Supplemental Material

Anomalous Attachment Behavior of Nanoparticles inside Narrow Channels

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Exact evaluation of DL energies between two planar surfaces per unit area

The one-dimensional nonlinear PB equation was solved to exactly calculate DL interaction energies between two planar surfaces per unit area \((E_{DL})\) by using the method of Devereux and de Bruyn (1963). Briefly, the nonlinear PB equation is written as

\[
\frac{d^2 \Psi}{d \xi^2} = \sinh \Psi \quad [S1]
\]

where \(\xi (= \kappa x, \kappa \) is inverse Debye screening length and \(x\) is distance from an interacting planar surface) is dimensionless distance, \(\Psi\) is dimensionless potential, given by

\[
\Psi = \frac{ve\psi}{kT} \quad [S2]
\]

where \(v\) is valence of ions in the electrolyte, \(e\) is charge of a proton, \(\psi\) is electrostatic potential in the double layer. Equation [S1] can be solved by using the following boundary conditions:

\[
\begin{align*}
\Psi &= \Psi_p \quad \text{at } \xi = 0 \\
\Psi &= \Psi_d \quad \text{at } \xi = \xi_{H} \\
\end{align*} \quad [S3]
\]

which correspond to the conditions:

\[
\begin{align*}
\psi &= \psi_p \quad \text{at } x = 0 \\
\psi &= \psi_d \quad \text{at } x = h \\
\end{align*} \quad [S4]
\]

where \(h\) is separation distance between the two planar surfaces. By integrating Equation [S1] once, the following equation can be obtained:

\[
\frac{d \Psi}{d \xi} = \pm \sqrt{2 \cosh \Psi + C} \quad [S5]
\]

where \(C\) is an integration constant.

When both interacting planar surfaces are positively charged and the value of \(\psi_p\) is greater than \(\psi_d\), the following expressions that describe the dimensional distance as a function of dimensionless potential can be derived from Equation [S5] for three ranges of \(C\):
\[ \xi = 2\exp\left(-\frac{\Psi_{mn}}{2}\right)\left[F\left[\exp(-\Psi_{mn}), \sin^{-1}\left(\sqrt{\exp(\Psi_{mn} - \Psi)}\right)\right] - F\left[\exp(-\Psi_{mn}), \sin^{-1}\left(\sqrt{\exp(\Psi_{mn} - \Psi_p)}\right)\right]\right] \]

where \( F \) represents the elliptic integral of the first kind, \( \Psi_{mn} \) is the minimum dimensionless potential between the two interacting surfaces for a given value of \( h \) in Equation [S6] or an imagined minimum dimensionless potential beyond the interacting surfaces in Equation [S7] (Devereux and de Bruyn, 1963). \( \Psi_{mn} \) and \( b \) are related to \( C \) by the following expressions:

\[ C = -2\cosh(\Psi_{mn}) \quad [S10] \]
\[ b = \sqrt{\frac{C}{2} + \frac{1}{2}\sqrt{C^2 - 4}} \quad [S11] \]

Substituting \( \xi_H \) and \( \Psi_d \) into Equations [S6]-[S9], the value of \( C \) (or \( \Psi_{mn} \) and \( b \)) can be obtained through iteration. Note that in order to decide which of these equations to use to obtain \( C \) for a given \( h \), the separation distance \( h_1 \) (or \( \xi_{h_1} = \kappa h_1 \)) corresponding to \( C=2 \) and the separation distance \( h_2 \) (or \( \xi_{h_2} = \kappa h_2 \)) corresponding to \( C=-2 \) have to be determined firstly.

The expressions used to determine \( \xi_{h_1} \) and \( \xi_{h_2} \) are in the following

\[ \xi_{h_1} = F\left[0, \pi - 2\tan^{-1}\left(\sqrt{\frac{\Psi_d}{2}}\right)\right] - F\left[0, \pi - 2\tan^{-1}\left(\sqrt{\frac{\Psi_p}{2}}\right)\right] \quad [S12] \]
\[ \xi_{h_2} = \ln\left[\frac{1 - \exp(-\Psi_p / 2)}{1 + \exp(-\Psi_p / 2)}\right] \quad [S13] \]

Equation [S8] and [S9] are used for \( \xi_{h_1} \leq \xi \leq \xi_{h_2} \) and \( \xi \leq \xi_{h_1} \), respectively. To determine
which equation (i.e., Equation [S6] or [S7]) to use to calculate \( \Psi_{\text{min}} \) at \( C \leq 2 \), an additional expression has to be adopted to determine \( \xi_{\text{min}} \) (i.e., the dimensionless distance at which the potential reaches minimum), given by

\[
\xi_{\text{min}} = 2\exp\left(-\frac{\Psi_d}{2}\right)\left[F\left(\exp(-\Psi_d), \frac{\pi}{2}\right) - F\left(\exp(-\Psi_d), \sin^{-1}\sqrt{\exp(\Psi_d - \Psi_p)}\right)\right]
\]

[S14]

Equation [S6] and [S7] are used to calculate \( \Psi_{\text{min}} \) or \( C \) at \( C \leq 2 \) for \( H_2 \leq \xi \leq \xi_{\text{min}} \) and \( \xi \geq \xi_{\text{min}} \), respectively.

If \( \Psi_{\text{min}} \) was obtained using Equation [S7] at \( C \leq 2 \), the value of \( E_{\text{DL}} \) can then be calculated using the following expression for \( C \leq 2 \):

\[
E_{\text{DL}} = -\frac{2nkT}{\kappa} \left[ \frac{\xi_{\text{min}}}{2} \left( 3\exp\Psi_{\text{min}} - 2 - \exp(-\Psi_{\text{min}}) \right) + 2\sqrt{2\cosh\Psi_p - 2\cosh\Psi_{\text{min}}} 
- 2\sqrt{2\cosh\Psi_d - 2\cosh\Psi_{\text{min}}} + 4\exp\left(\frac{\Psi_{\text{min}}}{2}\right) \left( E\left(\exp(-\Psi_{\text{min}}), \sin^{-1}\sqrt{\exp(\Psi_{\text{min}} - \Psi_p)}\right)\right) \right] - E^\infty_{\text{DL}}
\]

[S15]

where \( E \) represents the elliptic integral of the second kind, \( E^\infty_{\text{DL}} \) is the differential interaction energy when the separation distance is infinite, which is given by

\[
E_{\text{DL}} = -\frac{2nkT}{\kappa} \left[ 8 - 4\cosh(\frac{\Psi_p}{2}) - 4\cosh(\frac{\Psi_d}{2}) \right]
\]

[S16]

If \( \Psi_{\text{min}} \) was obtained using Equation [S6] (i.e., when \( \Psi_{\text{min}} \) is located beyond the interacting surfaces), the following expression has to be used to calculate \( E_{\text{DL}} \):

\[
E_{\text{DL}} = -\frac{2nkT}{\kappa} \left[ \frac{\xi_{\text{min}}}{2} \left( 3\exp(p) - 2 - \exp(-p) \right) + 2\sqrt{2\cosh\Psi_p - 2\cosh(p)} 
- 2\sqrt{2\cosh\Psi_d - 2\cosh(p)} + 4\exp\left(\frac{p}{2}\right) \left( E\left(\exp(-p), \sin^{-1}\sqrt{\exp(\frac{p - \Psi_p}{2})}\right)\right) \right] - E^\infty_{\text{DL}}
\]

[S17]
where \( p = \cosh^{-1}\left(-\frac{C}{2}\right) \).

By using Equation [S8] and [S9] to calculate \( C \), the following expressions can then be used to calculate \( E_{DL} \) at \(-2 \leq C \leq 2\) and \( C \geq 2\):

\[
E_{DL} = -\frac{2nkT}{\kappa} \left( \varepsilon_0 \left( \frac{C}{2} - 1 \right) - 2\sqrt{2} \sqrt{\frac{\cosh \Psi_p - 1}{\cosh \Psi_p + 1}} \frac{\cosh \Psi_p - 1}{\cosh \Psi_p + 1} \right) - 2\sqrt{2} \frac{\cosh \Psi_p - 1}{\cosh \Psi_p + 1} + 4 \left( 2E \left( \frac{2-C}{4}, \frac{\pi}{2} \right) \right) \text{ at } -2 \leq C \leq 2 \quad [S19]
\]

\[
E_{DL} = -\frac{2nkT}{\kappa} \left[ \varepsilon_0 \left( \frac{1}{2} - \frac{C}{2} \right) - 2\sqrt{2} \cosh \Psi_p + C + 2\sqrt{2} \cosh \Psi_d + C \right.
- \left. 4\exp\left( \frac{\Psi_p}{2} \right) \sqrt{\frac{1}{b^2 + \exp \Psi_p}} + 4\exp\left( \frac{\Psi_d}{2} \right) \sqrt{\frac{1}{b^2 + \exp \Psi_d}} \right) \text{ at } -2 \leq C \leq 2 \quad [S20]
\]

\[
+ 4b \left( E \left\{ \sqrt{1 - \frac{1}{b^2}}, \tan^{-1} \left[ \exp\left( -\frac{\Psi_d}{2} \right) \right] \right\} - E \left\{ \sqrt{1 - \frac{1}{b^2}}, \tan^{-1} \left[ \exp\left( -\frac{\Psi_p}{2} \right) \right] \right\} \right) \right) - E_{DL}^e
\]

It should be noted that the aforementioned method can also be used to calculate \( E_{DL} \) for \( \psi_p < \psi_d \) and for two negatively charged surfaces since the energy of a system can depend ultimately on neither the spatial coordinates of the system nor the sign conventions used to describe the system and surface charge (Devereux and de Bruyn, 1963).

**LSA expression for calculating DL energies between two planar surfaces per unit area**

\[
E_{DL}^{LSA} = 32\varepsilon_0\kappa \tanh(\Psi_p) \tanh(\Psi_d) \left( \frac{kT}{\varepsilon_0} \right)^2 \exp(-\kappa h) \quad [S21]
\]

where \( \varepsilon_0 \) is the dielectric permittivity in vacuum, \( \varepsilon \) is the relative dielectric permittivity of solvent.
Table S1. Zeta potentials (mV) of silica and iron oxide NPs, and nanotubes.

<table>
<thead>
<tr>
<th>IS (mM)</th>
<th>silica NPs</th>
<th>iron oxide NPs</th>
<th>nanotubes</th>
</tr>
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<tbody>
<tr>
<td>1</td>
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<td>-32.5</td>
</tr>
<tr>
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<td>-9.8</td>
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Figure S1. Calculated values of $U_{\text{pri}}$, $U_{\text{max}}$, and $U_{\text{sec}}$ for a silica NP with different diameters inside a channel of 80 nm inner diameter at different ISs. The thickness of the channel ($L$) is 5 nm.
Figure S2. Calculated values of $U_{\text{pri}}$, $U_{\text{max}}$, and $U_{\text{sec}}$ for a 70 nm silica NP inside a channel of 80 nm inner diameter with different thicknesses ($L$).
Figure S3. DLVO energy profiles for a 70 nm iron oxide NP interacting with (a) a negatively charge flat plate or inside a negatively charged channel of (b) 74 nm or (c) 200 nm inner diameter along a radial direction at various ISs. The Hamaker constant for the iron oxide-water-carbon system was taken as $1.76 \times 10^{-19}$ J (Wang et al., 2017), $L=5$ nm.
Figure S4. DLVO interaction energy profiles for a 70 nm iron oxide NP interacting with (a) a negatively charged flat plate or inside a negatively charged channel of (b) 74 nm or (c) 200 nm inner diameter along a radial direction at various ISs. L=5 nm.
Figure S5. DLVO energy profiles for a 70 nm silica NP outside a channel of (a) 74 nm or (b) 200 nm inner diameter at various ISs. $L=5$ nm.
Figure S6. Calculated values of $U_{\text{pri}}$, $U_{\text{max}}$, and $U_{\text{sec}}$ for a 70 nm silica NP outside a channel of 80 nm inner diameter with different thicknesses ($L$).
Figure S7. Calculated values of $U_{pri}$, $U_{max}$, and $U_{sec}$ for a 70 nm silica NP interacting with a channel of different inner diameters at different ISs. The thickness of the tube is 5 nm. The LSA expression (Equation [S21]) was used to calculate DL interaction.
Calculated values of $U_{pri}$, $U_{max}$, and $U_{sec}$ for a 70 nm silica NP interacting with a channel of different inner diameters at different ISs. The thickness of the tube is 5 nm. The value of $U^T$ was calculated as a sum of $U^{VDW}$, $U^{DL}$, and $U^{HR}$. $U^{HR}$ is hydration repulsion energy, which was calculated as $l_0P_0\exp(-h/l_0)$, where $l_0$ is a characteristic decay length, taken as 0.17 nm (Pazmino et al., 2014) and $P_0$ is a constant having the dimension of pressure, taken as $1.15\times10^8$ N/m$^2$ (Nabika et al., 2008).
References


