Notes: Surface potential difference and charge delocalization

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February 5, 2024

Consider the electric potential generated by two charge densities $\rho_1^e(z')$ and $\rho_2^e(z')$ in the bulk:

$$\phi(z) = \frac{1}{4\pi\varepsilon_0}\int_{-\infty}^{\infty} d\mathbf{r}'\,\rho^e(z')\frac{1}{|\mathbf{r}-\mathbf{r}'|}. \tag{1}$$

$\rho_1^e(z)$ and $\rho_2^e(z)$ have the same bulk charge number density ρ_{B}, but differ in their spatial distribution of charge. Specifically,

$$\rho_1^e(z) = |e|\cdot\rho_B(z)\star\delta(z), \tag{2}$$
$$\rho_2^e(z) = |e|\cdot\rho_B(z)\star G(\mathbf{r}). \tag{3}$$

$G(\mathbf{r})$ is the standard Gaussian distribution function:

$$G(\mathbf{r}) = \frac{1}{\sigma(\sqrt{2\pi})^3}e^{-\frac{r^2}{2\sigma^2}} \tag{4}$$

where σ is the standard deviation. The electrostatic potential generated by the Gaussian charge distribution can be transformed:

$$\begin{aligned}\phi(z) =& \frac{|e|}{4\pi\varepsilon_0}\int_{-\infty}^{\infty} d\mathbf{r}'\,\rho_B(z')\star G(\mathbf{r})\frac{1}{|\mathbf{r}-\mathbf{r}'|}\\ =& \frac{|e|}{4\pi\varepsilon_0}\int_{-\infty}^{\infty} d\mathbf{r}'\,\rho_B(z')\frac{\mathrm{erf}(\frac{|\mathbf{r}-\mathbf{r}'|}{\sigma\sqrt{2}})}{|\mathbf{r}-\mathbf{r}'|}\end{aligned} \tag{5}$$

The potential difference generated by two charge densities $\rho^e(z)$ with the same charge number density but different spatial distributions is:

$$\begin{aligned}\Delta\phi(z) =& \Phi_2(z)-\Phi_1(z)\\ =& -\frac{|e|}{4\pi\varepsilon_0}\int_{-\infty}^{\infty} d\mathbf{r}'\,\rho_B(z')\frac{\mathrm{erfc}(\frac{|\mathbf{r}-\mathbf{r}'|}{\sigma\sqrt{2}})}{|\mathbf{r}-\mathbf{r}'|}\end{aligned} \tag{6}$$

Then,

$$\Delta\phi(z) = -\frac{|e|}{4\pi\varepsilon_0}\int_{-\infty}^{\infty} dz'\,\rho_B(z')\int_{-\infty}^{\infty} dx'\int_{-\infty}^{\infty} dy'\,\frac{\operatorname{erfc}(\frac{\sqrt{x'^2+y'^2+(z-z')^2}}{\sigma\sqrt{2}})}{\sqrt{x'^2+y'^2+(z-z')^2}} \quad (7)$$

Applying a polar coordinate transformation,

$$\begin{aligned}\Delta\phi(z) &= -\frac{|e|}{4\pi\varepsilon_0}\int_{-\infty}^{\infty} dz'\,\rho_B(z')\int_0^{2\pi} d\varphi\int_0^{\infty} da\,a\cdot\frac{\operatorname{erfc}(\frac{\sqrt{a^2+(z-z')^2}}{\sigma\sqrt{2}})}{\sqrt{a^2+(z-z')^2}}\\ &= -\frac{|e|}{2\varepsilon_0}\int_{-\infty}^{\infty} dz'\,\rho_B(z')\int_0^{\infty} da\,a\cdot\frac{\operatorname{erfc}(\frac{\sqrt{a^2+(z-z')^2}}{\sigma\sqrt{2}})}{\sqrt{a^2+(z-z')^2}} \quad (8)\end{aligned}$$

Let $\tau^2 = a^2 + (z-z')^2$, so that when $a = 0$, $\tau = |z-z'|$,

$$\Delta\phi(z) = -\frac{|e|}{2\varepsilon_0}\int_{-\infty}^{\infty} dz'\,\rho_B(z')\int_{|z-z'|}^{\infty} d\tau\,\operatorname{erfc}\left(\frac{\tau}{\sigma\sqrt{2}}\right) \quad (9)$$

Performing integration by parts on the inner integral,

$$\begin{aligned}\Delta\phi(z) &= -\frac{|e|}{2\varepsilon_0}\int_{-\infty}^{\infty} dz'\,\rho_B(z')\left[\operatorname{erfc}\left(\frac{\tau}{\sigma\sqrt{2}}\right)\tau\Big|_{|z-z'|}^{\infty} - \int_{|z-z'|}^{\infty}\tau\,d\operatorname{erfc}\left(\frac{\tau}{\sigma\sqrt{2}}\right)\right]\\ &= -\frac{|e|}{2\varepsilon_0}\int_{-\infty}^{\infty} dz'\,\rho_B(z')\left[-|z-z'|\operatorname{erfc}\left(\frac{\tau}{\sigma\sqrt{2}}\right) - \int_{|z-z'|}^{\infty}\tau\,d\operatorname{erfc}\left(\frac{\tau}{\sigma\sqrt{2}}\right)\right] \quad (10)\end{aligned}$$

where

$$d\operatorname{erfc}\left(\frac{\tau}{\sigma\sqrt{2}}\right) = \frac{d\operatorname{erfc}(\frac{\tau}{\sigma\sqrt{2}})}{dt}\,\frac{dt}{d\tau}\,d\tau \quad (11)$$

and

$$\operatorname{erfc}\left(\frac{\tau}{\sigma\sqrt{2}}\right) = \frac{2}{\sqrt{\pi}}\int_{\frac{\tau}{\sigma\sqrt{2}}}^{\infty} e^{-t^2}\,dt \quad (12)$$

so

$$\begin{aligned}\frac{d\operatorname{erfc}(\frac{\tau}{\sigma\sqrt{2}})}{dt}\,\frac{dt}{d\tau}\,d\tau &= \frac{2}{\sqrt{\pi}}\Big|_{\frac{\tau}{\sigma\sqrt{2}}}^{\infty}\cdot\frac{d\frac{\tau}{\sigma\sqrt{2}}}{d\tau}\cdot d\tau\\ &= -\frac{\sqrt{2}}{\sigma\sqrt{\pi}}e^{-\frac{\tau^2}{2\sigma^2}}\cdot d\tau \quad (13)\end{aligned}$$

therefore

$$\Delta\phi(z) = -\frac{|e|}{2\varepsilon_0}\int_{-\infty}^{\infty} dz'\,\rho_B(z')\left[-|z-z'|\operatorname{erfc}\left(\frac{|z-z'|}{\sigma\sqrt{2}}\right) + \frac{\sqrt{2}\sigma}{\sqrt{\pi}}e^{-\frac{z-z'}{2\sigma^2}}\right] \quad (14)$$

Considering the charge number density along the z-axis in an interfacial system,

$$\rho_B(z) = \begin{cases} 0 & z \to \infty \\ \text{const} & z \to -\infty \end{cases} \tag{15}$$

Therefore, on both sides of the gas–liquid interface, the potential in the gas phase satisfies $\phi(+\infty) = 0$, while in the liquid phase:

$$\begin{aligned} \Delta\phi(-\infty) = -\frac{|e|}{2\varepsilon_0}\rho_B \cdot \Bigg[&- \int_{-\infty}^{\infty} dz' \, |z - z'| \operatorname{erfc}\left(\frac{|z - z'|}{\sigma\sqrt{2}}\right) \\ &+ \int_{-\infty}^{\infty} dz' \, \frac{\sqrt{2}\sigma}{\sqrt{\pi}} \, e^{-\frac{(z-z')^2}{2\sigma^2}} \Bigg] \end{aligned} \tag{16}$$

where

$$\begin{aligned} \int_{-\infty}^{\infty} dz' \, |z - z'| \operatorname{erfc}\left(\frac{|z - z'|}{\sigma\sqrt{2}}\right) &= 2\int_0^{\infty} dt \, t \operatorname{erfc}\left(\frac{t}{\sigma\sqrt{2}}\right) \\ &= \frac{\sqrt{2}}{\sigma\sqrt{\pi}} \int_0^{\infty} dt \, t^2 e^{-\frac{t^2}{2\sigma^2}} \\ &= \sigma^2 \end{aligned} \tag{17}$$

and

$$\begin{aligned} \int_{-\infty}^{\infty} dz' \, \frac{\sqrt{2}\sigma}{\sqrt{\pi}} e^{-\frac{(z-z')^2}{2\sigma^2}} &= 2\frac{\sigma\sqrt{2}}{\sqrt{\pi}} \int_0^{\infty} dt \, e^{-\frac{t^2}{2\sigma^2}} \\ &= 2\sigma^2. \end{aligned} \tag{18}$$

Therefore,

$$\Delta\phi(-\infty) = -\frac{|e|}{2\varepsilon_0}\rho_B \cdot \sigma^2. \tag{19}$$

Consequently, the potential drop across the interface is

$$\begin{aligned} \Delta\chi &= \Delta\phi(-\infty) - \Delta\phi(+\infty) \\ &= -\frac{|e|}{2\varepsilon_0}\rho_B \cdot \sigma^2. \end{aligned} \tag{20}$$

This derivation quantitatively demonstrates that, for a fixed interfacial charge-density profile, the surface potential difference is directly governed by the degree of charge delocalization (σ), as encapsulated in eq(20). Charge delocalization is therefore identified as the primary microscopic determinant of $\Delta\chi$.

A long-standing puzzle in interfacial electrostatics is the dramatic discrepancy between the surface potential of water predicted by classical force fields

(~ -0.5 V) and that from *ab initio* calculations ($\sim +4.0$ V). The central thesis of this work is that this discrepancy originates predominantly from the differing descriptions of *charge delocalization*—the spatial spreading of partial charges within a molecule. To isolate and quantify this effect, we employ the derived relation $\chi_{\text{deloc}} = -\frac{|e|}{2\varepsilon_0}\rho_B \cdot \sigma^2$, which explicitly links the surface potential shift to the variance σ^2 of the charge distribution.

Table 1: Parameters and calculated surface potential contributions for various water models.

	SPC/E[a]	TIP3P[b]	TIP4P[c]	SWM4-DP[d]	SWM4-NDP[e]	ab initio[f]	WFc[f]
q_{O}(e)	-0.8476	-0.830		-1.77185	1.71636	+6	+6
q_{D}(e)				1.77185	-1.71636		
q_{M}(e)			-1.040	-1.10740	-1.11466		
d_{OH}(Å)	1.0	0.9572	0.9572	0.9572	0.9572	$\langle 0.98584 \rangle$	$\langle 0.98584 \rangle$
d_{OM}(Å)			0.15	0.23808	0.24034		
θ_{HOH}(°)	109.47	104.52	104.52	104.52	104.52	$\langle 104.146 \rangle$	$\langle 104.146 \rangle$
μ(eÅ)	0.48937	0.48628	0.45332	0.51133	0.51237	$\langle 0.60832 \rangle$	$\langle 0.60832 \rangle$
σ_+ (Å)	0.47140	0.43703	0.43703	0.30718	0.32017	$\langle 0.27241 \rangle'$	$\langle 0.27116 \rangle$
σ_- (Å)	0	0	0	0.06687	0.03333	$\langle 0.48311 \rangle'$	$\langle 0.24085 \rangle$
χ_{deloc}(V)	-0.56966	-0.47944	-0.56237	-0.78038	-0.74986	3.85161	-0.37543
χ_{dipole}(V)	≈ 0	-0.07				0.295	0.295
χ(V)	-0.57	-0.55	-0.5	-0.540	-0.545	+4.18	-0.08

χ_{deloc} is obtained through eq(20), χ_{dipole} is obtained through dynamic sampling.
[a] Model from Ref.[X]. The bulk density is 1g/cm^3.
[b] Model from Ref.[X]'s model B. The bulk density is 1g/cm^3.
[c] Model and bulk density 0.936g/cm^3 from Ref.[X], χ from Ref.[X].
[d] Model, χ and bulk density is 0.997g/cm^3 from Ref.[X], $\sigma_\pm$ is derived via the μ in the bulk phase.
[e] Model, χ and bulk density is 0.997g/cm^3 from Ref.[X], $\sigma_\pm$ is derived via the μ in the bulk phase.
[f] The bulk density is 1g/cm^3. $\langle\rangle$ represents the average of molecules in the bulk phase, $\langle\rangle'$ represents the use of three bulk water molecules placed at 12Å × 12Å × 12Å for wave function analysis and averaged.

Table 1 presents a decisive test of this thesis. For each water model, we compute the delocalization contribution χ_{deloc} using the model's bulk charge density ρ_B and its charge delocalization parameters σ_+ and σ_-. The total surface potential χ (from literature or simulation) is compared against the sum of χ_{deloc} and the dipole-orientation contribution χ_{dipole}. The data reveal a clear trend: for classical point-charge-like models (SPC/E, TIP3P, SWM4-DP, SWM4-NDP), where σ_- is small, χ_{deloc} is negative and accounts for nearly the entire observed χ. The pivotal insight comes from comparing the 'ab initio' and 'WFc' results. Both describe the same total molecular charge, yet their predicted χ_{deloc} differ by over 4 V. This enormous difference is traced directly

to their vastly different σ_- values (see table), quantitatively proving that the representation of charge delocalization is the primary determinant of the surface potential sign and magnitude.