

Supplementary Information

Reversibility of NP localization at an ITIES was theoretically predicted^{1,2} by calculating the absorption isotherm using the following procedure. The free energy for a single NP as a function of distance from the interface includes the contribution of the surface tension W_{cap} , the solvation energy W_{solv} , the potential energy of the charged particle in the external electric field present in the interfacial region W_{ext} , and the three phase line tension W_{line} .

$$\begin{aligned}
 W &= W_{\text{cap}} + W_{\text{solv}} + W_{\text{ext}} + W_{\text{line}} \\
 W_{\text{cap}} &= -\pi R^2 \sigma_{12} \left(\frac{4 \cos \theta_{\text{contact}}}{1 + \exp(-2x/R)} + \exp(-x^2/R^2) \right) \\
 W_{\text{solv}} &= k_B T \frac{z^2 L_B}{2R} \frac{1}{1 + \exp(-x/R)} \left(\frac{\epsilon_1}{\epsilon_2} \frac{1}{1 + \kappa_2 R} - \frac{1}{1 + \kappa_1 R} \right) \\
 W_{\text{ext}} &= \int_{-\infty}^{\infty} dX \Phi(X) \rho(x - X) \\
 \frac{e\Phi(x)}{k_B T} &= 4 \tanh^{-1} \left(e^{\kappa_1 x} f_1 \left(\frac{eV}{k_B T} \right) \right) \Theta(-x) + \left[\frac{eV}{k_B T} - 4 \tanh^{-1} \left(e^{-\kappa_2 x} f_2 \left(\frac{eV}{k_B T} \right) \right) \right] \Theta(x) \\
 W_{\text{line}} &= 2\pi R \mu \exp \left(-\frac{x^2}{R^2} \right)
 \end{aligned}$$

where x is the position of the NP centre with respect to the interface, in water for $x < 0$ and in oil for $x > 0$, R the radius of the NP, σ_{12} the surface tension between the two media, θ_{contact} the contact angle though the oil, $z = -q_{\text{np}}/e$ is the average number of electrons on a NP, $\epsilon_{1,2}$ the dielectric constants of the two media, $\kappa_{1,2}$ the inverse Debye lengths in the media, $L_B = e^2/(\epsilon_1 k_B T)$ the Bjerrum length in water, and μ the line tension. V is the potential drop between oil and water, and $\Phi(x)$ is the potential profile, obtained from the Verwey-Niessen³ expression for the electrostatic potential for two diffuse double layers. The contributions are smeared over the size of the particle, giving rise to the exponential dependences on R .

$$\begin{aligned}
 f_1(v) &= \frac{\sqrt{1 + \tau e^{v/2}} - \sqrt{1 + \tau e^{-v/2}}}{\sqrt{1 + \tau e^{v/2}} + \sqrt{1 + \tau e^{-v/2}}} \\
 f_2(v) &= \frac{\sqrt{\tau + e^{v/2}} - \sqrt{\tau + e^{-v/2}}}{\sqrt{\tau + e^{v/2}} + \sqrt{\tau + e^{-v/2}}} \\
 \tau &= \frac{\epsilon_2 \kappa_2}{\epsilon_1 \kappa_1} \\
 \rho(x) &= \frac{2z}{\pi R^2} \sqrt{R^2 - x^2} \Theta(R^2 - x^2)
 \end{aligned}$$

The applied voltage tunes the depth of the energy well at the ITIES and the relative magnitudes of the two barriers on either side of the well. Depending on the system parameters (NP size and charge, contact angle with the two liquids, magnitude and polarity of the applied field) a stable or metastable bound state for the NP arises at the interface.

Localized NPs interact pairwise exclusively via screened electrostatic forces. This interaction, together with the single particle energy profile, leads to the formulation of an absorption isotherm. The coverage of an ITIES as a function of the applied potential is implicitly given by:

$$-u = \ln\left(\frac{\Gamma}{1-\Gamma}\right) + \frac{L_B Z^2 \Gamma}{4R^5 \kappa^4} \left(1 + \frac{\kappa R}{\sqrt{\Gamma}}\right)^2 \exp\left(-2\kappa R \left(\frac{1}{\sqrt{\Gamma}} - 1\right)\right)$$

where $\Gamma = N/N_{\max}$ is the coverage of the interface, with N the number of particles localized at the interface and N_{\max} the number of particles required to form a full monolayer. $-u$ is the energy difference between the depth of the energy well and the height of the barrier for desorption, in units of $k_B T$, obtained from the single particle profile as a function of the applied potential V . Polarizing the aqueous phase negatively relative to the oil phase increases the coverage of the interface, whereas sufficiently positive polarizations draw the particles away from the interface, into the water.

References

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- 3 E. Verwey and K. Niessen, *Phil. Mag.*, 1939, **28**, 435–446.