# Supplementary Information for

# Incorporating Ion-Specific van der Waals and Soft Repulsive Interactions in the Poisson-Boltzmann Theory of Electrical Double Layers

Aniruddha Seal,<sup>a,b,‡</sup> Utkarsh Tiwari,<sup>c,b,‡</sup> Ankur Gupta<sup>d</sup> and Ananth Govind Rajan<sup>b\*</sup>

<sup>a</sup> School of Chemical Sciences, National Institute of Science Education and Research Bhubaneswar, Homi Bhabha National Institute, Khurda, Odisha 752050, India

- <sup>b</sup> Department of Chemical Engineering, Indian Institute of Science, Bengaluru, Karnataka 560012, India
- <sup>c</sup> Department of Chemical Engineering, Birla Institute of Technology and Science Pilani, K K Birla Goa Campus, Zuarinagar, Goa 403726, India

<sup>d</sup> Department of Chemical and Biological Engineering, University of Colorado Boulder, Boulder, Colorado 80309, United States

Corresponding Email: ananthgr@iisc.ac.in

‡ Both authors (A.S. and U.T.) contributed equally to this work

## Contents

S1 Lennard-Jones parameters of $SO_4^{2-}$	2
S2 Derivation of the entropy expression	<b>2</b>
S3 Conversion of the 12-6 LJ potential to a 10-4 LJ potential	3
S4 Derivation of dimensionless parameters to quantify the effect of ion-ion and wall-ion interactions on the EDL	4
S5 Double layer characteristics with hydrated radii	4
S6 Comparison with molecular dynamics simulation results	7
S7 Ion radii from Marcus and silver LJ parameters from the interface force field	8

# S1. Lennard-Jones parameters of $SO_4^{2-}$

The inter-ionic Lennard-Jones (LJ) parameters for the poly-atomic species were obtained via two different approaches – best-fit and physics-based – using the LJ parameters of the constituent atoms. These two sets of LJ parameters of  $SO_4^{2-}$  are shown in Table S1.

Table S1: LJ interac	ction parameters of $\mathrm{SO_4}^{2-}$	$^{-}$ obtained using $^{1}$	best-fit and physic	cs-based approaches

Fitting approach	LJ parameter $\sigma$ (in nm)	LJ parameter $\epsilon$ (in kJ/mol)	
Physics-based	0.51775	2.7963	
Least-square fitting	0.50862	2.8947	

#### S2. Derivation of the entropy expression

The configurational entropy S is derived using a lattice gas model, by employing the Boltzmann entropy formula:

$$S = k_B \ln \omega \tag{S1}$$

where  $k_B$  is the Boltzmann constant and  $\omega$ , the number of ways of arranging  $N_+$  cations with diameter  $a_+$  and  $N_-$  anions with diameter  $a_-$  in a space of volume V, with  $a_- > a_+$ . It can be calculated as follows:

$$\omega = {}^{V/a_{-}^{3}} C_{N_{-}} {}^{(V-N_{-}a_{-}^{3})/a_{+}^{3}} C_{N_{+}}$$
(S2)

where  ${}^{m}C_{n}$  denotes the number of ways of choosing n cells out of a total of m cells in the lattice.

Substituting the expression for  $\omega$  in Equation S1, using Stirling approximation for factorials  $(\ln n! \approx n \ln n - n)$ , for a large number of ions in the solution

$$\frac{S}{k_B} = \frac{V}{a_-^3} \ln\left(\frac{V}{a_-^3}\right) + \frac{V - N_- a_-^3}{a_+^3} \ln\left(\frac{V - N_- a_-^3}{a_+^3}\right) - \left(\frac{V}{a_-^3} - N_-\right) \ln\left(\frac{V}{a_-^3} - N_-\right) - \left(\frac{V - N_- a_-^3}{a_+^3} - N_+\right) \ln\left(\frac{V - N_- a_-^3}{a_+^3} - N_+\right) - N_+ \ln N_+ - N_- \ln N_-$$
(S3)

After some re-arrangements of the entropy expression, we get:

$$\frac{S}{k_B} = \frac{V}{a_-^3} \ln\left(\frac{V}{a_-^3} \times \frac{a_-^3}{V - N_- a_-^3}\right) + \frac{V - N_- a_-^3}{a_+^3} \ln\left(\frac{V - N_- a_-^3}{a_+^3} \times \frac{a_-^3}{V - N_+ a_+^3 - N_- a_-^3}\right) + N_- \ln\left(\frac{V}{a_-^3} - N_-\right) + N_+ \ln\left(\frac{V - N_- a_-^3 - N_+ a_+^3}{a_+^3}\right) - N_+ \ln N_+ - N_- \ln N_-$$
(S4)

Dividing both sides of Equation S4 by V, and using  $N_+ = c_+V$  and  $N_- = c_-V$ , where  $c_+$  and  $c_-$  are the cation and anion concentrations, respectively, in the electrolyte, we obtain:

$$\frac{S}{Vk_B} = -\frac{1}{a_-^3} \ln\left(1 - c_-a_-^3\right) + \frac{1 - c_-a_-^3}{a_+^3} \ln\left(\frac{1 - c_-a_-^3}{1 - c_+a_+^3 - c_-a_-^3}\right) - c_-\ln\left(\frac{c_-a_-^3}{1 - c_-a_-^3}\right) - c_+\ln\left(\frac{c_+a_+^3}{1 - c_-a_-^3 - c_+a_+^3}\right)$$
(S5)

Adding and subtracting  $c_+ \ln \left(\frac{a_+^3 c_+}{1-a_-^3 c_-}\right)$  from both sides of Equation S5 leads to:

$$\frac{-S}{Vk_B} = -c_{-}\ln c_{-}a_{-}^3 + \left(\frac{1-a_{-}^3c_{-}}{a_{-}^3}\right)\ln\left(1-a_{-}^3c_{-}\right) + c_{+}\ln\left(\frac{a_{+}^3c_{+}}{1-a_{-}^3c_{-}}\right) + c_{+}\ln\left(\frac{1-a_{-}^3c_{-}}{a_{+}^3c_{+}} \times \frac{a_{+}^3c_{+}}{1-c_{-}a_{-}^3-c_{+}a_{+}^3}\right) + \left(\frac{1-a_{-}^3c_{-}}{a_{-}^3}\right)\ln\left(\frac{1-c_{-}a_{-}^3-c_{+}a_{+}^3}{1-c_{-}a_{-}^3}\right)$$
(S6)

After simplification, we obtain the entropy equation used in the main text (Equation 5):

$$-\frac{S}{Vk_B} = c_{-} \ln\left(a_{-}^3 c_{-}\right) + \frac{1 - a_{-}^3 c_{-}}{a_{-}^3} \ln\left(1 - a_{-}^3 c_{-}\right) + c_{+} \ln\left(\frac{a_{+}^3 c_{+}}{1 - a_{-}^3 c_{-}}\right) + \frac{1 - a_{-}^3 c_{-} - a_{+}^3 c_{+}}{a_{+}^3} \ln\left(\frac{1 - a_{-}^3 c_{-} - a_{+}^3 c_{+}}{1 - a_{-}^3 c_{-}}\right)$$
(S7)

#### S3. Conversion of the 12-6 LJ potential to a 10-4 LJ potential

We work out the integration of the pairwise 12-6 LJ potential leading to the 10-4 LJ potential used in Sections 2.4 and 2.5 in the main text for incorporating ion-ion/wall-ion LJ interactions in our PB-LJ framework. The LJ interaction between a wall (or an infinitesimally thin section of the electrolyte) and ions separated by a distance x (Figure S1) is integrated over the entire wall (or the sheet of the electrolyte) giving rise to a 10-4 potential (Eq. S8).



Figure S1: A. Side view of an ion interacting with a wall, separated by distance x and B. front view of the wall showing an infinitesimal ring of thickness dr.

The total LJ interaction energy is given as

$$U = \int_0^\infty -4\epsilon \left( \frac{\sigma^6}{\left(\sqrt{x^2 + r^2}\right)^6} - \frac{\sigma^{12}}{\left(\sqrt{x^2 + r^2}\right)^{12}} \right) 2\pi \rho_w r dr$$
(S8)

where  $\rho_w$  is the density of the atoms in the wall. The expression can be simplified to get

$$U = -8\pi\epsilon\rho_w \left(\sigma^6 \int_0^\infty \frac{rdr}{(x^2 + r^2)^3} - \sigma^{12} \int_0^\infty \frac{rdr}{(x^2 + r^2)^6}\right)$$
(S9)

Finally, we obtain

$$U = -4\pi\epsilon\rho_w \left(\frac{\sigma^6}{2x^4} - \frac{\sigma^{12}}{5x^{10}}\right) \tag{S10}$$

### S4. Derivation of dimensionless parameters to quantify the effect of ion-ion and wall-ion interactions on the EDL

The ratios of the ion-ion and wall-ion interaction energies contributed by LJ interactions and the electrostatic potential energy of an ion ( $\eta_{\text{ion}}$  and  $\eta_{\text{wall}}$ ) were computed as follows. The ion-ion LJ interaction energy ( $u_{\text{LJ}}^{\text{ion-ion}}$ ) is given by Eq. 23 in the main text. We have approximated the value of this integral by considering the electrolyte concentration scale to be the bulk electrolyte concentration ( $c_0$ ), the length scale to be the Debye length ( $\lambda_D$ ), and the ion-ion interaction scale as its maximum value, attained at a distance of  $\sigma_{ii}$ . Hence the ion-ion LJ interaction energy can be estimated as

$$u_{\rm LJ}^{\rm ion-ion} \sim -4\pi\epsilon_{ii}c_0 \left[\frac{\sigma_{ii}^6}{2\sigma_{ii}^4} - \frac{\sigma_{ii}^{12}}{5\sigma_{ii}^{10}}\right]\lambda_D = -\frac{6\pi\epsilon_{ii}c_0\sigma_{ii}^2\lambda_D}{5} \tag{S11}$$

Following a similar procedure starting from the one-wall contribution in Eq. 30 in the main text, the wall-ion LJ interaction energy  $(u_{\rm LJ}^{\rm wall-ion})$  can be estimated as

$$u_{\rm LJ}^{\rm wall-ion} \sim -4\pi\epsilon_{iw}\rho_w \left[\frac{\sigma_{iw}^6}{2\sigma_{iw}^4} - \frac{\sigma_{iw}^{12}}{5\sigma_{iw}^{10}} + \frac{\sigma_{iw}^6}{2L^4} - \frac{\sigma_{iw}^{12}}{5L^{10}}\right] \approx \frac{6\pi\epsilon_{iw}\rho_w\sigma_{iw}^2}{5}$$
(S12)

The electrostatic interaction energy  $(u_{\text{elec}})$  scale can be simply written as

$$u_{\rm elec} = ze\psi_D \tag{S13}$$

Combining Eqs. S11 and S13,  $\eta_{ion}$  can be written as

$$\eta_{\rm ion} = \frac{u_{\rm LJ}^{\rm ion-ion}}{u_{\rm elec}} = \frac{6\pi\epsilon_{ii}c_0\sigma_{ii}^2\lambda_D}{5ze\psi_D} \sim \frac{\epsilon_{ii}\sigma_{ii}^2c_0\lambda_D}{ze\psi_D} \quad \text{(numerical factors removed)} \tag{S14}$$

Combining Eqs. S12 and S13,  $\eta_{\text{wall}}$  can be written as

$$\eta_{\text{wall}} = \frac{u_{\text{LJ}}^{\text{wall-ion}}}{u_{\text{elec}}} = \frac{6\pi\epsilon_{iw}\sigma_{iw}^2\rho_w}{5ze\psi_D} \sim \frac{\epsilon_{iw}\sigma_{iw}^2\rho_w}{ze\psi_D} \quad \text{(numerical factors removed)} \tag{S15}$$

#### S5. Double layer characteristics with hydrated radii

The double layer characteristics (electric potential and counter/co-ion concentrations) of the case studies investigating the chemical identity of the electrolyte (Figure 5 in the main text), electrolyte concentration (Figure 6 in the main text), and electrode potential (Figure 7 in the main text) are re-computed with the hydrated radii of the electrolyte ion species given in Table 1. Note that there is a limit on the maximum concentration of the electrolyte that can be considered in the PB framework. This is detailed in Table 2 of the main text. As seen in Table 2, when using hydrated ion radii, the maximum allowable ion concentration is lower as compared to when we use bare ion radii, due to the larger ion sizes. For this reason, the plots for MgSO<sub>4</sub> are made using a concentration of 0.5 M in Figure S3D (as opposed to 1 M in Figure 5D of the main text). Similarly, the plots for NaCl are made using a concentration of 2 M in Figure S4.



Figure S2: I. Electric Potential and II, III. normalized cation and anion concentrations showing the effect of the chemical makeup of the electrolyte on the EDL structure: A. 1:1 electrolyte (KCl), B. 2:1 electrolyte (MgCl<sub>2</sub>), C. 1:2 electrolyte (Na<sub>2</sub>SO<sub>4</sub>) and D. 2:2 electrolyte (MgSO<sub>4</sub>) present at a concentration of 1 M (0.5 M for MgSO<sub>4</sub>) between the two graphene electrodes with  $\Psi_D$  set to 5, computed with the hydrated radii of the ionic species given in Table 1 of the main text.



Figure S3: I. Electric Potential and II, III. cation and anion concentration profiles computed at three different electrolyte concentrations with 0.5, 1, and 2 M NaCl between the graphene electrodes with  $\Psi_D$  set to 5. The solid lines represent the results with the wall-ion LJ terms included, and the dotted lines denote the results with the wall-ion LJ terms set to zero in the chemical potential equations, computed with the hydrated radii of the ionic species given in Table 1 of the main text.



Figure S4: I. Electric potential and II, III. normalized cation and anion concentrations computed at different values of boundary potential  $\Psi_D$  showing A. the effect of switching from positive to negative potential:  $\Psi_D = +5$  to  $\Psi_D = -5$  and B. the effect of changing the magnitude of wall potential:  $\Psi_D = 5$  to  $\Psi_D = 0.5$  for 1 M NaCl present as the electrolyte between the two graphene electrodes. The solid lines represent the results with the wall-ion Lennard-Jones terms included, and the dotted lines denote the wall-ion Lennard-Jones terms set to zero in the chemical potential equations, computed with the hydrated radii of the ionic species given in Table 1 of the main text.

#### S6. Comparison with molecular dynamics simulation results

We compare the counter and co-ion concentration profiles obtained using our PB-LJ model with the molecular dynamics (MD) results obtained by Mashayak and Aluru.<sup>1</sup> We model the double layer structure for two NaCl concentrations (0.25 M and 1 M) present between two oppositely charged graphene electrodes with a surface charge density of 0.12 C/m<sup>2</sup> and 0.18 C/m<sup>2</sup> for ion concentrations of 0.25 and 1 M NaCl respectively. The ionic diameters are taken from Marcus<sup>2</sup>, and the LJ interaction parameters for the PB-LJ model are taken from Mashayak and Aluru.<sup>1</sup> The dimensionless inter-electrode distance (L) was set to 6.87 to match the wall separation of 3.804 nm used in that work, and the dimensionless electrode wall potential ( $\Psi$ ) was set to 4.5 and 2.838, respectively, for the 1 M and 0.25 M NaCl cases, to match the surface charge density using the relation  $\frac{\sigma}{\kappa_r \kappa_0} = -d\psi/dx$ . We let go the approximation that  $u_{LJ}^{iw}(L/2) \approx 0$ , since we are dealing with smaller inter-wall spacing here and  $\Delta u_{LJ}^{iw}(x)$  is taken to be  $u_{LJ}^{iw}(x) - u_{LJ}^{iw}(L/2)$ .



Figure S5: Comparison of the PB-LJ model results with MD simulation results in terms of cation and anion concentrations computed for different bulk concentrations of NaCl electrolyte present between two graphene electrodes. (A) PB-LJ results for 0.25 M NaCl, (B) MD results for 0.25 M NaCl, (C) PB-LJ results for 1 M NaCl, and (D) MD results for 1 M NaCl. The MD simulation results, i.e., panels B and D are reproduced with permission from Mashayak and Aluru, J. Chem. Phys. 146, 044108 (2017),<sup>1</sup> Copyright © 2017, AIP Publishing.

From Figure S5, we can see that the peak position of the cation and anion concentrations, as well as the peak height for the cations, matches well with that obtained from MD simulations (better match than the classical density functional theory, i.e., CDFT, predictions). However, the

anion concentration peak heights are much lower than the MD predictions, but they do match with the CDFT predictions. Future work can unravel how the prediction of the anion concentration profiles can be improved.

# S7. Ion radii from Marcus and silver LJ parameters from the interface force field

The parameters used to compute the EDL capacitance in panels B, C, and D in Figure 10 in the main text are given here. In the interface force field (IFF) developed by Heinz et al.,<sup>3</sup> the  $\epsilon$  and  $\sigma$  values for silver are 19.079 kJ/mol and 0.263 nm, respectively. The hydrated diameters of the electrolyte ions extracted from Marcus (twice the value of  $d_{\rm ion-W}$  from Table XIII in ref. 2) are given in Table S2 below. The hydrated ion diameters for Na<sup>+</sup> and Cl<sup>-</sup> are used to generate the plots in Figure S5A,C.

Table S2: D	iameters of	the electroly	vte ions	extracted	from	Marcus. <sup>2</sup>	2
		•	/				

Ion	Hydrated Diameter
	(nm)
Na <sup>+</sup>	0.471
F <sup>-</sup>	0.526
Cl <sup>-</sup>	0.637

## References

- [1] S. Mashayak and N. Aluru, J. Chem. Phys., 2017, 146, 044108.
- [2] Y. Marcus, Chem. Rev., 1988, 88, 1475–1498.
- [3] H. Heinz, R. Vaia, B. Farmer and R. Naik, J. Phys. Chem. C, 2008, 112, 17281–17290.