Supplementary information:
An explanation for the charge on water's surface

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The following material is not in itself new, but we include it here because it is useful background to the work described in the main paper.

1   A Poisson-Boltzmann equation

The Poisson-Boltzmann (PB) equation couples the electric potential to the Boltzmann distribution of ions through Poisson's equation. A mean-field approach such as this breaks down at high ionic strengths like those often present in computer simulations, but works well at the low concentrations that are relevant to our work [1]. The equation is improved by giving the ions a finite size [2]. The version of the Poisson-Boltzmann equation that we use is based on the work of Borukhov *et al.* [3, 4].

1.1   Background

Poisson's equation in water is,

$$\nabla_{\mathbf{r}}^2 \phi\left(\mathbf{r}\right) = -\frac{4\pi}{\epsilon_{\mathrm{w}}} \rho(\mathbf{r}), \tag{1}$$

where $\phi(\mathbf{r})$ is the electrostatic potential, $\rho(\mathbf{r})$ is the charge density, $\nabla_{\mathbf{r}}$ the gradient operator, and ϵ_{w} the relative permittivity of water. We have chosen the permittivity of free space to be $(4\pi)^{-1}$. Atomic units are used. If we use a mean-field approximation for the ions' concentrations, $c_i(\mathbf{r})$,

$$c_i(\mathbf{r}) = c_{0i} \exp\left(-\frac{z_i\phi(\mathbf{r}) + V_i(z)}{k_{\mathrm{B}}T}\right), \tag{2}$$

where z_i the charge on species i, c_{0i} the number density of species i where the potentials vanish, k_{B} is Boltzmann's constant and T the absolute temperature, then we obtain the customary form of the Poisson-Boltzmann equation for N species [5],

$$\nabla_{\mathbf{r}}^2 \phi\left(\mathbf{r}\right) = -\frac{4\pi}{\epsilon_{\mathrm{w}}} \sum_{i=1}^{N} e z_i c_{0i} \exp\left(-\frac{e z_i\phi(\mathbf{r}) + V_i(z)}{k_{\mathrm{B}}T}\right), \tag{3}$$

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where $\phi(\mathbf{r})$ is the mean electrostatic potential at a point $\mathbf{r}$, and we have included a non-electrostatic potential acting on each species, $V_i(z)$. These equations for the potential ϕ and the ion concentrations are useful, but based on the assumption that the ions are infinitesimally small. This allows high charge densities and diverging potentials. One approach to this problem is to split interface structure into two regions, a Stern layer of relatively high density, and a diffuse layer of lower density that is adequately described by the equations 2 and 3 [6]. We instead modify the Poisson-Boltzmann equation to forbid divergent potentials.

1.2   Free-energy density

We follow Borukhov *et al.* in placing the ions on a lattice, as a simple way of introducing a finite size [3]. We will only treat this model at the mean-field level, so the only effect on the results is to impose a maximum density of ions. We choose the lattice spacing to be a, which in our treatment of polarisation fluctuations is the region around the ion within which the fluctuations are suppressed. Our results are insensitive to this parameter provided it has roughly this magnitude. The nonlinear Poisson-Boltzmann equation that we used was derived from a simple free-energy functional which included electrostatic terms, a lattice-based configurational entropy that prevents unphysically large ion concentrations, and an external potential, $V_i(\mathbf{r})$ for species i, including self-image repulsions from the interface and the fluctuation suppression force. These are given by,

$$U \;=\; \int d\mathbf{r} \left\{ -\frac{\epsilon_{\mathrm{w}}}{8\pi}|\nabla_{\mathbf{r}}\phi(\mathbf{r})|^2 + \sum_i ez_ic_i(\mathbf{r})\phi(\mathbf{r}) + \sum_i V_i(\mathbf{r})c_i(\mathbf{r}) \right\}, \tag{4}$$

$$S \;=\; -k_{\mathrm{B}}a^{-3}\int d\mathbf{r} \left\{ \sum_i \left[a^3c_i(\mathbf{r})\ln\left(a^3c_i(\mathbf{r})\right)\right] + \left[1 - a^3\sum_i c_i(\mathbf{r})\right]\ln\left[1 - a^3\sum_i c_i(\mathbf{r})\right]\right\}, \tag{5}$$

$$L \;=\; -k_{\mathrm{B}}T\sum_i \ln\left(\xi_i\right)\int d\mathbf{r}\, c_i(\mathbf{r}), \tag{6}$$

where the integrations are over our region of interest, U is the internal energy, S the entropy, and the terms in L produce a Legendre transformation to the desired ensemble. The free energy is $F = U - TS + L$, and the ξ_i are varied to obtain the desired bulk concentrations. The chemical potentials of the ions are given by,

$$\mu_i = k_{\mathrm{B}}T\ln\xi_i. \tag{7}$$

Other symbols are defined above. The ordinary Poisson-Boltzmann equation, and equations for the ion densities (equations 3 and 2), are obtained as the Euler-Lagrange equations from F with the second term in the entropy's integrand is neglected. The results in the main paper are obtained using the Euler-Lagrange equations for the full free energy F. These equations are described in the next section.

1.3   Equation for the potential and ion concentrations

We then take the Debye length, Λ, as the unit of length, using as a coordinate $\mathbf{s} = \mathbf{r}/\Lambda$. We rewrite Poisson's equation in terms of the dimensionless scaled potential $\psi = e\phi/k_\mathrm{B}T$, and the volume fractions $x_i(\mathbf{s}) = a^3 c_i(\mathbf{r})$. The total volume fraction of ions where the potentials vanish is $\eta = \sum_i x_{i0}$. We shall only be interested in problems in one dimension.

With these substitutions and simplifications, Poisson's equation becomes for the case of monovalent cations, monovalent anions, and hydroxides,

$$\eta\psi''(s) = - \left[x_+(s) - x_-(s) - x(s) \right] \tag{8}$$

where we have explicitly chosen three species, cations with volume fraction x_+, hydroxides with volume fraction x, and all other anions with volume fraction x_-. We choose θ to be the fraction of all anions present that are hydroxides. The isoelectric point is insensitive to η, and the shape of the ζ-potential with pH is little altered unless η is very large.

The volume fractions occupied by the ions are related to the scaled potential by the equations,

$$x_+(s) = \frac{\eta}{2C(s)} \exp\left(-\psi(s) - u(s)\right), \tag{9}$$

$$x_-(s) = \frac{\eta(1-\theta)}{2C(s)} \exp\left(+\psi(s) - u(s)\right), \tag{10}$$

$$x(s) = \frac{\eta\theta}{2C(s)} \exp\left(+\psi(s) - u(s) - v(s)\right), \tag{11}$$

where θ is the fraction of anions that are hydroxides, $u(s)$ is the self-image repulsion, and $C(s)$ a common factor,

$$\begin{aligned}
C(s) = {} & 1 + \frac{\eta}{2} \left[\exp\left(-\psi(s) - u(s)\right) - 1 \right], \\
& + \frac{\eta(1-\theta)}{2} \left[\exp\left(+\psi(s) - u(s)\right) - 1 \right], \\
& + \frac{\eta\theta}{2} \left[\exp\left(+\psi(s) - u(s) - v(s)\right) \right].
\end{aligned} \tag{12}$$

These equations are solved at first for ψ and the x_i, which are converted to the mean electric potential ϕ and the concentrations c_i. The physical quantities reported in the main paper are obtained as described in section 3.4.

1.4   Numerical solution

The differential equation governing the electric potential was obtained as an Euler-Lagrange equation from the full free-energy functional described in the previous section, and solved using the numerical differential equation solvers built into Mathematica 7.0 [7]. All results were obtained

for an infinite region $z > 0$ with interface at $z = 0$. Naturally, we only solved the full nonlinear differential equation out to some $z_{\max}$, where the potential was small enough to switch to the linearised solution. Typically $z_{\max}$ was 18Λ, where Λ is the Debye length. The coordinate transformation $w = \exp(-s)$ is useful. The boundary conditions were,

$$\lim_{s \to \infty} \psi(s) = 0 \tag{13}$$
$$\psi'(0) = 0 \tag{14}$$

We satisfied these with the shooting method to one part in a million or better, using Brent's method to bracket and seek the desired boundary conditions. The consequence of the second boundary condition is the overall neutrality of the interface. The results are not sensitive to the choice of numerical integration algorithm or to the accuracy and precision settings. The drawback of this approach is that we are unable to give a simple, closed form for the ζ-potential or the surface tension, but this is outweighed by the accuracy of this modified Poisson-Boltzmann equation [4].

2 The size of the polarisation fluctuation 'hole' around the ion

We estimated the size of the polarisation-fluctuation hole carried by the hydroxide using a formula that relates the dielectric constant to spontaneous polarisation fluctuations [8]. Here we discuss two issues relating to the choice of this formula: the sample-shape dependence of a dielectric material's response to an external field, and the contribution of electronic polarisation.

A dielectric material is polarised when subjected to an applied field, but the relative permittivity relates the polarisation not to this applied field, but to the total, or internal, or Maxwell field. This fact makes the connection between the dielectric constant and the spontaneous fluctuations in dipole moment depend on the shape of our sample, and on the medium in which it is immersed [9]. Many different fluctuation formulae for the dielectric constant have been published. We have taken care to use the one appropriate to our system of interest. Here we point out that our results are not in fact sensitive to the choice of this formula. The discussion in this section applies to dilute, bulk, electrolyte solutions with only two ionic species present.

2.1 Non-conducting system

We discuss first a system without freely moving charges. This discussion, strictly speaking, applies to the effect of neutral solutes on the dielectric constant of their solution. Kirkwood gave a formula for the spontaneous polarisation fluctuations of a sphere of volume V and dielectric constant ϵ embedded in a medium of the same dielectric constant [8],

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{3\epsilon} = \frac{4\pi \left\langle |\mathbf{M}|^2 \right\rangle}{3V k_{\mathrm{B}} T}, \tag{15}$$

where all symbols are defined either above or in the main article. We use this equation to calculate the relation between the dielectric decrement, δ_-, and the reduction in polarisation fluctuations near the ion, Δ.

We set out this last step in detail. It is also discussed in the main paper. We have from experiment the dependence of the relative permittivity on the concentration of ions, for dilute solutions,

$$\begin{aligned}
\epsilon(c) &= \epsilon_{\mathrm{w}} - \delta \times c + \dots, & (16) \\
&= \epsilon_{\mathrm{w}} - \delta_+ \times c_+ - \delta_- \times c_- + \dots, & (17) \\
&= \epsilon_{\mathrm{w}} - (\delta_+ + \delta_-) \times c + \dots, & (18)
\end{aligned}$$

where the relation between the solution's dielectric decrement, δ, and those of the individual ions, $\delta_\pm$, is as discussed in the main paper. The dots denote higher order terms in the concentration. We expand the left-hand side of equation 15 to the same order,

$$\frac{(\epsilon(c) - 1)(2\epsilon(c) + 1)}{3\epsilon(c)} = \frac{(\epsilon_{\mathrm{w}} - 1)(2\epsilon_{\mathrm{w}} + 1)}{3\epsilon_{\mathrm{w}}} - \delta \times \frac{(2\epsilon_{\mathrm{w}}^2 + 1)\,c}{3\epsilon_{\mathrm{w}}^2} + \dots \tag{19}$$

We now assume that each ion reduces the fluctuations in the solution's collective dipole moment by some amount $\Delta_\pm$. This assumption is discussed in the main article, and supported by the work of Gavryushov and Linse, amongst others [10]. That the mean-squared moment of our spherical sample is,

$$\left\langle |\mathbf{M}|^2 \right\rangle = \left\langle |\mathbf{M}|^2 \right\rangle_0 - n_+ \Delta_+ - n_- \Delta_- + \dots, \tag{20}$$

where the $n_\pm$ are the numbers of ions in the spherical sample, and $\langle \cdot \rangle_0$ is the average in the limit of low concentrations of the ions. We now have expansions to linear order in c of both sides of equation 15. We may therefore equate the coefficients of c on the right-hand sides of equations 19 and 20, to find,

$$\Delta_\pm = \frac{k_{\mathrm{B}} T \left(2\epsilon_{\mathrm{w}}^2 + 1\right)}{4\pi \epsilon_{\mathrm{w}}^2} \delta_\pm, \tag{21}$$

where the expression holds for either type of ion, but in the main article we are interested only in the hydroxide.

We obtain the same result as in the main article provided ϵ is large enough. This is because the factor on the right-hand side of equation 21,

$$\frac{(2\epsilon_{\mathrm{w}}^2 + 1)}{\epsilon_{\mathrm{w}}^2} \tag{22}$$

approaches two for large ϵ, and in this limit we recover equation 5 of the main paper. The calculation using the Kirkwood formula is simple and likely reasonably accurate, but we have neglected two aspects: the high-frequency response of the electrons, and the dipole moment of the ions' distribution. In the next two sections we examine both of these.

2.2 Electrolyte system

The calculation that includes the response of the ions' configurations is identical in principle to the one in the previous section, but considerably more mathematically elaborate [11]. Let the electrical conductivity of our electrolyte solution due to motions of ions be σ, its relative permittivity be ϵ. Denote the same quantities for the medium surrounding our spherical sample with a prime: ϵ' *etc*. Then the dielectric response is related to the polarisation fluctuations by,

$$(\epsilon(\omega) - 1) \; \frac{2\Sigma'(\omega) + 3}{2\Sigma'(\omega) + \Sigma(\omega) + 3} - \frac{(\epsilon_\infty - 1)\,(2\epsilon'_\infty + 1)}{2\epsilon'_\infty + \epsilon_\infty} \tag{23}$$

$$= \frac{4\pi}{3Vk_{\mathrm{B}}T} \left[\left\langle |\mathbf{M}|^2 \right\rangle + i\omega \left\langle \mathbf{M} \cdot \mathbf{M} \right\rangle_\omega + \left\langle \mathbf{M} \cdot \mathbf{J} \right\rangle_\omega \right] \tag{24}$$

where the dipolar dielectric response, $\epsilon(\omega)$ and ionic conductivity, $\sigma(\omega)$, now depend on the angular frequency of the applied field, ω, a typographical error in Caillol's equation 77 has been corrected, and,

$$\Sigma(\omega) \;=\; \epsilon(\omega) - 1 + \frac{4\pi i}{\omega}\sigma(\omega) \tag{25}$$

$$\Sigma'(\omega) \;=\; \epsilon'(\omega) - 1 + \frac{4\pi i}{\omega}\sigma'(\omega). \tag{26}$$

$\langle \cdot \rangle_\omega$ is the Fourier-Laplace transform of a correlation function [11]:

$$\langle AB \rangle_\omega = \int\limits_0^\infty \langle A(t)B(0) \rangle \exp(i\omega t)\mathrm{d}t. \tag{27}$$

The limit of low frequency gives,

$$\frac{(\epsilon - 1)\,2\sigma'}{(2\sigma' + \sigma)} - \frac{(\epsilon_\infty - 1)\,(2\epsilon'_\infty + 1)}{2\epsilon'_\infty + \epsilon_\infty} = \frac{4\pi}{3Vk_{\mathrm{B}}T} \left[\left\langle |\mathbf{M}|^2 \right\rangle + \left\langle \mathbf{M} \cdot \mathbf{M}_{\mathrm{I}} \right\rangle \right] \tag{28}$$

where $\mathbf{M}_{\mathrm{I}}$ is the moment of the distribution of ions in the spherical sample region. We neglect the cross-correlation term because it has been repeatedly shown to be small in simulations of model electrolytes [12, 13], and because Gavryushov and Linse show that the dielectric decrement produced by an ion is due to a local change in the mean-squared solvent moment term (*i.e.* the first on the right hand side of equation 28).

We now drop the term in the high-frequency response (see next section). We might assume that our spherical sample is surrounded by a medium of high conductivity, or alternatively a

medium of the same conductivity as the sample. The latter case is the one we are interested in, and leads to a formula for $\epsilon - 1$,

$$\epsilon - 1 = \frac{2\pi \langle |\mathbf{M}|^2 \rangle}{V k_{\mathrm{B}} T}, \tag{29}$$

which is equation 2 of the main paper. We then expand and equate coefficients of c as in section 2.1 above or in section 3.2 of the main paper.

2.3 Electronic dipole-moment fluctuations

In the above equations a term involving the high-frequency dielectric response appears, and if $\epsilon_\infty = \epsilon_\infty'$, it becomes,

$$\frac{(\epsilon_\infty - 1)(2\epsilon_\infty + 1)}{3\epsilon_\infty}, \tag{30}$$

This term is about two orders of magnitude smaller than the others and so may be safely neglected. We therefore assume that the moment fluctuations, $\langle |\mathbf{M}|^2 \rangle$, include electronic moment fluctuations and drop the expression in equation 30 from our response formula. This is a good approximation when the static dielectric constant is so much higher than the high-frequency one [14].

Because we use the experimental dielectric decrement to estimate Δ, we have included all contributions to the polarisation-fluctuation hole around the ion. Comparison of the values of the dielectric decrement of the hydroxide to its polarisability shows that it is the fluctuations in the arrangements of waters' permanent moments that dominate.

3 The strength of the fluctuation-suppression force

We seek the simplest possible estimate of the free energy of interaction of the constrained water molecules in an ion's solvation environment with a hydrophobic interface. This will be an estimate of the free energy of the fluctuation hole around the ion, Δ, at various distances, z, from the interface. We will assume that the reduction of fluctuations associated with the ion is concentrated at the ion's position, and that fluctuations are otherwise uniformly distributed. As with other approximations we have made this underestimates the strength of the force.

We want the free energy change on removing both the fluctuations Δ from the ion's position, and all the fluctuations in the $z < 0$ region. This is equivalent to the free energy of interaction of dipole-moment fluctuations of intensity Δ, at a distance z from an infinite region of water-like polarisation fluctuations, $z < 0$.

Consider first two classical Drude oscillators with point polarisabilities, α, separated by some distance r, with potential energy,

$$V(\mu, \mu', \mathbf{r}) = \frac{|\mu|^2}{2\alpha} + \frac{|\mu'|^2}{2\alpha} - \frac{3\mu \cdot \hat{r}\hat{r} \cdot \mu' - \mu \cdot \mu'}{r^3} \tag{31}$$

where μ and μ' are the dipole moments. The first two terms lead to restoring forces on the dipoles and the third is the dipole-dipole interaction. We may regard a small region of the fluid as a harmonic oscillator for these purposes because we can always expand its free energy to second order in its dipole moment. The partition function for this system is easily obtained as a product of Gaussian integrals over the components of the two dipole moments. It can be done automatically with Mathematica [7]:

$$Q = \int \mathrm{d}\mu \, \mathrm{d}\mu' \, \exp\left(-\frac{V(\mu, \mu', \mathbf{r})}{k_{\mathrm{B}}T}\right) \tag{32}$$

The corresponding free energy to lowest order in r^{-3} and neglecting a physically irrelevant constant is given by,

$$A(r) = -\frac{\langle|\mu|^2\rangle\langle|\mu'|^2\rangle}{3k_{\mathrm{B}}Tr^6} \tag{33}$$

Now suppose that the fluctuating dipole μ interacts not with another similar oscillator but with a region filled with a uniform density of dipolar fluctuations, corresponding to a dielectric constant. Assume this region fills all space for $Z < 0$, and place the reduction Δ at $z > 0$. We must integrate equation 33 over the region,

$$v(z) = \int_{-\infty}^{+\infty} \mathrm{d}X \int_{-\infty}^{+\infty} \mathrm{d}Y \int_{-\infty}^{0} \mathrm{d}Z \, A\left(\sqrt{X^2 + Y^2 + (Z-z)^2}\right) \tag{34}$$

$$= -\int_{-\infty}^{+\infty} \mathrm{d}X \int_{-\infty}^{+\infty} \mathrm{d}Y \int_{-\infty}^{0} \mathrm{d}Z \, \frac{\langle|\mathbf{M}|^2\rangle_0 \Delta}{3Vk_{\mathrm{B}}T}\left(X^2 + Y^2 + (Z-z)^2\right)^{-3}. \tag{35}$$

Here we have replaced $\langle|\mu'|^2\rangle$ with Δ, and $\langle|\mu|^2\rangle$ with the uniform density of polarisation fluctuations $\langle|\mathbf{M}|^2\rangle_0/V$, so as to obtain the interaction of Δ with the half space. Integrating over the whole region $z < 0$ gives the desired potential, equation 6 of the main paper. This form is typical of dispersion interactions between a wall and a particle. Our discussion here has been brief, but we refer the reader to Hunter's discussion of the theory of dispersion interactions based on pair sums [5].

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