Supporting Information: Theory of Surface Forces in Multivalent Electrolytes

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1 Derivation of the expression for the Helmholtz free energy

In this section, we derive the expression for the electrostatic and hydration field energies using the approach described in refs. 1 and 2. The expressions for the field energies derived here contribute to the Helmholtz free energy of the system. Note that the Helmholtz free energy serves as the starting point in the derivation of the disjoining pressure operating between two charged surfaces.

1.1 Electrostatic Field Energy

We assume that two point charges interact via a Coulomb potential, along with a local interaction potential attributed to ion-ion correlations which decays according to the length scale, l_{ij}, for each pair interaction between ions i and j.[3,4] The interaction potential, $U_{i,j}$ is given by:

$$\frac{U_{i,j}(\mathbf{r})}{k_B T} = \frac{z_i z_j l_b (1 - e^{-|\mathbf{r}|/l_{i,j}})}{\mid \mathbf{r} \mid} \tag{S1}$$

where k_B is the Boltzmann constant, T is the absolute temperature, z_i and z_j are the valencies of ion i and ion j, respectively, l_b is the Bjerrum length, and $\mathbf{r}$ is a spatial coordinate.

The linear operator which corresponds to the Green's function, $G(\mathbf{r}, \mathbf{r}') = \frac{1-e^{-|\mathbf{r}-\mathbf{r}'|/l_{i,j}}}{4\pi|\mathbf{r}-\mathbf{r}'|}$, such that $LG(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')$ is $L = ({l_{i,j}}^2\nabla^2 - 1)\nabla^2$ where δ is the Dirac delta function. The mean potential, $\phi_{i,j}$, resulting from the interaction of the point charges, as described in Eq. S1, is given by,

$$z_i e \phi_{i,j} = \int_V d\mathbf{r}' [U_{i,j}(\mathbf{r} - \mathbf{r}') c_j(\mathbf{r}')] \tag{S2}$$

where c_j is the number density of ions of type j (number of ions of type j per unit volume). By applying the linear operator $L_{i,j}$ on both sides of Eq. S2, the potential resulting from the interaction of ion i with ion j obeys the following differential equation:

$$\epsilon L_{i,j} \phi_{i,j} = z_j e c_j(r) \tag{S3}$$

Summing over the index i from 1 to N where N is the number of ion types in the system, Eq. S3 can be expressed as follows:

$$\sum_{i=1}^{N} \sum_{j=1}^{N} \epsilon L_{i,j} \phi_{i,j} = N \sum_{j=1}^{N} z_j e c_j(r) = N\rho \tag{S4}$$

where ρ is the charge density. Note that the correlation lengths for a pair interaction is symmetric, namely $l_{i,j} = l_{j,i}$. If the correlation length for each pair of species is equal,

$l_{i,j} = l_c$, then the linear operators are equivalent, $L_{i,j} = L = ({l_c}^2\nabla^2 - 1)\nabla^2$. Therefore, we can define the potential as:

$$\phi = \frac{1}{N}\sum_i \sum_j \phi_{i,j} \tag{S5}$$

The governing equation for the electrostatic potential is given by:

$$\epsilon({l_c}^2\nabla^2 - 1)\nabla^2\phi = \rho \tag{S6}$$

We can then derive the form of the electrostatic field energy via a charging process. The field energy changes as we place charges in a potential field. The change in the electrostatic field energy, δW_{elec}, upon introducing a differential amount of charge, $\delta\rho$, into the system is given by:

$$\delta W_{elec} = \int_V d\mathbf{r}[\phi\delta\rho] \tag{S7}$$

Substituting ρ in Eq. S6 into Eq. S7, we obtain:

$$\begin{aligned} \delta W_{elec} &= \int_V d\mathbf{r}[\epsilon\phi\delta(\nabla\cdot({l_c}^2\nabla^3\phi - \nabla\phi))] \\ &= \int_V d\mathbf{r}[\epsilon\phi\nabla\cdot({l_c}^2\delta\nabla^3\phi - \delta\nabla\phi)] \end{aligned} \tag{S8}$$

Note that throughout the main text and the SI, we assume that the solvent permittivity, ϵ, is constant. Invoking the vector identity that: $a\nabla\cdot v = \nabla\cdot(av) - \nabla a\cdot v$, where a is a scalar and v is a vector, Eq. S8 can be rewritten as follows:

$$\begin{aligned} \delta W_{elec} = \int_V d\mathbf{r}[&\epsilon\nabla\cdot(\phi({l_c}^2\delta\nabla^3\phi - \delta\nabla\phi)) \\ &- \epsilon\nabla\phi\cdot({l_c}^2\delta\nabla^3\phi - \delta\nabla\phi)] \end{aligned} \tag{S9}$$

Note that Eq. S9 was obtained using, $a = \phi$ and $v = ({l_c}^2\delta\nabla^3\phi - \delta\nabla\phi)$, in the vector identity discussed above. Next, implementing the divergence theorem on the 1st integral in Eq. S9,

Eq. S9 can be rewritten as follows:

$$\delta W_{elec} = \int_S d\mathbf{r_s} n \cdot [\epsilon\phi({l_c}^2 \delta\nabla^3\phi - \delta\nabla\phi)] + \int_V d\mathbf{r}[-\epsilon\nabla\phi \cdot ({l_c}^2\delta\nabla^3\phi - \delta\nabla\phi)] \tag{S10}$$

Next, we choose an arbitrary reference surface for which we will evaluate the surface integral in Eq. S10. Note that the expression for the integrand in the surface integral is of the form, $n \cdot \delta D$, where D is the electric displacement field, given by, $D = -\epsilon\nabla\phi + {l_c}^2\epsilon\nabla^2\nabla\phi$. By choosing an arbitrary reference surface where the displacement field is zero, we can cancel out the surface term (1st term in Eq. S10, which is of the form, $\int_S d\mathbf{r_s}\phi(n \cdot \delta D)$, and obtain the following simplified relation,

$$\delta W_{elec} = \int_V d\mathbf{r}[-\epsilon\nabla\phi \cdot ({l_c}^2\delta\nabla^3\phi - \delta\nabla\phi)] \tag{S11}$$

Substitution of $\delta\nabla^3\phi = \nabla\delta\nabla^2\phi$ in Eq. S11:

$$\delta W_{elec} = \int_V d\mathbf{r}[-\epsilon {l_c}^2\nabla\phi \cdot \nabla\delta\nabla^2\phi + \epsilon\nabla\phi \cdot \delta\nabla\phi] \tag{S12}$$

Utilizing the vector identity used above, and using the divergence theorem, and neglecting surface terms, we obtain:

$$\delta W_{elec} = \int_V d\mathbf{r}[\epsilon\nabla\phi \cdot \delta\nabla\phi + \epsilon {l_c}^2(\nabla^2\phi)\delta\nabla^2\phi] \tag{S13}$$

Integrating Eq. S13 from 0 to W_{elec}, we obtain:

$$W_{elec} = \int_V d\mathbf{r}[\frac{\epsilon}{2}(\nabla\phi)^2 + \frac{\epsilon {l_c}^2}{2}(\nabla^2\phi)^2] \tag{S14}$$

The underlying assumption is that we can locally integrate from 0 to W_{elec}, where $W_{elec} = \int \delta W_{elec}$, at each local point within the volume V. Note that the field energy is universally

convex such that $\delta^2 W_{elec} > 0$. However, in the minimization of the functional in Eq. S14, we need to enforce Maxwell's equations for a bulk charge distribution ρ bounded by surfaces of fixed surface charge density q_s, $\nabla \cdot D = \rho$ and $n \cdot D = -q_s$, with Lagrange multipliers, λ_1 and λ_2, where D is the displacement field. After incorporating these additional constraints in Eq. S14, we obtain the following expression:

$$\begin{aligned} W_{\text{elec}} = &\int_V d\mathbf{r}[\frac{\epsilon}{2}(\nabla\phi)^2 + \frac{\epsilon {l_c}^2}{2}(\nabla^2\phi)^2] \\ &+ \int_V d\mathbf{r}[\lambda_1(\rho - \nabla \cdot D)] + \int_S d\mathbf{r}_s[\lambda_2(q_s + n \cdot D)] \end{aligned} \tag{S15}$$

where n is the unit vector pointing outward from the surface. It can be shown that λ_1 and λ_2 must satisfy $\lambda_1 = \lambda_2 = \phi$ by minimizing the functional in Eq. S15 with respect to the electrostatic potential. After applying the divergence theorem and substituting in Eq. S6, we arrive at the final form of the electrostatic field energy:

$$W_{\text{elec}} = \int_V d\mathbf{r}[\rho\phi - \frac{\epsilon}{2}(\nabla\phi)^2 - \frac{\epsilon {l_c}^2}{2}(\nabla^2\phi)^2] + \int_S d\mathbf{r_s}[q_s\phi] \tag{S16}$$

1.2 Hydration Field Energy

We can follow a similar procedure to derive the field energy for the hydration potential. The expression for the water-mediated hydration interaction between two ions, $V_{i,j}$, is given by:

$$\frac{V_{i,j}(\mathbf{r})}{k_B T} = \frac{l_h e^{-\kappa_h(|\mathbf{r}| - l_h)}}{|\ \mathbf{r}\ |} \tag{S17}$$

In this case, we define a new potential, the hydration potential, arising from the repulsion between two ions mediated by ordered water layers. In Eq. S17 l_h is the hydration length and κ_h is the inverse length scale associated with ordered water layers. The linear operator that corresponds to the Green's function $G(\mathbf{r}, \mathbf{r}') = \frac{-e^{-\kappa_h|\mathbf{r}-\mathbf{r}'|}}{4\pi|\mathbf{r}-\mathbf{r}'|}$ such that $LG(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')$

is $L = \nabla^2 - \kappa_h^2$. If we define the hydration potential $\boldsymbol{\psi_h}$, as follows:

$$\boldsymbol{\psi_h} = \frac{1}{k_B T} \int_V d\mathbf{r}' [V_{i,j}(\mathbf{r} - \mathbf{r}') \sum_n \alpha_n c_n(\mathbf{r}')], \tag{S18}$$

we can show that the potential in Eq. S18 will obey the following differential equation by applying the linear operator L to both sides of Eq. S18:

$$(\nabla^2 - \kappa_h^2)\boldsymbol{\psi_h} = -4\pi l_h e^{\kappa_h l_h} \sum_n \alpha_n c_n \tag{S19}$$

where, c_n, is the number density of ions of type n and α_n is a size parameter for each ion given by the relation, $\alpha_n = \frac{l_n}{l_h} e^{\kappa_h (l_n - l_h)}$. In α_n, l_n is the hydrated size of ion n, so that $\alpha_n = 1$ $\forall n$ corresponds to the case of equally hydrated ion sizes. Note that this derivation is similar to that of Bohinc et al.[5] It is convenient to solve for the difference in the hydration potential relative to a reservoir, instead of solving for its absolute value, because the chemical potential contribution due to hydration will always be computed relative to a reservoir concentration. To this end, we introduce the relative hydration potential, $\psi_h = \boldsymbol{\psi_h} - \boldsymbol{\psi_{h,ref}}$, which results in the following expression:

$$(\nabla^2 - \kappa_h^2)\psi_h = -4\pi l_h e^{\kappa_h l_h} \sum_n \alpha_n (c_n - c_{n,ref}) \tag{S20}$$

Beginning with Eq. S20, we can mimic the electrostatic charging procedure for the non-electrostatic hydration interaction to obtain the field energy for the hydration potential. To this end, instead of placing ions in an electric field, we place them in a hydration field, which results in the following expression for the change in the hydration field energy, δW_{hydr}, for the hydration process,

$$\begin{aligned}\delta W_{\text{hydr}} &= k_B T \int_V d\mathbf{r} \left[\psi_h \delta\big(\sum_n \alpha_n (c_n - c_{n,ref}) \big) \right] \\ &= k_B T \int_V d\mathbf{r} \left[\psi_h \delta\Big(\frac{-\nabla^2 \psi_h + \kappa_h^2 \psi_h}{4\pi l_h e^{\kappa_h l_h}} \Big) \right]\end{aligned} \tag{S21}$$

For convenience, defining a constant $A = k_B T/(4\pi l_h e^{\kappa_h l_h})$, and then implementing the vector identity discussed earlier, Eq. S21 can be recast as follows:

$$\begin{aligned}\delta W_{\text{hydr}} &= \int_V d\mathbf{r} \Big[- A\psi_h \delta \nabla^2 \psi_h + A\kappa_h^2 \psi_h \delta \psi_h \Big] \\ &= \int_V d\mathbf{r} \Big[- A\nabla \cdot (\psi_h \delta \nabla \psi_h) \\ &\qquad + A\nabla \psi_h \delta \nabla \psi_h + A\kappa_h^2 \psi_h \delta \psi_h \Big]\end{aligned} \tag{S22}$$

Next, we first apply the divergence theorem on the 1st term in Eq. S22. We then note that similar to our analysis of the surface integral in Eq. S10 to derive the expression for the electrostatic field energy, we can move the term on the second line of Eq. S22 to a reference surface such that it takes the form, $\int_S d\mathbf{r_s} A\psi_h (n \cdot \delta D_h)$, where $D_h = -\nabla \psi_h$, is the equivalent of the electric displacement field for the hydration potential. Similar to the analysis presented in the case of the electrostatic field energy where the surface term containing the electric displacement field got eliminated, we can also eliminate this term containing the displacement field for the hydration potential. Subsequently, we integrate the two final terms in the third line of Eq. S22 to obtain,

$$W_{\text{hydr}} = \int_V d\mathbf{r} \left[\frac{A}{2} (\nabla \psi_h)^2 + \frac{A}{2} \kappa_h^2 \psi_h^2 \right] \tag{S23}$$

Note that we still need to enforce Eq. S20 in the hydration field energy. This can be done using two Lagrange multipliers at the surface and in the bulk, similar to what we did to

derive the electrostatic field energy. Following a procedure similar to the one used to obtain the Lagrange multipliers in the case of the electrostatic field energy, here, we find that the Lagrange multipliers are equal to the hydration potential, ψ_h. Substituting the Lagrange multipliers along with the expressions of the constraints in Eq. S23, we obtain:

$$\begin{aligned} W_{\text{hydr}} = &\int_V d\mathbf{r}\left[\frac{A}{2}(\nabla\psi_h)^2 + \frac{A}{2}\kappa_h^2\psi_h^2\right] \\ &+ \int_V d\mathbf{r}\left[\psi_h k_B T\big(\sum_n \alpha_n(c_n - c_{n,ref})\big)\right] \\ &+ \int_V d\mathbf{r}\left[A\psi_h\nabla^2\psi_h - A\kappa_h^2\psi_h^2)\right] \\ &+ \int_S d\mathbf{r}_s\left[\psi_h(-n\cdot A\nabla\psi_h + \sigma_h)\right] \end{aligned} \tag{S24}$$

Equation S24 can be further simplified by using the divergence theorem, which yields the following expression for the hydration potential:

$$\begin{aligned} W_{\text{hydr}} = &\int_V d\mathbf{r}\left[-\frac{A}{2}(\nabla\psi_h)^2 - \frac{A}{2}\kappa_h^2\psi_h^2\right] + \\ &\int_V d\mathbf{r}\psi_h k_B T\sum_n \alpha_n(c_n - c_{n,ref}) \\ &+ \int_S d\mathbf{r}_s\left[\psi_h\sigma_h\right] \end{aligned} \tag{S25}$$

Because we assumed that the hydration interactions act only between the counterions, i.e., between the cations in the case of two negatively-charged surfaces, $\alpha_+ = 1$ for cations, while for the cation-anion and the anion-anion interactions, $\alpha_n = 0$. This results in the following expression for the hydration field energy:

$$\begin{aligned} W_{\text{hydr}} = &\int_V d\mathbf{r}\left[-\frac{A}{2}(\nabla\psi_h)^2 - \frac{A}{2}\kappa_h^2\psi_h^2 + \psi_h k_B T\big(c_+ - c_0\big)\right] \\ &+ \int_S d\mathbf{r}_s\left[\psi_h\sigma_h\right] \end{aligned} \tag{S26}$$

1.3 The Total Free Energy Functional

The total internal energy of the system is given by: $U = W_{elec} + W_{hydr}$. In addition, we retain the entropic contribution in the PB model, $-TS = \int_V d\mathbf{r} g$, where,

$$g = k_B T \sum_{i=\pm} \left[c_i \left(\ln \left(\frac{c_i}{c_{0i}} \right) - 1 \right) \right] \tag{S27}$$

We assume that the entropy of the ions is unaffected by the electrostatic correlations which only influence the internal energy, U. Finally, we include a contribution to the Helmholtz free energy which results from the exchange of ions between the bulk reservoir and the region confined between the two charged surfaces, $\mathbb{F}_{exch.}$, which is given by: $\mathbb{F}_{exch.} = -\int_V d\mathbf{r} \Big(\mu_+ c_+ + \mu_- c_- \Big)$. Adding up $U - TS + \mathbb{F}_{exch.}$, the expression for the Helmholtz free energy, $\mathbb{F}$, of the system is given by:

$$\begin{aligned} \mathbb{F} = & \int_V d\mathbf{r} \left\{ \rho\phi - \frac{\epsilon}{2} \Big[|\nabla\phi|^2 + {l_c}^2 \left(\nabla^2 \phi \right)^2 \Big] + g\left(c_+, c_-\right) \right\} \\ & + \oint_S d\mathbf{r}\, q_s \phi \\ & + \int_V d\mathbf{r} \left\{ \Big[\frac{-\kappa^2 \psi_h^2 - (\nabla\psi_h)^2}{8\pi l_h e^{\kappa l_h}} \Big] k_B T + \left(c_+ - c_0\right) \psi_h k_B T \right\} \\ & + \oint_S d\mathbf{r}\, \sigma_h \psi_h - \int_V d\mathbf{r} (\mu_+ c_+ + \mu_- c_-) \end{aligned} \tag{S28}$$

Note that Eq. S28 is the same as Eq. 3 used in the main text to predict the disjoining pressure.

2 Derivation of Eq. 15 in our article describing the relation between the electrostatic potential, hydration potential and their higher order derivatives

At thermodynamic equilibrium, $\frac{\delta \mathbb{F}}{\delta \phi} = 0$ and $\frac{\delta \mathbb{F}}{\delta \psi_h} = 0$ for the bulk variation. Using the calculus of variations, the functional derivative of $\mathbb{F}[\phi]$ and $\mathbb{F}[\psi_h]$, can be expressed as:

$$\frac{\delta \mathbb{F}}{\delta \phi} = \frac{\partial f}{\partial \phi} - \frac{d}{dx}\left(\frac{\partial f}{\partial \phi'}\right) + \frac{d^2}{dx^2}\left(\frac{\partial f}{\partial \phi''}\right) = 0 \tag{S29}$$

$$\frac{\delta \mathbb{F}}{\delta \psi_h} = \frac{\partial f}{\partial \psi_h} - \frac{d}{dx}\left(\frac{\partial f}{\partial \psi_h'}\right) = 0 \tag{S30}$$

The total derivative of f is given by:

$$\begin{aligned}\frac{df}{dx} =& \frac{\partial f}{\partial x} + \frac{\partial f}{\partial \phi}\phi' + \frac{\partial f}{\partial \phi'}\phi'' + \frac{\partial f}{\partial \phi''}\phi''' \\ &+ \frac{\partial f}{\partial \psi_h}\psi_h' + \frac{\partial f}{\partial \psi_h'}\psi_h''\end{aligned} \tag{S31}$$

Because f does not depend explicitly on x, it follows that $\frac{\partial f}{\partial x} = 0$. In addition, we utilize the following mathematical relations:

$$\frac{\partial f}{\partial \phi'}\phi'' = \frac{d}{dx}\left(\frac{\partial f}{\partial \phi'}\phi'\right) - \frac{d}{dx}\left(\frac{\partial f}{\partial \phi'}\right)\phi' \tag{S32}$$

$$\frac{\partial f}{\partial \phi''}\phi''' = \frac{d}{dx}\left(\frac{\partial f}{\partial \phi''}\phi''\right) - \frac{d}{dx}\left(\frac{\partial f}{\partial \phi''}\right)\phi'' \tag{S33}$$

$$\frac{\partial f}{\partial \psi_h'}\psi_h'' = \frac{d}{dx}\left(\frac{\partial f}{\partial \psi_h'}\psi_h'\right) - \frac{d}{dx}\left(\frac{\partial f}{\partial \psi_h'}\right)\psi_h' \tag{S34}$$

Now, substituting the results for $\frac{\partial f}{\partial \phi'}\phi''$, $\frac{\partial f}{\partial \phi''}\phi'''$, and $\frac{\partial f}{\partial \psi_h'}\psi_h''$ from Eqs. S32, S33 and S34, respectively, into Eq. S31, we obtain:

$$\begin{aligned}\frac{df}{dx} =& \frac{\partial f}{\partial \phi}\phi' + \frac{d}{dx}\left(\frac{\partial f}{\partial \phi'}\phi'\right) + \frac{d}{dx}\left(\frac{\partial f}{\partial \phi''}\phi''\right) \\ &- \frac{d}{dx}\left(\frac{\partial f}{\partial \phi'}\right)\phi' - \frac{d}{dx}\left(\frac{\partial f}{\partial \phi''}\right)\phi'' \\ &+ \frac{\partial f}{\partial \psi_h}\psi_h' + \frac{d}{dx}\left(\frac{\partial f}{\partial \psi_h'}\psi_h'\right) - \frac{d}{dx}\left(\frac{\partial f}{\partial \psi_h'}\right)\psi_h'\end{aligned} \tag{S35}$$

Now multiplying Eq. S29 with ϕ' and Eq. S30 with ψ_h', and then substituting the resulting expressions in Eq. S35, we obtain:

$$\begin{aligned}\frac{df}{dx} =& \frac{d}{dx}\left(\frac{\partial f}{\partial \phi'}\phi'\right) + \frac{d}{dx}\left(\frac{\partial f}{\partial \phi''}\phi''\right) \\ &- \frac{d^2}{dx^2}\left(\frac{\partial f}{\partial \phi''}\right)\phi' - \frac{d}{dx}\left(\frac{\partial f}{\partial \phi''}\right)\phi'' \\ &+ \frac{d}{dx}\left(\frac{\partial f}{\partial \psi_h'}\psi_h'\right)\end{aligned} \tag{S36}$$

Using the relation: $\frac{d}{dx}\left(\frac{d}{dx}\left(\frac{\partial f}{\partial \phi''}\right)\phi'\right) = \frac{d^2}{dx^2}\left(\frac{\partial f}{\partial \phi''}\right)\phi' + \frac{d}{dx}\left(\frac{\partial f}{\partial \phi''}\right)\phi''$, Eq. S36 can be rewritten as:

$$\begin{aligned}\frac{df}{dx} =& \frac{d}{dx}\left(\frac{\partial f}{\partial \phi'}\phi'\right) + \frac{d}{dx}\left(\frac{\partial f}{\partial \phi''}\phi''\right) \\ &- \frac{d}{dx}\left(\frac{d}{dx}\left(\frac{\partial f}{\partial \phi''}\right)\phi'\right) + \frac{d}{dx}\left(\frac{\partial f}{\partial \psi_h'}\psi_h'\right)\end{aligned} \tag{S37}$$

Next, integrating Eq. S37 yields the following relation:

$$f - \frac{\partial f}{\partial \phi'}\phi' - \frac{\partial f}{\partial \phi''}\phi'' + \frac{d}{dx}\left(\frac{\partial f}{\partial \phi''}\right)\phi' - \frac{\partial f}{\partial \psi_h'}\psi_h' = \text{constant} \tag{S38}$$

Substituting the expression for f from Eq. 3 in our article, and solving for the various terms in Eq. S38, we obtain:

$$\begin{aligned}&\frac{\epsilon}{2}\phi'^2 + \frac{\epsilon {l_c}^2}{2}\phi''^2 - \epsilon {l_c}^2 \phi''' \phi' + \rho\phi + g - \mu_+ c_+ - \mu_- c_- \\ &+ \psi_h k_B T \left(c_+ - c_0\right) + k_B T \left[\frac{-\kappa_h^2 \psi_h^2 + {\psi_h'}^2}{8\pi l_h e^{\kappa_h l_h}}\right] = \text{constant}\end{aligned} \tag{S39}$$

Eq. S39 is the same as Eq. 15 in our article.

3 Contour plots showing the dependence of the predicted disjoining pressure on the salt concentration and surface charge density

To explore the full parameter space of the dependence of the predicted disjoining pressure on salt concentration and surface charge density, two contour plots are presented in Fig. S1 for a 2:1 electrolyte solution. The contour plots show the regions in which the phenomenon of like-charge attraction may be expected based on our proposed theory. In particular, like-charge attraction is prominent at close separations of 1-3 nm, even for low to moderate charge densities ranging from -0.05 C/m^2 to -0.1 C/m^2. As the two charged surfaces are pulled apart from intimate contact, there is first a strong repulsive pressure, followed by an attractive well that relaxes to zero over a few nanometers of separation distance. The topological complexity of the concentration-dependent disjoining pressure arises from the interplay between the attractive pressure resulting from ion-ion correlations and the entropic repulsion. According to Eq. 2 in our article, increasing the salt concentration results in a decrease in the magnitude of the correlation length, which in turn decreases the attractive pressure contribution resulting from ion-ion correlations (2nd term of Eq. 21 in our article). However, the dimensionless correlation length in Eq. 12 in our article, which controls the variation of the electrostatic potential, and consequently, determines the value of the second derivative

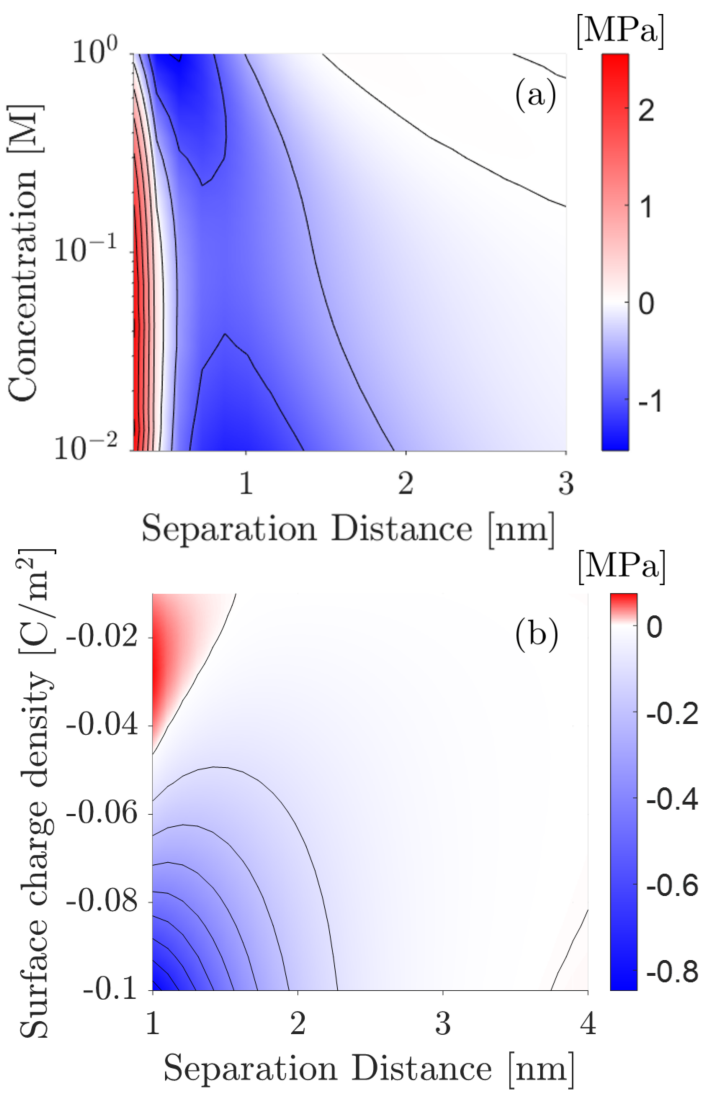

Figure S1: Contour plots of the predicted disjoining pressure for a 2:1 electrolyte solution ($\epsilon_r = 80$) with (a) changing bulk salt concentration, and (b) surface charge density. In (a), the surface charge density is fixed at $q_s = -0.1$ C/m^2. In (b), the bulk salt concentration is fixed at $c_0 = 0.1$ M. The scales of the contour plots are adjusted so that red indicates a repulsive predicted disjoining pressure, and blue indicates an attractive predicted disjoining pressure. Note that the disjoining pressure is expressed in units of MPa.

of the electrostatic potential in the 2nd term of Eq. 21 in our article, gets enhanced upon increasing the salt concentration. Furthermore, the entropic contribution to the predicted disjoining pressure (4th term in Eq. 21 in our article) decreases with an increase in the salt concentration of the bulk reservoir. This explains why we observe a complex non-monotonic dependence of the predicted disjoining pressure with varying salt concentration.

4 Comparison to experimental data for reduced Hamaker constant

The Hamaker constant reported by Plassard et al. (A_h) is approximately 70-fold larger than the reported value for silica, $A_h \approx 2 \times 10^{-21}$ J based on previous studies.[6,7] To ascertain whether our model can work in the case of lower A_h values, we repeated the calculations used to obtain Fig. 8 in the main text using $A_h = 2 \times 10^{-21}$ J instead of $A_h = 14 \times 10^{-20}$ J, the value measured experimentally by Plassard et al. The disjoining pressure profiles are shown below in Fig. S2. In order to fit the qualitative trends in the data, all the parameter values were kept constant, but the value of σ_h was changed from $\sigma_h = 5/nm^2$ (the original value used to generate Fig. 8 in the main text) to $\sigma_h = 4/nm^2$. As can be seen, the BSK theory can still describe the qualitative trends even when the Hamaker constant is reduced, due to the attractive disjoining pressure resulting from ion-ion correlations.

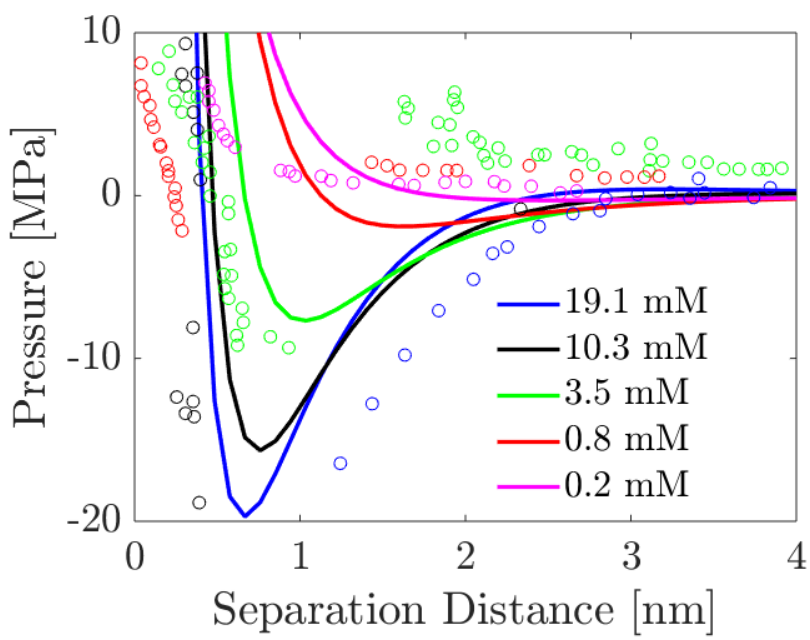

Figure S2: Comparison of the disjoining pressure versus the surface separation distance predicted by our complete theory (solid lines) with the experimental data of Plassard et al.[8] (circles) for five $Ca(OH)_2$ salt concentrations. Note that we used $A_h = 2 \times 10^{-21}$ J to generate the disjoining pressure profiles using our theory (solid lines).

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