Supporting Information

Nano-ellipsoids at fluid-fluid interface: effect of surface charge on adsorption, buckling and emulsification

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DLVO interaction calculation:

When a charged particles is approaching a fluid-fluid interface, it exhibits different type of interactions near the interface. These interactions are 1) interaction between the particles and interface 2) interaction between the particle and the image charge. The overall interaction between the interface and particles is the sum of van der waal and electrostatic interaction between the particles and interface. In case of charged particle, the image charge effect is an important phenomenon to understand the adsorption of particles at interface.\(^1\) If a charged particle moving from the high dielectric medium (water dielectric constant ~78) to the low dielectric medium (air or oil), the particle experience a same image charge on the other side. These electrostatic interactions are called as image charge interaction. The nature of the image charge interaction depends on the image charge sign. The image charge is given as\(^1\)

\[
q_{\text{image}} = q \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2}
\]  

(S1)

Where, \(\varepsilon_1\) is the medium dielectric constant which contains the charged particle and \(\varepsilon_2\) is the particle free medium dielectric constant. The overall interaction near the interface is the sum of particle-interace and image charge interaction.
Fig. S1 Schematic diagram of image charge interaction at oil-water interface. Image charge interactions are calculated for side by side configuration. The distance between the real and image charge particles is \( l \). Particle-interface interactions are calculated for the configuration of particle major axis parallel to the interface. The distance between the particle and interface is \( l/2 \).

The overall interactions between anisotropic particles depend on the orientation of the particles. The schematic diagram of image charge interaction at oil-water interface is shown in Fig. S1. The pair wise interaction between ellipsoid particles is calculated by using the Derjaguin’s approximation. This method is applicable if the separation distances are smaller than the particle size. The particle-particle interaction is estimated by
\[
U = \frac{2\pi}{\sqrt{K_a + K_b + 2H_aH_b - 2S_{ab}}} \int_0^\infty w(z)dz \hspace{2cm} (S2)
\]

where

\[
S_{ab} = \sqrt{(H_a^2 - K_a)(H_b^2 - K_b)} \hspace{2cm} (S3)
\]

\(k_i\) and \(H_i\) are Gaussian and mean curvature of ellipsoidal particle at point \(T_i\) \((i=a,b)\), and \(w(z)\) is the interaction potential between the flat surfaces. Similarly, the interaction between the particle and interface is calculated by

\[
U = \frac{2\pi A^2 B}{A^2 \sin^2 \eta + B^2 \cos^2 \eta} \int_0^\infty w(z)dz \hspace{2cm} (S4)
\]

Where \(\eta\) is the angle between the interface and particle, \(B\) and \(A\) are the length of major and minor axes of the ellipsoid respectively. The particle-particle and particle-interface interactions are calculated by substituting the \(w(z)\) in eq \((S2)\) and eq\((S4)\) respectively. The electrostatic interaction between the flat plate is given by

\[
w_e(d) = \frac{2\varepsilon \phi \phi_i}{k_d} \exp\left(-\frac{l}{k_d}\right) \hspace{2cm} (S5)
\]

Where, \(\varepsilon\) is the product of water dielectric constant and vacuum permittivity, \(\phi\) is the surface potential on the particle or interface (i.e. image charge interaction: 1- particle and 2- image charge; particle-interface interaction: 1-particle and 2- interface), \(k_d\) is the Debye length, and \(l\) is the surface to surface distance. The van der waal interaction between the flat plate is

\[
w_v(z) = \frac{H}{12\pi d^2} \hspace{2cm} (S6)
\]
Where, $H$ is the Hamaker constant of the system, $d$ is the distance between the surfaces. The image interactions are calculated for side by side configuration and particle-interface interactions are calculated for major axis parallel to interface. Hematite particles charge at different pH is measured at 1mM salt concentration and interface charge from literature. The angle between the particle and interface is $\eta = 90^\circ$. The overall interaction is calculated for pH 2, 4 and 6.5 and shown in Fig. S2, S3 and S4. The Hamaker constant for particle-oil across water is calculated by using mixing rule.

\[
H_{wp} = \left(\sqrt{H_{oo}} - \sqrt{H_{ww}}\right)\left(\sqrt{H_{pp}} - \sqrt{H_{ww}}\right)
\]  

(S7)

Where, $H_{oo}, H_{ww}$ and $H_{pp}$ are the Hamaker constants of decane, water and hematite across the vacuum, respectively.$^3$
Fig. S2 Overall DLVO and image charge interaction near the interface at pH 2.

![Graph](image1)

Fig. S3 Overall DLVO and image charge interaction near the interface at pH 4.

![Graph](image2)

Fig. S4 Overall DLVO and image charge interaction near the interface at pH 6.5.

![Graph](image3)
Reference