Theoretical description of the electrical double layer for a mixture of n ionic species with arbitrary size and charge asymmetries. I. Spherical geometry

Article *in* The Journal of Chemical Physics · June 2023

DOI: 10.1063/5.0151140

CITATIONS
3

READS
137

3 authors, including:

Jonathan Josué Elisea Espinoza
Universidad Autónoma de San Luis Potosí
3 PUBLICATIONS **12** CITATIONS
SEE PROFILE

Guillermo Ivan Guerrero-Garcia
Universidad Autónoma de San Luis Potosí
51 PUBLICATIONS **787** CITATIONS
SEE PROFILE

Supplementary Material of "Theoretical description of the electrical double layer for a mixture of n ionic species with arbitrary size- and charge-asymmetry: I. Spherical geometry"

Jonathan Josué Elisea-Espinoza,[†] Enrique González-Tovar,[†] and Guillermo Iván Guerrero-García[*,‡]

[†]*Instituto de Física de la Universidad Autónoma de San Luis Potosí, Álvaro Obregón 64, 78000 San Luis Potosí, San Luis Potosí, México.*

[‡]*Facultad de Ciencias de la Universidad Autónoma de San Luis Potosí, Av. Chapultepec 1570, Privadas del Pedregal, 78295 San Luis Potosí, San Luis Potosí, México.*

E-mail: givan@uaslp.mx

I. Interaction potentials between particles used in the molecular dynamics simulations

In order to illustrate the behaviour of the repulsive-core potential and its relationship with the bare Coulomb and DLVO potential, the corresponding colloid-colloid, colloid-ion, and ion-ion interaction potentials are plotted here.

The colloid-colloid interaction potential is plotted in Fig. 1(a) considering either a bare Coulombic interaction or a screened DLVO interaction for the Debye lengths of the salt free (SF) and the added salt (AS) systems, namely, 648 and 469 Å, respectively. Here, it is

assumed that the valence and diameter of both macroions are $Z_M = 10$ and $R_M = 1000$ Å, respectively. The repulsive-core parameter is $\sigma_{rc} = 1$ Å.

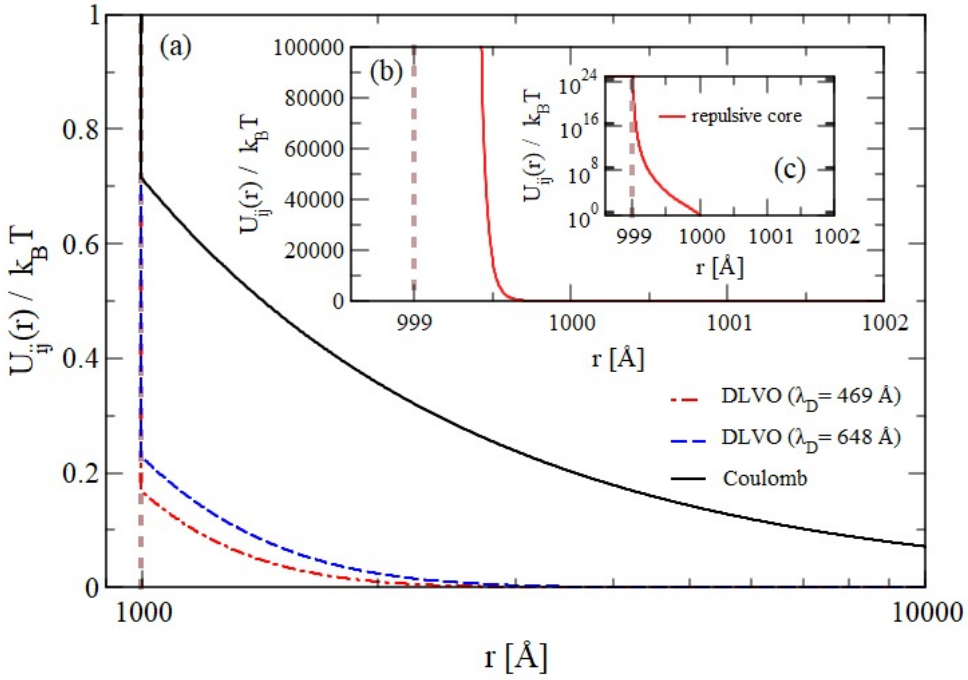

Figure 1: (Color online) Electrostatic and repulsive-core colloid-colloid interaction potentials. The valence and diameter of both macroions are $Z_M = 10$ and $R_M = 1000$ Å, respectively. (a) Bare Coulomb and screened DLVO interactions. For the DLVO potentials, the Debye lengths of the salt free (SF) and added salt (AS) systems are 648 and 469 Å, respectively; (b) repulsive-core interaction potential; (c) asymptotic limit of the repulsive-core interaction potential shown in panel (b) when r approaches to $\Delta_{ij} = 999$ Å.

The colloid-ion and the ion-ion bare Coulomb and repulsive core potentials are plotted in Figs. 2 and 3, respectively. In these cases, the valence and the diameter of the colloid are $Z_M = 10$ and $R_M = 1000$ Å, respectively; whereas the valence and the diameter of the ion are $z_s = 1$ and $R_s = 3$ Å, respectively. In both instances the repulsive-core parameter $\sigma_{rc} = 1$ Å.

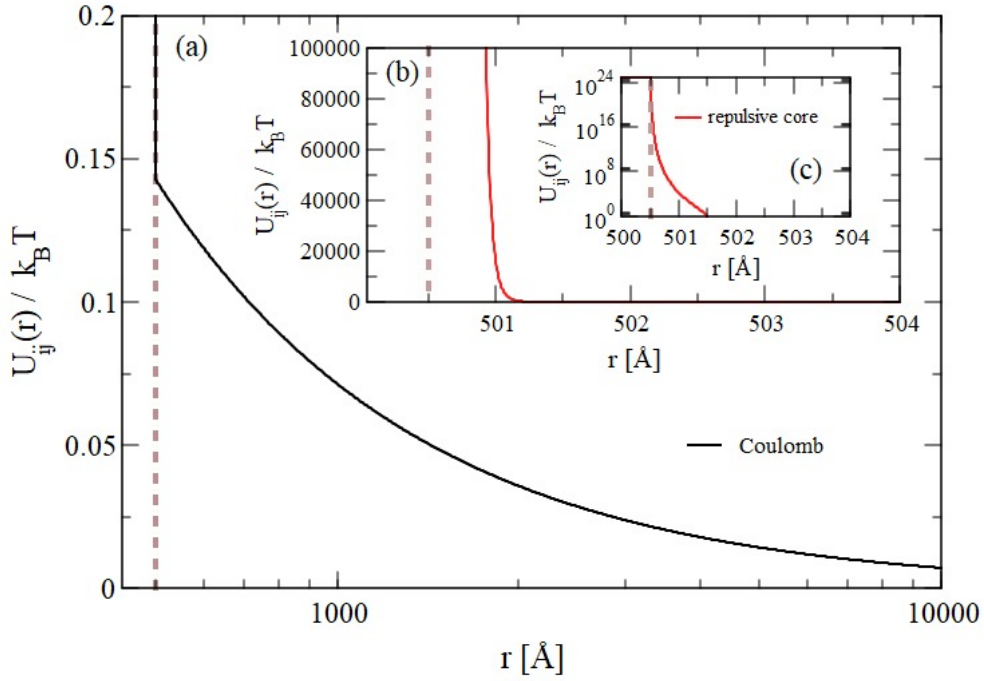

Figure 2: (Color online) Electrostatic and repulsive-core colloid-ion interaction potentials. The valence and the diameter of the colloid are $Z_M = 10$ and $R_M = 1000$ Å, respectively. The valence and the diameter of the ion are $z_s = 1$ and $R_s = 3$ Å, respectively. In both instances, the repulsive-core parameter is $\sigma_{rc} = 1$ Å. (a) Bare Coulombic interaction potential, (b) repulsive-core interaction potential, (c) asymptotic limit of the repulsive-core interaction potential shown in panel (b) when r approaches to $\Delta_{ij} = 500.5$ Å.

II. Validation of the theoretical approach with previous HNC/MSA studies

In order to corroborate that the theory presented in this paper was consistently implemented, we have compared the results provided by our computational implementation by reproducing results from some previous HNC/MSA studies.

Our first test consisted in comparing the theoretical results obtained via the proposed finite element scheme with those published by Guerrero-García, González-Tovar and Olvera

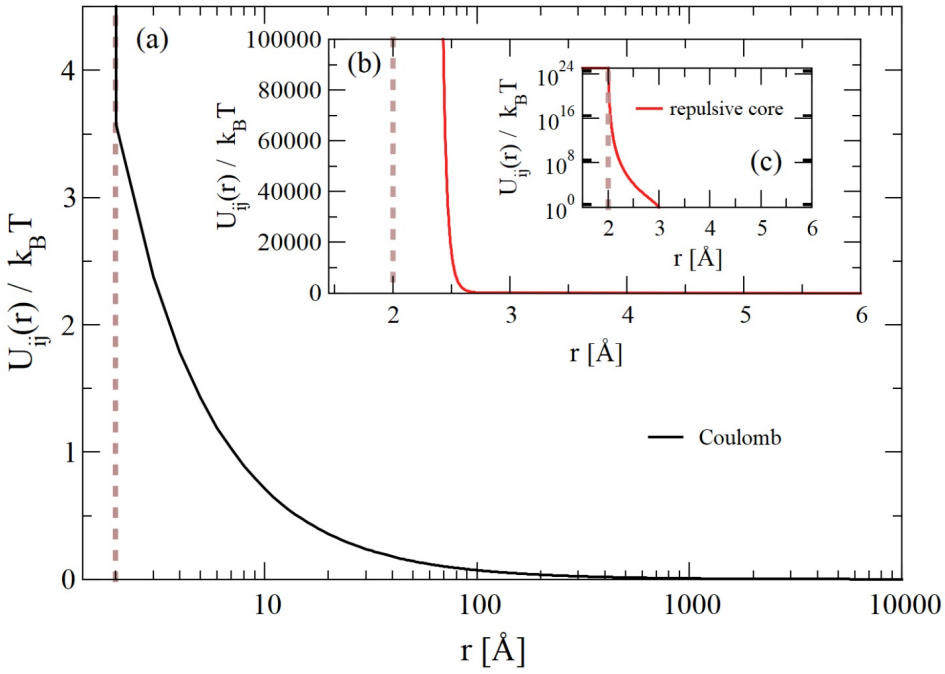

Figure 3: (Color online) Electrostatic and repulsive-core ion-ion interaction potentials. The valence and the diameter of the both ions are $z_s = 1$ and $R_s = 3$ Å, respectively. In both instances, the repulsive-core parameter is $\sigma_{rc} = 1$ Å. (a) Bare Coulombic interaction potential, (b) repulsive-core interaction potential, (c) asymptotic limit of the repulsive-core interaction potential shown in panel (b) when r approaches to $\Delta_{ij} = 2$ Å.

de la Cruz[1] in 2010, where the authors studied the effects of ionic size-asymmetry around a charged nanoparticle M. In that study, a central macroion of radius $\widetilde{r}_M = 15$ Å and valence z_M was considered. This macroion was immersed in a continuous solvent medium with dielectric constant $\varepsilon_r = 78.5$ and temperature $T = 298\,K$, in the presence of a monovalent size-asymmetric electrolyte, as shown in Table 1.

Based on the above data, we build an input file for our algorithm and run it for three z_M valences, specifically, for $z_M = -12$, 0, 12. In Fig. 4, we show a comparison between the profiles of the radial distribution functions $g_{Mj}(r)$ produced by our algorithm and those reported by Guerrero-García *et al.*[1]

Table 1: Parameters of the ionic species considered in the primitive model representation of a macroion at infinite dilution investigated by Guerrero-García et al[1] .

species	z_i	$\widetilde{r}_i$	ρ_i^{bulk}
$+$	1	2.125 Å	1 [M]
$-$	-1	4.25 Å	1 [M]
$\boldsymbol{M}$	$-12, 0, 12$	30.0 Å	0 [M]

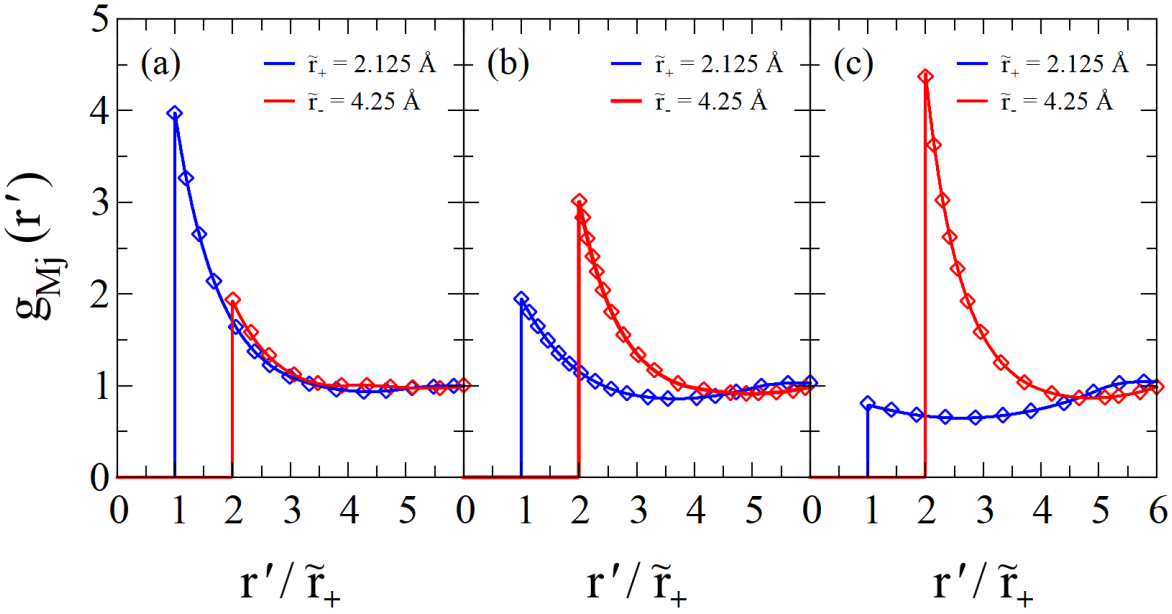

Figure 4: (Color online) Radial distribution functions $g_{Mj}(r')$ as a function of the distance $r' = r - \widetilde{r}_M$, for a central macroion of radius $\widetilde{r} = 15$ Å and valence **(a)** $z_M = -12$, **(b)** $z_M = 0$ and **(c)** $z_M = 12$, immersed in a $1:1$ binary electrolyte at 1 molar concentration. The empty diamonds correspond to the digitized HNC/MSA data reported by Guerrero-García *et al.*[1] while the solid lines correspond to the results obtained using our computational implementation.

The $g_{Mj}(r)$ profiles shown in Fig. 4 show an identical agreement between our numerical results and the data published by Guerrero-García[1] using the HNC/MSA equations.

As a second test, we have chosen an article written by González-Calderón, Chávez-Páez, González-Tovar and Lozada-Cassou[2], where the authors used the HNC/MSA approximation restricted to one species of macroions at finite concentration and two equally-sized small

ionic species around a central macroion. In particular, the system reported by González-Calderón et al. considers a central spherical macroion of diameter $R_M = 42.5$ Å and valence z_M, immersed in a ternary electrolyte composed of positive ions (+), negative ions (−) and macroions (M), dispersed in a continuous solvent with dielectric constant $\varepsilon_r = 78.5$ and temperature $T = 298\ K$. The macroions M were considered as positive spherical particles with the same characteristics as those of the central macroion M, while the + and − ions were considered as spherical particles of diameter $R = R_+ = R_- = 4.25$ Å. A summary of the characteristics of the ionic species considered in this model is presented below, where the colloidal volume fraction ϕ is defined as $\phi = \frac{\pi}{6}\,\rho_M^{bulk}\,R_M$, with ρ_M^{bulk} being the concentration of particles of species M.

Table 2: Characteristics of the ionic species considered in the primitive model studied by González-Calderón and others[2] for $\phi = 0.24$.

	$\boldsymbol{\sigma_0 = 0.01\ C/m^2}$			$\boldsymbol{\sigma_0 = 0.05\ C/m^2}$		
species	z_i	R_i	ρ_i^{bulk}	z_i	R_i	ρ_i^{bulk}
+	1	4.25 Å	0.1 [M]	1	4.25 Å	0.1 [M]
−	−1	4.25 Å	0.13512 [M]	−1	4.25 Å	0.27558 [M]
$\boldsymbol{M}$	3.54175	42.5 Å	0.00992 [M]	17.70873	42.5 Å	0.00992 [M]

Based on the above data, we have calculated the radial distribution functions $g_{Mj}(r)$ for both σ_0 values. Afterwards, we have computed the integrated charge[2], $Q(r)$, normalized regarding the bare charge, Q_0, on the surface of the central macroion M. The profiles $Q(r)/Q_0$ obtained using our theoretical approach for n species with arbitrary size- and valence-asymmetry are shown as solid lines, whereas those reported by González-Calderón *et al.*[2] are plotted as empty diamonds in Fig. 5. An almost identically match, for the two surface charge densities σ_0 considered here, it is observed at the level of the normalized integrated charge.

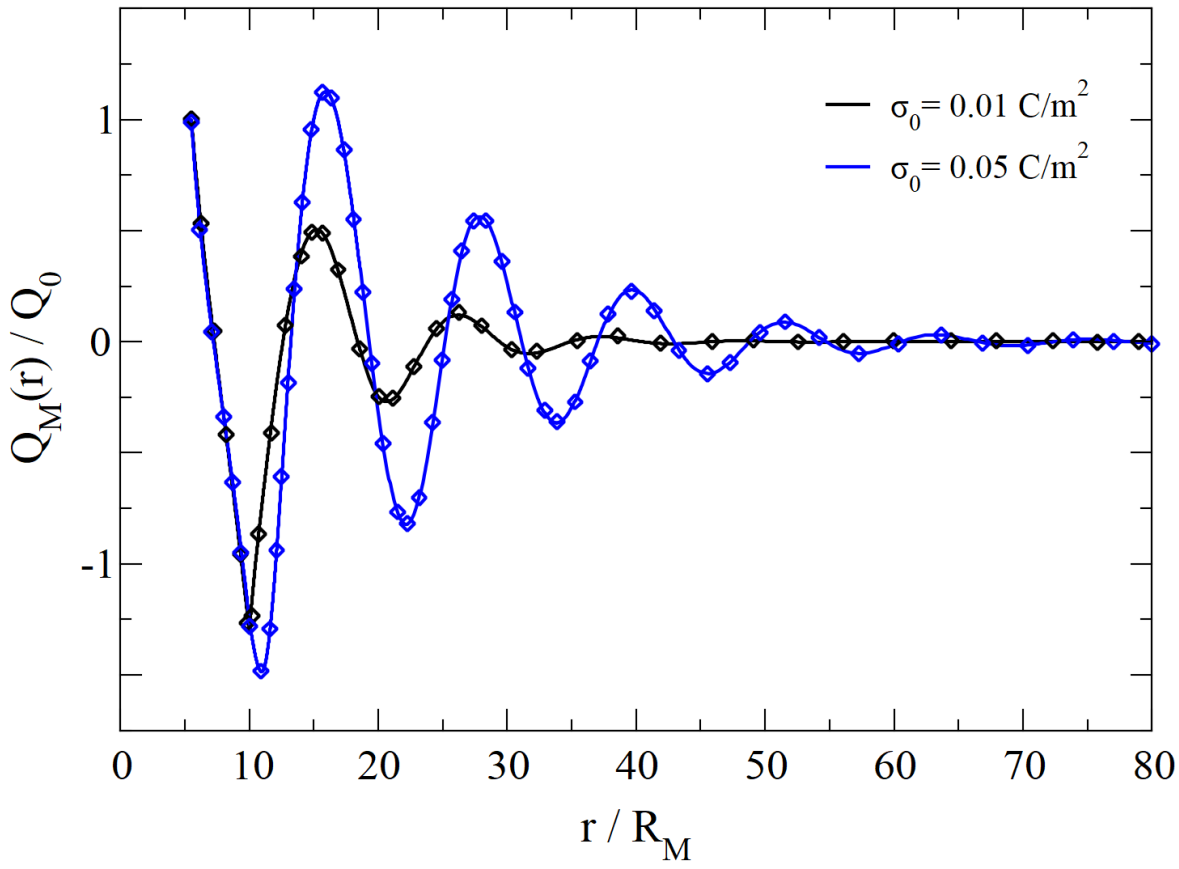

Figure 5: (Color online) Profiles of the integrated charge $Q(r)$ normalized regarding the charge Q_0 on the surface of the central macroion M. The empty diamonds correspond to the digitized HNC/MSA data reported by González-Calderón *et al.*,[2] while the solid lines correspond to the results obtained using our computational implementation.

References

(1) G. I. Guerrero-García, E. González-Tovar, and M. Olvera de la Cruz, Soft Matter **6**, 2056 (2010).

(2) A. González-Calderón, M. Chávez-Páez, E. González-Tovar, and M. Lozada-Cassou, J. Phys. Chem. B, **122**, 27, 7002–7008 (2018).