Supporting Information

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

Venkateshwar Rao Dugyala, Thiriveni G. Anjali, Siliveru Upendar, Ethayaraja Mani, Madivala G. Basavaraj
Polymer Engineering and Colloid Science Llab (PECS Lab), Department of Chemical Engineering,
Indian Institute of Technology Madras, Chennai-600036, India

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 particlesand 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]

$$q_{image} = q\frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \quad \text{(S1)}$$

Where, ε_1 is the medium dilectric constant which contains the charged particle and ε_2 is the particle free medium dielectric constant. The overall interaction near the interfcae is the sum of particle-interace and image charge interaction.

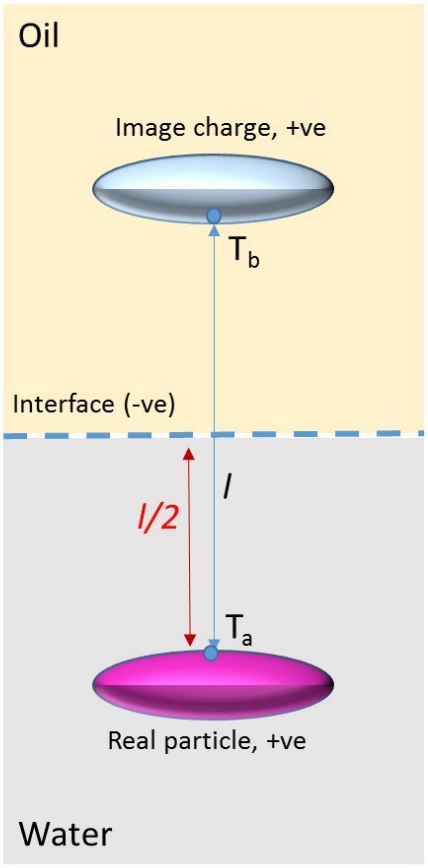

Fig. S1 Schematic diagram of image charge interaction at oil-water interface. Image charge interactions are calculated for side by side configuration. The distance between the real and image charge particles is *l*. Particle-interface interactions are calculated for the configuration of particle major 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.[2] This method is applicable if the separation distances are smaller than the particle size. The particle-particle interaction is estimated by

$$U = \frac{2\pi}{\sqrt{K_a + K_b + 2H_aH_b - 2S_{ab}}} \int_d^\infty w(z)dz \tag{S2}$$

where

$$S_{ab} = \sqrt{\left(H_a^2 - K_a\right)\left(H_b^2 - K_b\right)} \tag{S3}$$

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 surfces. Similary, the interaction between the particle and interfcae is calculated by

$$U = \frac{2\pi A^2 B}{A^2 \sin^2\eta + B^2 \cos^2\eta} \int_d^\infty w(z)dz \tag{S4}$$

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

$$w_e(d) = \frac{2\varepsilon\phi_1\phi_2}{k}\exp\left(-\frac{l}{k}\right) \tag{S5}$$

Where, ε is the product of water dielectric constant and vacuum permitvity, ϕ is the surface potential on the particle or interfcae (i.e image charge interaction: 1- particle and 2- image charge ; particle-interface interaction: 1-particle and 2- interface), $k$is the Debye length, and $l$is the surface to surface distance. The van der waal interaction between the flat plate is

$$w_v(z) = \frac{H}{12\pi d^2} \tag{S6}$$

Where, H is the Hamker 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 differnet pH is measured at 1mM salt concentration and interface charge from literature. The angle between the particle and interface is $\eta = 90^{0}$. The overall interaciton is calculated for pH 2, 4 and 6.5 and shown in Fig. S2, S3 and S4.The Hamaker constant for partcle-oil across water is calculated by using mixing rule.

$$H_{owp} = \left(\sqrt{H_{oo}} - \sqrt{H_{ww}}\right)\left(\sqrt{H_{pp}} - \sqrt{H_{ww}}\right) \quad \text{(S7)}$$

Where, H_{oo}, H_{ww} and H_{pp} are the Hamker constants of decance, water and hematitie across the vacuum, respectively.[3]

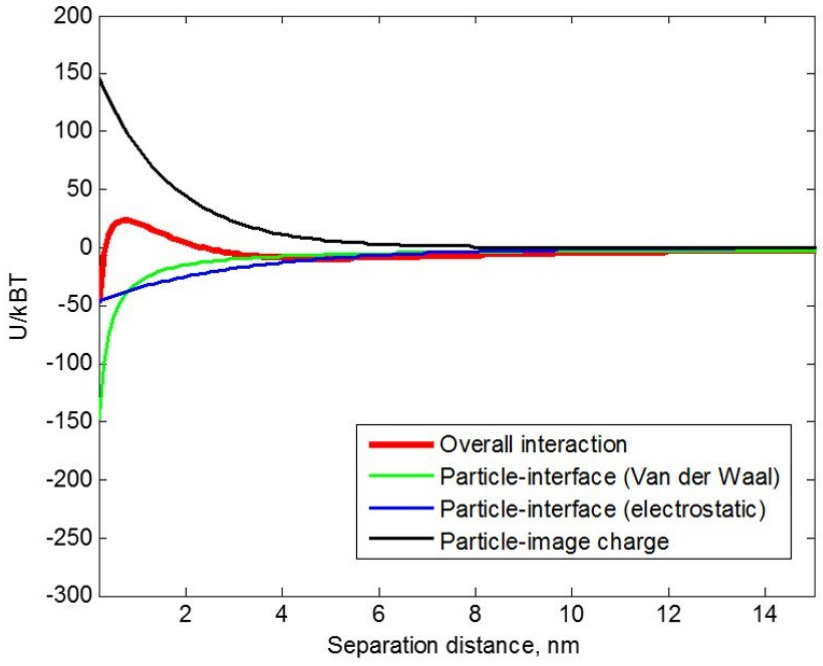

Fig. S2 Overall DLVO and image charge interaction near the interface at pH 2.

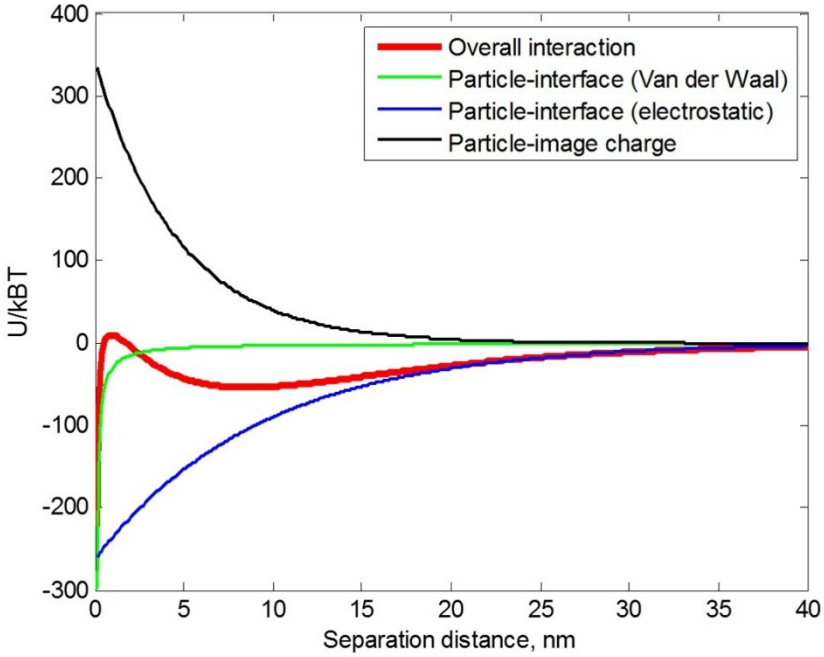

Fig. S3 Overall DLVO and image charge interaction near the interface at pH 4.

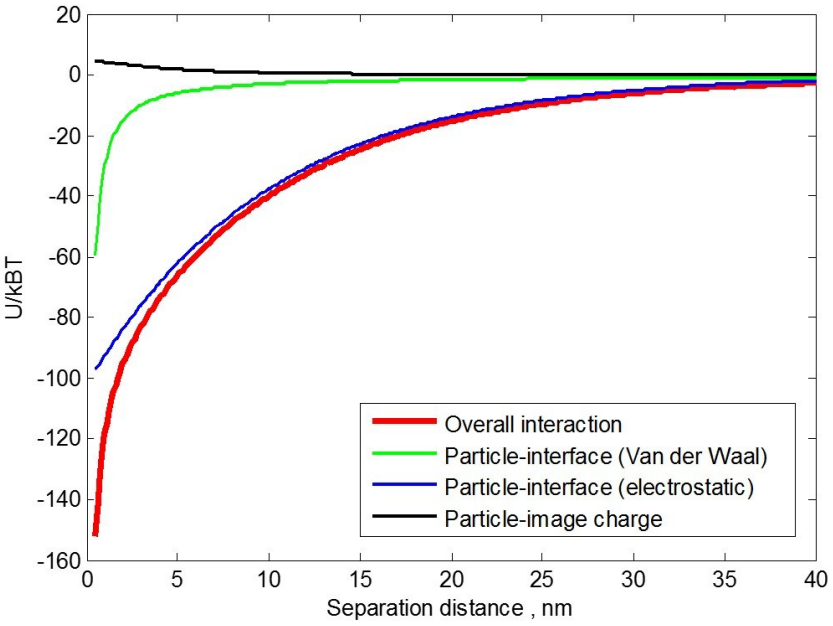

Fig. S4 Overall DLVO and image charge interaction near the interface at pH 6.5.

Reference

1. H. Wang, V. Singh and S. H. Behrens, *The Journal of Physical Chemistry Letters*, 2012, 3, 2986-2990.
2. P. Schiller, S. Kruger, M. Wahab and H.-J. Mögel, *Langmuir*, 2011, 27, 10429-10437.
3. J. N. Israelachvili, *Intermolecular and surface forces: revised third edition*, Academic press, 2011.