Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Grand canonical simulations of ions between charged conducting surfaces using exact 3D Ewald summations

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The minimum image (MI) method

Using this rather approximate MI model, we can write the total interaction energy (U_C) of our C system, for a specific ion concentration $\{\mathbf{r}_i\} \equiv \{x_i, y_i, z_i\}$, as:

$$\beta U_C = \frac{l_b}{2} \sum_i \sum_{j \neq i} \frac{\xi_i \xi_j}{\left[\rho_{ij}^2 + (z_i - z_j)^2\right]^{1/2}} + + \beta U_{im}\left(\{\mathbf{r}_i\}\right) + \beta U_{ex} \tag{1}$$

where β is the inverse thermal energy, $\rho_{ij}^2 = (x_i - x_j)^2 + (y_i - y_j)^2$, ξ_i is the valency of ion i, and $\beta U_{im}(\{\mathbf{r}_i\})$ is the reduced total image charge interaction energy, resulting from multiple reflections across the left and right surfaces. U_{ex} is the interaction energy with a mean-field charge distribution from the region outside the central box + its images. This distribution is established from a previous MI simulation, carried out in absence of any long-range correction. The external potential is symmetrized, adjusted so that it is zero at the electrode surfaces (where we know that the locally determined potential should be zero). Details can be found in refs.[1,2]

Defining $\Delta \equiv |z_j - z_i|$ and $\alpha \equiv |z_i + z_j|$, we have:

$$\begin{aligned}
\frac{2\beta U_{im}^{i,j}}{l_B} &= -\sum_{k=1,3,...} \left[\left(\rho^2 + ((k-1)\,h + \alpha)^2\right)^{-1/2} + \left(\rho^2 + ((k+1)\,h - \alpha)^2\right)^{-1/2}\right] + \\
&+ \sum_{m=2,4,...} \left[\left(\rho^2 + (mh - \Delta)^2\right)^{-1/2} + \left(\rho^2 + (mh + \Delta)^2\right)^{-1/2}\right] \qquad (2)
\end{aligned}$$

where we have explicitly noted that the infinite sum has to be truncated in practice. We let n_{max} define the total number of reflections, where $n_{max} = max(k_{max}, m_{max})$. The interactions are thus truncated by n_{max} along the z direction, and by the size of the simulation box (utilizing a minimum image cutoff), along the (x, y) directions.

Calculating the potential profile

We can rewrite equation (2) as:

$$\begin{aligned}
\frac{2\beta U_{im}^{i,j}}{l_B} &= -\left((\rho^2 + \alpha)^2\right)^{-1/2} - \sum_{n=1,2,...} \left[\left(\rho^2 + (2nh + \alpha)^2\right)^{-1/2} + \left(\rho^2 + (2nh - \alpha)^2\right)^{-1/2}\right] + \\
&+ \sum_{n=1,2,...} \left[\left(\rho^2 + (2nh - \Delta)^2\right)^{-1/2} + \left(\rho^2 + (2nh + \Delta)^2\right)^{-1/2}\right]
\end{aligned}$$

Now, for the total potential, there is of course also the direct interaction, $\left((\rho^2 + \alpha)^2\right)^{-1/2}$. If we smear out the charges in a mean-field manner, with an effective surface charge density $\sigma_s(z_j)$ at z_j, then the average potential $\Psi(z_i)$ at z_i,from the charge density at z_j, becomes:

$$\frac{e\Psi(z_i)}{2\pi l_B \sigma_s(z_j)} = -\left[\Delta - \alpha + \sum_{n=1,2,...} 2nh + \Delta + 2nh - \Delta - 2nh - \alpha - 2nh + \alpha\right] = \alpha - \Delta$$

In other words, we can consider (say) the left half cell, and sum up the interaction difference with the charged sheet from z_j, and its nearest image (across the left wall). Combining this with a similar approach for the right half cell, will naturally reduce the statistical noise.

Image Ewald simulations of an RPM 3:1 salt

For completeness, we include results that are analogous to those reported in Figure 2 of the main paper, but with trivalent cations, i.e. a 3:1 salt. The chosen separation, $h = 145$ Å was perhaps somewhat small, but it is still clear that the mid plane value of $\Psi(z) - \Psi_{ref}$ will match $-\Psi_{bias}$ at wide enough separations.

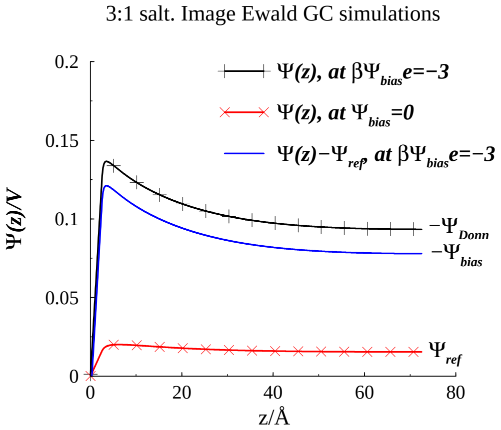

Figure 1: Average potential profiles, as obtained from Image Ewald simulations at $\beta\Psi_{bias}e = -3$, and at $\Psi_{bias} = 0$. The salt chemical potential was $\beta\mu_{salt} = -12$.

Image Ewald simulations of a 1:1 salt, where the cations have a non-central charge

Finally, we give a numerical example, demonstrating that $\Psi_{ref} = 0$, for a charge-symmetric salt. Rather than treating a simple RPM model, we have chosen to study a monovalent salt, where the charge is displaced a distance 2Å from the hard-sphere centre (the anions have central charges). This leads to non-trivial and asymmetric distributions also at neutral surfaces, since the cations can approach their image charge more closely that the anions, at the electrode interfaces. This is highlighted in graph (a) of Figure 3. In graph (b), we show that the average potential profile nevertheless (i.e. despite the ion asymmetry) vanishes when $\Psi_{bias} = 0$, which means that the reference potential also vanishes.

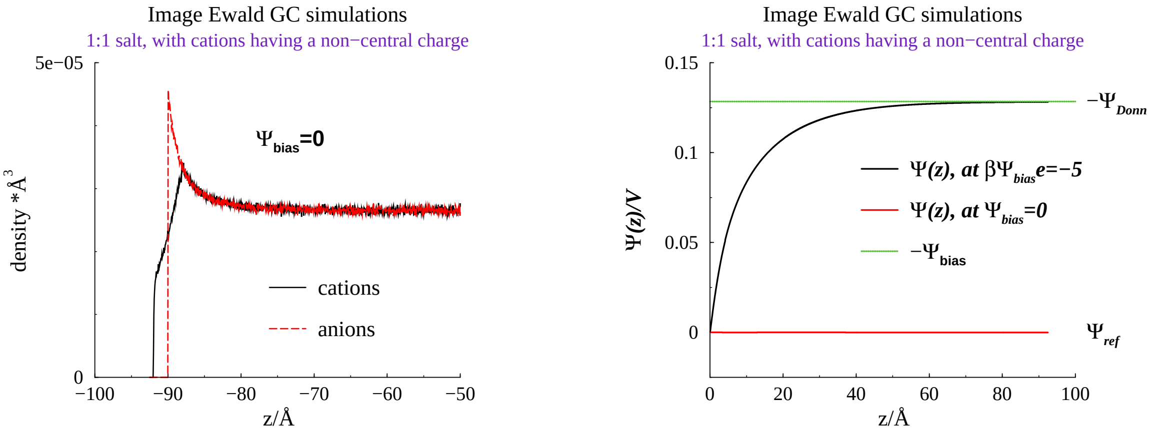

Figure 2: Image Ewald GC simulations of an aqueous 1:1 salt solution, in which the cations have their charged displaced a distance 2 Å from the hard-sphere centre. The salt chemical potential was $\beta\mu_{salt} = -10.7$.
(a) Ion density distributions, at zero applied bias potential.
(b) Average potential profiles. The finite bias potential was set to $\beta\Psi_{bias}e = -5$.

References

(1) Torrie, G. M.; Valleau, J. P. Electrical double layers. I. Monte Carlo study of a uniformly charged surface. *J. Chem. Phys.* **1980**, *73*, 5807–5816.

(2) Jönsson, B.; Wennerström, H.; Halle, B. *J. Phys. Chem.* **1980**, *84*, 2179.