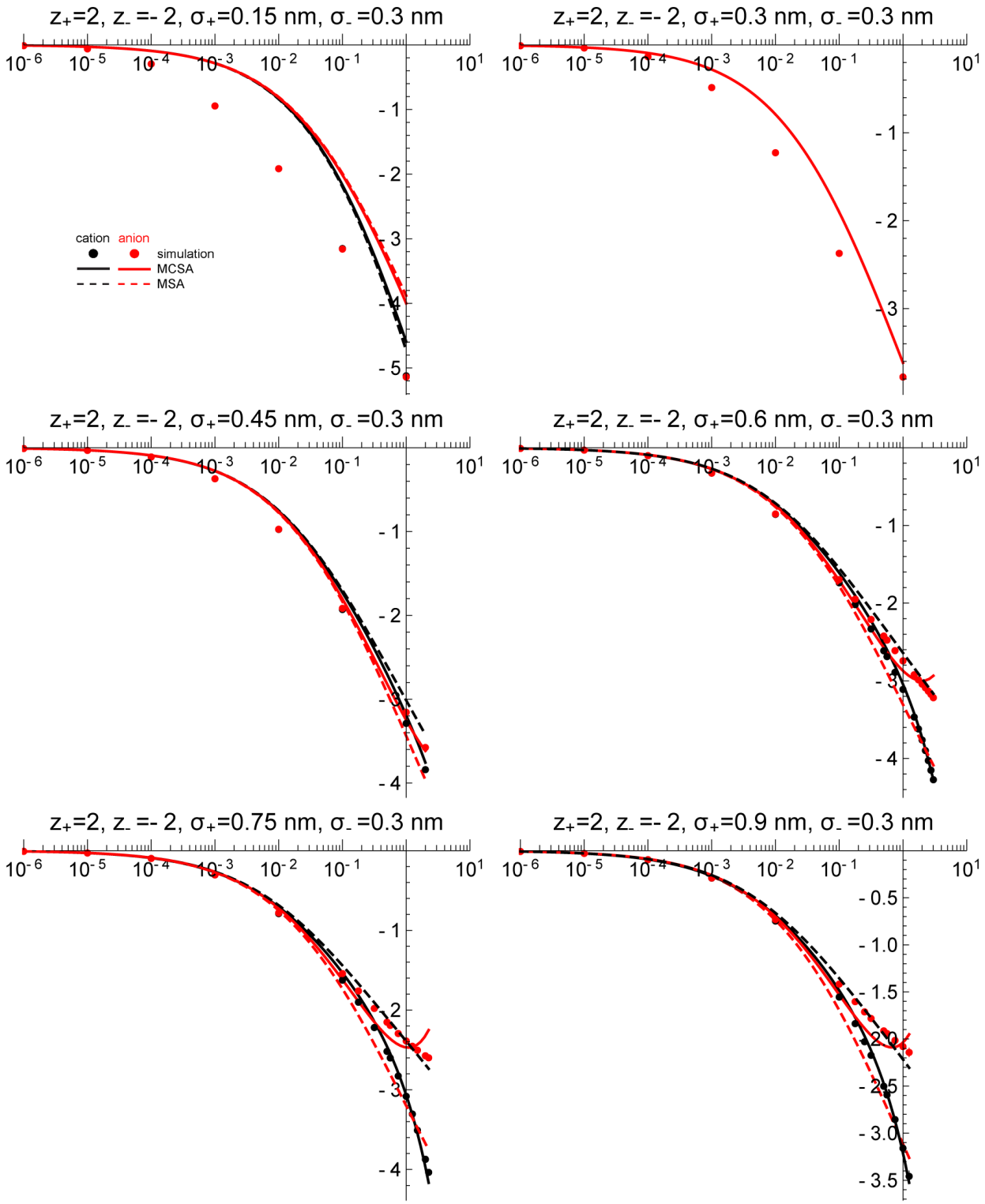
1:1 electrolyte. The screening component of the excess chemical potential in kT (y-axis) as a function of cation concentration in Molar (x-axis) for the different ion diameters (σ_+ and σ_-) with $\varepsilon = 78.45$ and $T = 298.15$ K. MC (symbols), MSA (dashed lines), and MCSA (solid lines) for cations (black) and anions (red). Ion diameters and valences are listed at the top. Each panel has a different sized cation while other ion parameters remain constant.



2:1 electrolyte. The screening component of the excess chemical potential in kT (y-axis) as a function of cation concentration in Molar (x-axis) for the different ion diameters (σ_+ and σ_-) with $\varepsilon = 78.45$ and $T = 298.15$ K. MC (symbols), MSA (dashed lines), and MCSA (solid lines) for cations (black) and anions (red). Ion diameters and valences are listed at the top. Each panel has a different sized cation while other ion parameters remain constant.



3:1 electrolyte. The screening component of the excess chemical potential in kT (y-axis) as a function of cation concentration in Molar (x-axis) for the different ion diameters (σ_+ and σ_-) with $\varepsilon = 78.45$ and $T = 298.15$ K. MC (symbols), MSA (dashed lines), and MCSA (solid lines) for cations (black) and anions (red). Ion diameters and valences are listed at the top. Each panel has a different sized cation while other ion parameters remain constant.



2:2 electrolyte. The screening component of the excess chemical potential in kT (y-axis) as a function of cation concentration in Molar (x-axis) for the different ion diameters (σ_+ and σ_-) with $\varepsilon = 78.45$ and $T = 298.15$ K. MC (symbols), MSA (dashed lines), and MCSA (solid lines) for cations (black) and anions (red). Ion diameters and valences are listed at the top. Each panel has a different sized cation while other ion parameters remain constant.