Brownian dynamics simulations for charged fluids using the Wolf potential

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Abstract

The Wolf method, a computational approach for charged-stabilized fluids, is faster than the standard Ewald summation technique. Recent Monte Carlo simulations showed that the Wolf potential for strong electrolytes satisfies Stillinger-Lovett sum rules, which are a consequence of perfect screening, local electroneutrality, and electrostatic screening within the Debye-Hückel regime. This study adapts the Wolf potential to Brownian dynamics simulations to investigate the structural and dynamic properties of charged fluids. The Ornstein-Zernike equation is solved using the Wolf potential and the HNC closure relation. This approach enables the study of transport phenomena in low Reynolds and Peclet regimes.

Ermak-McCammon algorithm [1]

$$r_i(t + \Delta t) = r_i(t) + \beta \sum_j D^0 F^0_{ij} \Delta t + \mathcal{R}_i(\Delta t) ,$$

whit

$$\langle \mathcal{R}_i \rangle = 0, \quad \left\langle \mathcal{R}_i(t) \mathcal{R}_j(t') \right\rangle = 2\delta_{ij} D_0 \delta(t - t') \Delta t .$$

Wolf potential and HNC approximation

• **Model (Wolf potential).**

In our model, we have used the Wolf potential [6] plus pairwise repulsive soft-core interactions,

$$\frac{\beta \mathcal{U}_{WF}}{K} = \frac{B_{ij}}{r^9} + \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i}^N V_{WF}(r_{ij}) - \left(\frac{\text{erfc}(\alpha r_c)}{2r_c} + \frac{\alpha}{\pi^{1/2}} \right) \sum_{i=1}^N z_i^2 ,$$

with

$$V_{WF}(r_{ij}) = \begin{cases} z_i z_j \left(\frac{\text{erfc}(\alpha r_{ij})}{2r_{ij}} - \frac{\text{erfc}(\alpha r_c)}{r_c} \right) , & r_{ij} \leq r_c \\ 0 , & r_{ij} > r_c \end{cases} ,$$

here α is the Wolf screening parameter [6], which is taken as $\alpha = 4/L$, L is the simulation box, r_c is the cut-off radius, z_i is the valence. B_{ij} is an adjustable parameter [5].

• **HNC Approximation.**

The hyper-netted chain (HNC) approximation is a closure for the Ornstein-Zernike (OZ) equation. For multi-component mixtures, the OZ equation reads

$$h_{ij}(r) = c_{ij} + \sum_k \rho_k \int h_{ik}(|\mathbf{r} - \mathbf{r}'|) c_{kj}(\mathbf{r}') d\mathbf{r}'$$

where $h(r)$ and $c(r)$ are the total and direct correlation functions, respectively.
A general closure relation between $h(r)$ and $c(r)$ for the OZ equation is

$$\ln\left[h_{ij}(r) + 1 \right] = -\beta u_{ij}(r) + h_{ij}(r) - c_{ij}(r) + \mathcal{B}_{ij}(r)$$

$\mathcal{B}_{ij}(r)$ is in literature known as the "bridge function" and cannot be written in closed form. Within the HNC approximation, the bridge function is taken as zero.

Static structural (electrolytes)

One of the goals of this contribution is to understand the local structure and the diffusivity properties of low-valence electrolytes [2]. Through Brownian dynamic (BD) and Monte Carlo (MC) simulations, we have computed the ion-ion pair correlation functions for each electrolyte presented [2, 5].
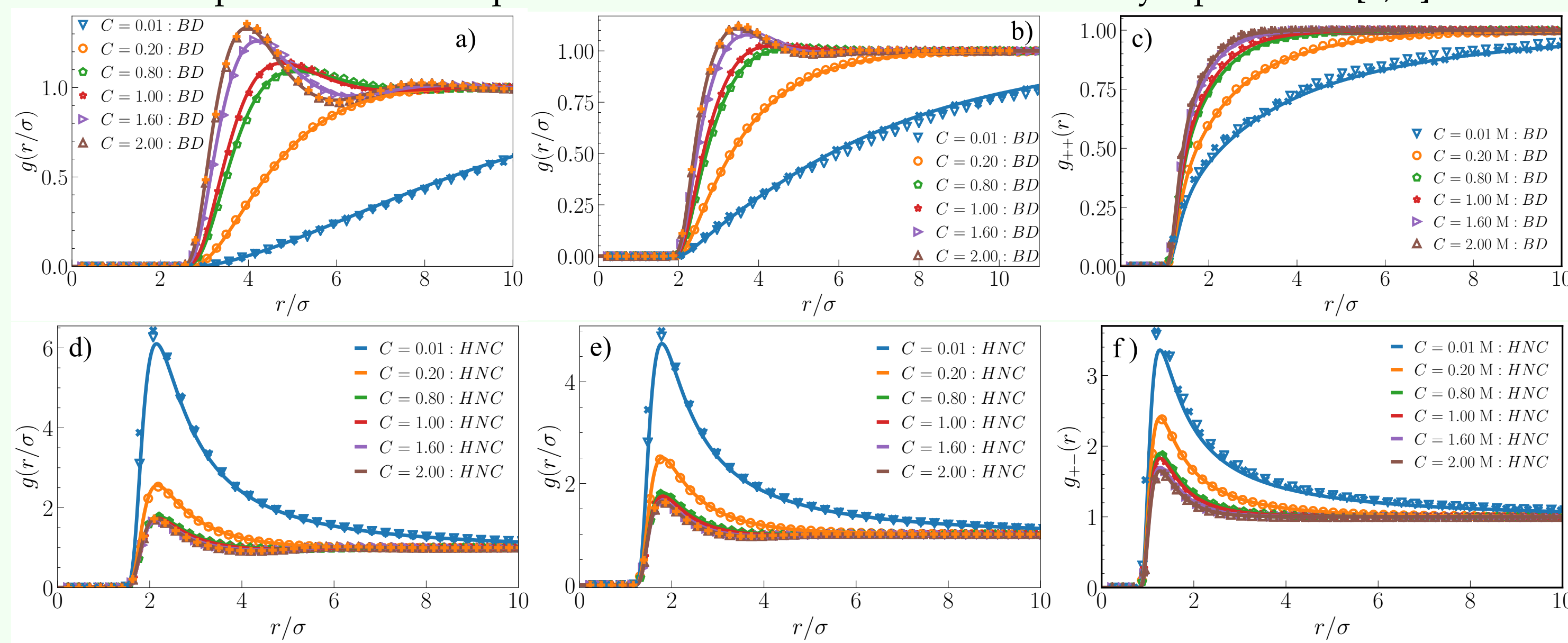
The results of the lowest and highest concentrations explicitly compared with the MC data.

Dynamical properties in electrolytes (MSD and $F^{\text{self}}(t)$)

The self-intermediate scattering function, $F^{\text{self}}(t)$, is computed at $\sigma q \equiv q^* = 1$ since that q value is associated with the principal peak of the structure factor (not shown here), both $F^{\text{self}}(t)$ and MSD calculated for concentrations ranging from 0.01 M to 2.00 M
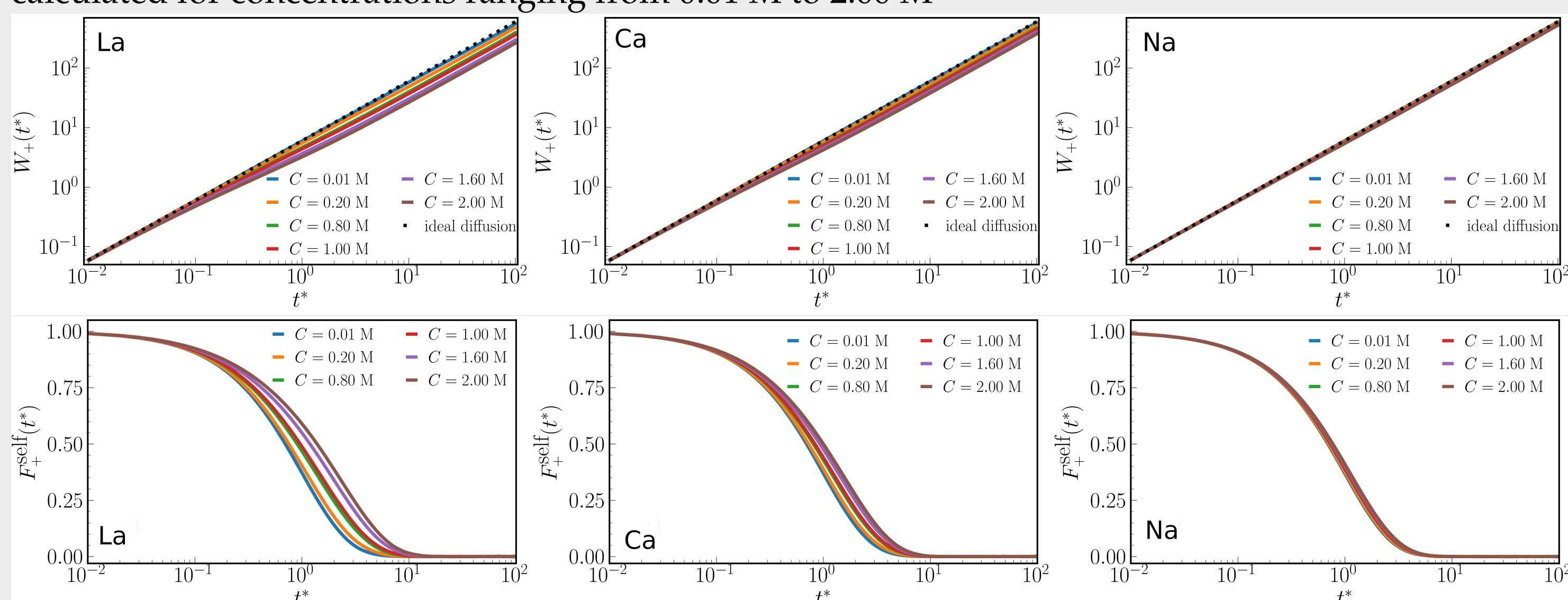
• **Ions**. As the charge asymmetry increases, the diffusion of the cations at intermediate and long times decreases with the concentration, whereas the diffusion of the anions slightly decreases [5].

Electrolytes and colloidal systems
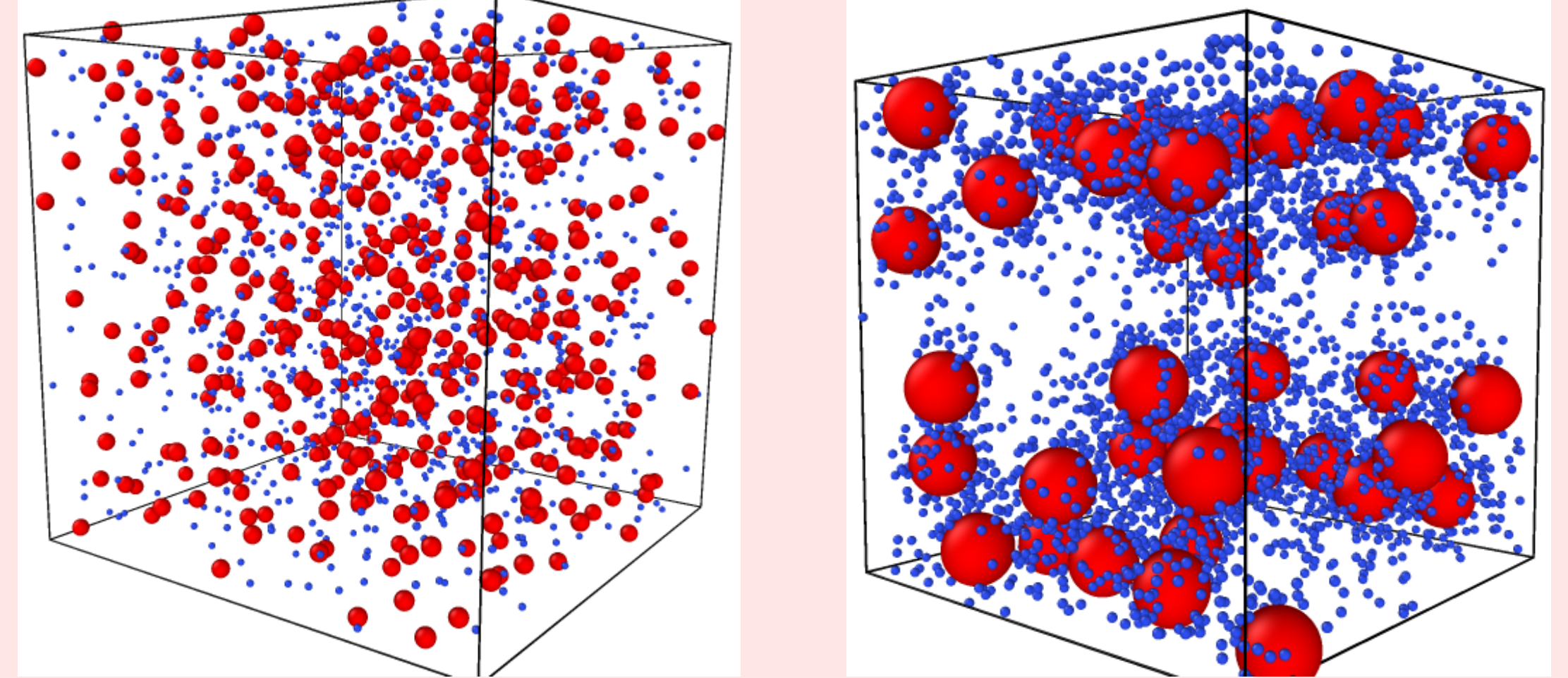
Snapshots of the electrolyte (on the left) and colloidal (on the right) systems shown. For the electrolyte, the ratio of charges is 1:2, and the size ratio is 2.57. In the colloidal case, the charge ratio is 60:1, and the size ratio is 10:1.

Static structural (Weakly charged colloids)

As far as we know, this is the first time that the structural and dynamical properties of weakly charged colloids are calculated using the Wolf method in a BD simulation [3, 4, 5]. Our findings showcase scenarios wherein the macroions bear a positive charge while the counterions are monovalent.
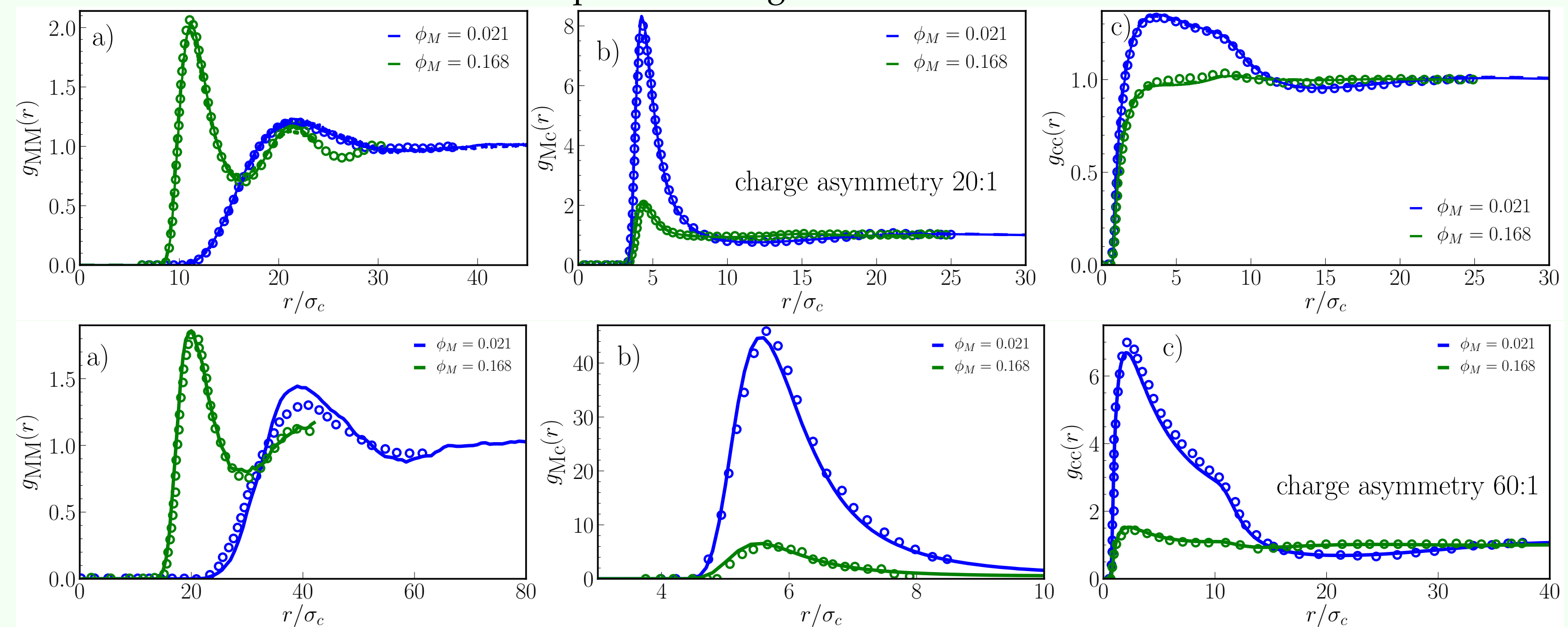
We consider two cases of size asymmetry, namely 15:2 for 20:1 in charge ratio and 10:1 considering the charge ratio of 60:1.

Dynamical properties in weakly charged colloids (MSD and $F^{\text{self}}(t)$)

In all cases, we consider a temperature of 298 K ($T^* = 0.5594$). The charge 60:1 and size 10:1 case are essential to assess the accuracy of the Wolf potential in dealing with colloidal dispersions that exhibit stronger electrostatic couplings. Following Linse [3, 4], we consider $N_M = 80$ and 40 macroions when $Z_M = 20$ and 60, respectively.
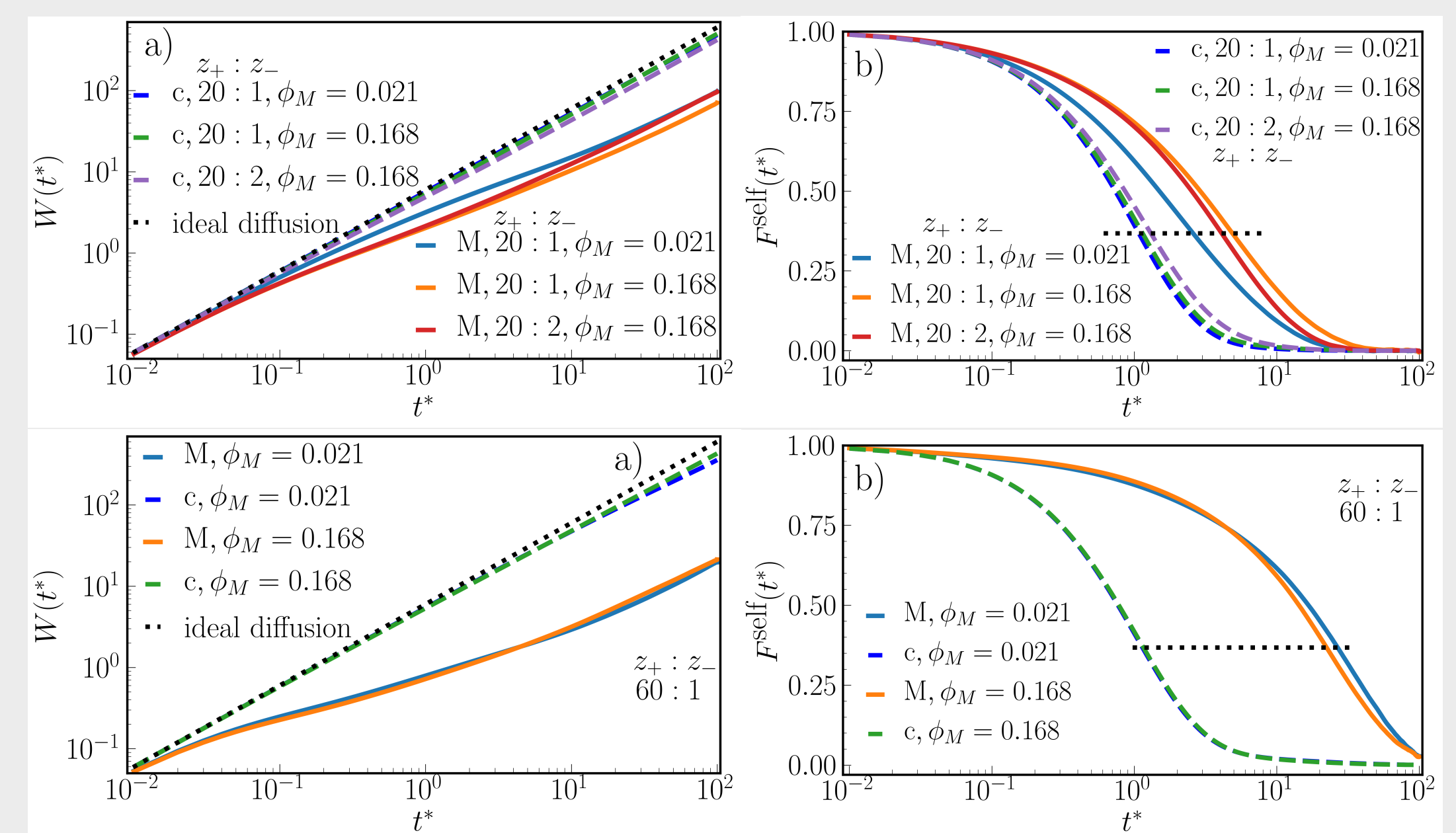
This scenario can be understood as follows: at short times, macroions only experience friction from the solvent, so their dynamics do not depend on any other physical parameter. However, at intermediate times, they have to overcome the barrier created by the counterions that are part of the double layer. According the RDF, particularly from the $g_{Mc}(r)$, the number of counterions bonded to a macroion increases as we increase the valence of the macroion.

References

[1] Donald L. Ermak and J. A. McCammon. *J. Chem. Phys.*, 69(4):1352, 1978.

[2] J. M. Falcón-González et al. *J. Chem. Phys.*, 153(23):234901, 2020.

[3] Vladimir Lobaskin and Per Linse. *J. Chem. Phys.*, 111(9):4300, 1999.

[4] Vladimir Lobaskin, Per Linse, et al. *J. Chem. Phys.*, 109(9):3530, 1998.

[5] Fidencio Pérez-Hernández et al. *J. Mol. Liq.*, 390:123106, 2023.

[6] D. Wolf et al. *J. Chem. Phys.*, 110(17):8254, 1999.