SUPPORTING INFORMATION

Electrostatic Interactions Between Diffuse Soft Multi-Layered (Bio)Particles: Beyond Debye-Hückel Approximation and Deryagin Formulation

Jérôme F.L. Duval,* Jenny Merlin, Puranam A. L. Narayana

Laboratoire Environnement et Minéralurgie, Nancy-Université, UMR7569 CNRS, BP 40 – F-54501 Vandoeuvre-lès-Nancy Cedex, France.

1. Analytical expression for the electrostatic potential profile within Debye-Hückel and Deryagin approximations assuming homogeneous distribution and complete dissociation for ionogenic groups within each layer composing the interphases 1 and 2.

Under conditions of low electrostatic potentials ($y(x) << 1$), complete dissociation ($\mu_k(y) \rightarrow 1$) and homogeneous distribution ($\alpha_k \rightarrow 0$) of ionogenic groups within each layer composing the multi-layered interphases 1 and 2, the potential distribution profile reads as

$$y_1(x) = \tilde{\rho}_1 + \frac{\cosh(\kappa x)}{\sinh(\kappa x_{N+M+1})} \sum_{m=2}^{N+M+1} (\tilde{\rho}_{m-1} - \tilde{\rho}_m) \sinh\left[\kappa (x_{m-1} - x_{N+M+1})\right] \quad \text{(S1)}$$

$$y_{2\le m\le N+M}(x) = \tilde{\rho}_m + \frac{1}{\sinh(\kappa x_{N+M+1})} \left\{ \cosh\left[\kappa (x - x_{N+M+1})\right] \sum_{u=2}^{m} (\tilde{\rho}_{u-1} - \tilde{\rho}_u) \sinh(\kappa x_{u-1}) + \cosh(\kappa x) \sum_{u=m+1}^{N+M+1} (\tilde{\rho}_{u-1} - \tilde{\rho}_u) \sinh\left[\kappa (x_{u-1} - x_{N+M+1})\right] \right\} \quad \text{(S2)}$$

$$y_{N+M+1}(x) = \tilde{\rho}_{N+M+1} + \frac{\cosh\left[\kappa (x - x_{N+M+1})\right]}{\sinh(\kappa x_{N+M+1})} \sum_{m=2}^{N+M+1} (\tilde{\rho}_{m-1} - \tilde{\rho}_m) \sinh\left[\kappa x_{m-1}\right] \quad \text{(S3)}$$

, where $y_{1\le m\le N+M+1}(x) = y(x_{m-1} \le x \le x_m)$, $\tilde{\rho}_{1\le i\le N} = \rho_{1\le i\le N} / (2Fzc^{\infty})$, $\tilde{\rho}_{N+1} = 0$ and $\tilde{\rho}_{N+2\le u\le N+M+1} = \rho_{1\le j=u-N-1\le M} / (2Fzc^{\infty})$ with ρ_i and ρ_j defined in the main text.

2. Semi-analytical formulation of $\Pi(H)$, $\Delta G_{\text{el}}^{\text{p-p}}(H)$ and $\Delta G_{\text{el}}^{\text{sp-sp}}(H)$ within Debye-Hückel and Deryagin approximations under the conditions $\alpha_k \rightarrow 0$ and $\mu_k(y) \neq 1$.

For $y(x) << 1$, $\alpha_k \to 0$ and $\mu_k(y) \neq 1$, the linearized form of eq 14 in the space region $x_{m-1} \le x \le x_m$ with $m = 1,...,N+M+1$ is provided by

$$x_{m-1} \le x \le x_m: \qquad \frac{d^2 y_m(x)}{dx^2} - \kappa^2 \left[1 + \frac{\tilde{\rho}_m \gamma_m \tilde{\varepsilon}_m}{z(1+\gamma_m)^2}\right] y(x) = -\kappa^2 \frac{\tilde{\rho}_m}{(1+\gamma_m)}, \tag{S4}$$

In eq S4, $y_{1\le m\le N+M+1}(x)$ and $\tilde{\rho}_m$ are defined below eq S3 and $\tilde{\varepsilon}_{1\le i\le N} = \varepsilon_{1\le i\le N}$, $\tilde{\varepsilon}_{N+1} = 0$, $\tilde{\varepsilon}_{N+2\le m\le N+M+1} = \varepsilon_{j=m-N-1}$, $\gamma_{1\le m\le M+N+1} = 10^{-\tilde{\varepsilon}_m(\mathrm{p}\tilde{K}_m - \mathrm{pH})}$ with $\tilde{K}_{1\le i\le N} = K_{1\le i\le N}$, $\mathrm{p}\tilde{K}_{N+1} = 0$ and $\tilde{K}_{N+2\le m\le N+M+1} = K_{j=m-N-1}$. It is here recalled that index *i* and *j* pertain to layer *i* and *j* within interphase 1 and 2, respectively (see main text and Glossary therein). The solutions of eq S4 then read as

$$x_{m-1} \le x \le x_m: \qquad y_{1\le m\le N+M+1}(x) = A_m \cosh(\lambda_m x) + B_m \sinh(\lambda_m x) + \omega_m \tag{S5}$$

where A_m and B_m are constants to be determined and $\lambda_m = \kappa \left[1 + \frac{\tilde{\rho}_m \gamma_m \tilde{\varepsilon}_m}{z(1+\gamma_m)^2}\right]^{1/2}$, $\omega_m = \left(\frac{\kappa}{\lambda_m}\right)^2 \frac{\tilde{\rho}_m}{(1+\gamma_m)}$. Applying adequately the boundaries given by eqs 15-16 together with the continuity equations for the potential and electric field at the positions $x_{m=1,...,M+N+1}$, we show that the A_m and B_m are solutions of the algebraic equations written in the matrix form

$$T.\vec{S} = \vec{C}, \tag{S6}$$

where $\vec{S}$ and $\vec{C}$ are the $2(N+M+1)$ column vectors defined by

$$\vec{S} = \begin{pmatrix} A_1 \\ A_2 \\ \vdots \\ A_{N+M+1} \\ B_1 \\ B_2 \\ \vdots \\ B_{N+M+1} \end{pmatrix}, \quad \vec{C} = \begin{pmatrix} \omega_2 - \omega_1 \\ \omega_3 - \omega_2 \\ \vdots \\ \omega_{N+M+1} - \omega_{N+M} \\ 0 \\ \vdots \\ 0 \end{pmatrix} \tag{S7}$$

and T the $2(N+M+1) \times 2(N+M+1)$ matrix of which the elements $t_{i,j}$ are defined by the relationships

$$i = 1,...,N+M: \qquad \begin{cases} t_{i,i} = \cosh(\lambda_i x_i) \\ t_{i,i+N+M+1} = \sinh(\lambda_i x_i) \\ t_{i,i+1} = -\cosh(\lambda_{i+1} x_i) \\ t_{i,i+N+M+2} = -\sinh(\lambda_{i+1} x_i) \end{cases} \tag{S8-S11}$$

$$i = N + M + 1, ..., 2N + 2M : \begin{cases} t_{i,i-M-N} = \lambda_{i-N-M} \sinh\left(\lambda_{i-N-M} x_{i-N-M}\right) \\ t_{i,i+1} = \lambda_{i-N-M} \cosh\left(\lambda_{i-N-M} x_{i-N-M}\right) \\ t_{i,i-N-M+1} = -\lambda_{i-N-M+1} \sinh\left(\lambda_{i-N-M+1} x_{i-N-M}\right) \\ t_{i,i+2} = -\lambda_{i-N-M+1} \cosh\left(\lambda_{i-N-M+1} x_{i-N-M}\right) \end{cases} \quad \text{(S12-S15)}$$

$$t_{2N+2M+1,N+M+2} = 1 \quad \text{(S16)}$$

$$\begin{cases} t_{2N+2M+2,N+M+1} = \sinh\left(\lambda_{N+M+1} x_{N+M+1}\right) \\ t_{2N+2M+2,2N+2M+2} = \cosh\left(\lambda_{N+M+1} x_{N+M+1}\right) \end{cases} \quad \text{(S17-S18)}$$

and $t_{i,j} = 0$ for couples (i, j) which are not specified in eqs S8-S18. For a given separation distance $H = x_{N+1} - x_N$, the sets of solution A_m and B_m may be obtained from eqs S6-S18 using Newton-Raphson method.[1] Combining eq S5 and eq 21, we further obtain for the disjoining pressure

$$\Pi(H) = \frac{\kappa^2 \varepsilon_o \varepsilon_r}{2} \left(\frac{RT}{zF}\right)^2 \left\{\left[A_{N+1}(H)\right]^2 - \left[B_{N+1}(H)\right]^2\right\} \quad \text{(in N m}^{-2}\text{)} \quad \text{(S19)}$$

where we explicitly indicated that A_{N+1} and B_{N+1} both depend on H. Once $\Pi(H)$ determined, the integrations given by eqs 18-19 in the main text may be carried out using Simpson's rule,[1] which in turn yields $\Delta G_{el}^{p\text{-}p}(H)$ and $\Delta G_{el}^{sp\text{-}sp}(H)$.

3. Computation of 2D potential distribution between soft multi-layered particles using COMSOL Multiphysics environment.

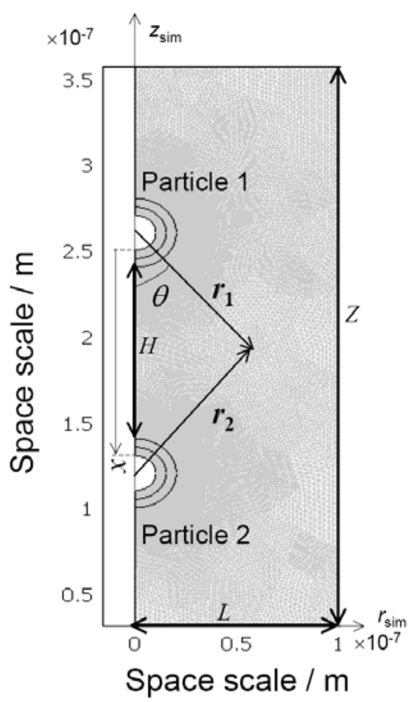

Figure S1. Typical simulation box used within Comsol Multiphysics environment for the evaluation of the potential distribution between two soft multi-layered particles separated by distance H. The example is given for the situation considered in Figure 9 of the main text ($N = 2$, $M = 2$). For the sake of convenience, calculations were performed in *axi-symmetric cylindrical geometry* with the coordinate system (r_{sim}, z_{sim}) as indicated in the figure. Because of symmetry argument, the problem is indeed invariant upon rotation around the axis r_{sim}=0. It was systematically verified that the obtained numerical solutions for the potential profiles were independent of the size/local density of the chosen mesh (an example of which is given in the figure) and size of the simulation box as subsumed in the variables L and Z. In particular for positions far from the particles, bulk condition for the electrostatic potential was assigned (*i.e.* $y \rightarrow 0$). The situation is therefore that of two spherical multi-layered particles enclosed in a large cylinder of height Z and radius L. Computation of the volume integral involved in eq 29 of the main text was of course performed using the appropriate integral definition in cylindrical geometry. Also, depending on the geometry adopted for the interacting systems (spherical or planar), eqs 33-36 or eqs 37-38 were expressed in terms of the coordinates (r_{sim}, z_{sim}) using straightforward geometrical relations existing between r_1, r_2, r_{sim}, z_{sim} or r_1, x, r_{sim}, z_{sim} where r_1, r_2 and x are defined in Figure 1 of the main text and are recalled in Figure S1.

References.

1. Press, W. H.; Teukolsky, S. A.; Vetterling, W. T.; Flannery, B. P. in *Numerical recipes in Fortran, The Art of Scientific Computing*, 2nd ed.; Cambridge University Press: New-York, 1986.