Supplementary Information

Nanoparticle-stabilised emulsions: droplet armouring vs. droplet bridging

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DLVO model:

- **Debye length:**

The inverse Debye length (κ) is computed from the following equation for each ionic strength [1, 2]

$$\kappa = \sqrt{\frac{\sum_i (z_i e)^2 C_i^*}{\varepsilon_0 \varepsilon_r k_B T}} \tag{S1}$$

where e is the elementary charge (i.e., 1.602x10^{-19} C), z is the valance charge of ions (i.e., one for NaCl), C_i^* is the number concentration of ions (in m^3) which varies with ionic strength.

- **Derivation of hydrophobic energy for two interacting oil drops:**

An exponential form for hydrophobic interaction energy ($\phi_{hydrophobic}$) per unit area between two semi-infinite plates is shown to be more accurate than a power law. This exponential form is reported below [3]

$$\left[d\phi_{hydrophobic}(x)\right]_{plate-plate} = -\frac{2\gamma_{ow}}{D_0}\exp\left(-x/D_0\right)dx \tag{S2}$$

$$\Rightarrow \left[\phi_{hydrophobic}(h)\right]_{plate-plate} = -\frac{2\gamma_{ow}}{D_0}\int_h^\infty \exp\left(-x/D_0\right)dx = -2\gamma_{ow}\exp\left(-h/D_0\right) \tag{S3}$$

For hydrophobic force ($F_{hydrophobic}$) between two identical spheres (with a radius of R) we approximately have

$$\left[F_{hydrophobic}(h)\right]_{sphere-sphere} = 2\pi R\left[\phi_{hydrophobic}(h)\right]_{plate-plate} \tag{S4}$$

$$\Rightarrow \left[F_{hydrophobic}(h)\right]_{sphere-sphere} = -4\pi\gamma_{ow}R\exp\left(-h/D_0\right) \tag{S5}$$

Using the Derjaguin approximation (i.e., $\phi(h) = \int_h^\infty F(x)dx$), one finds

$$\Rightarrow \left[\phi_{hydrophobic}(h)\right]_{sphere-sphere} = -4\pi\gamma_{ow}D_0R\exp\left(-h/D_0\right) \tag{S6}$$

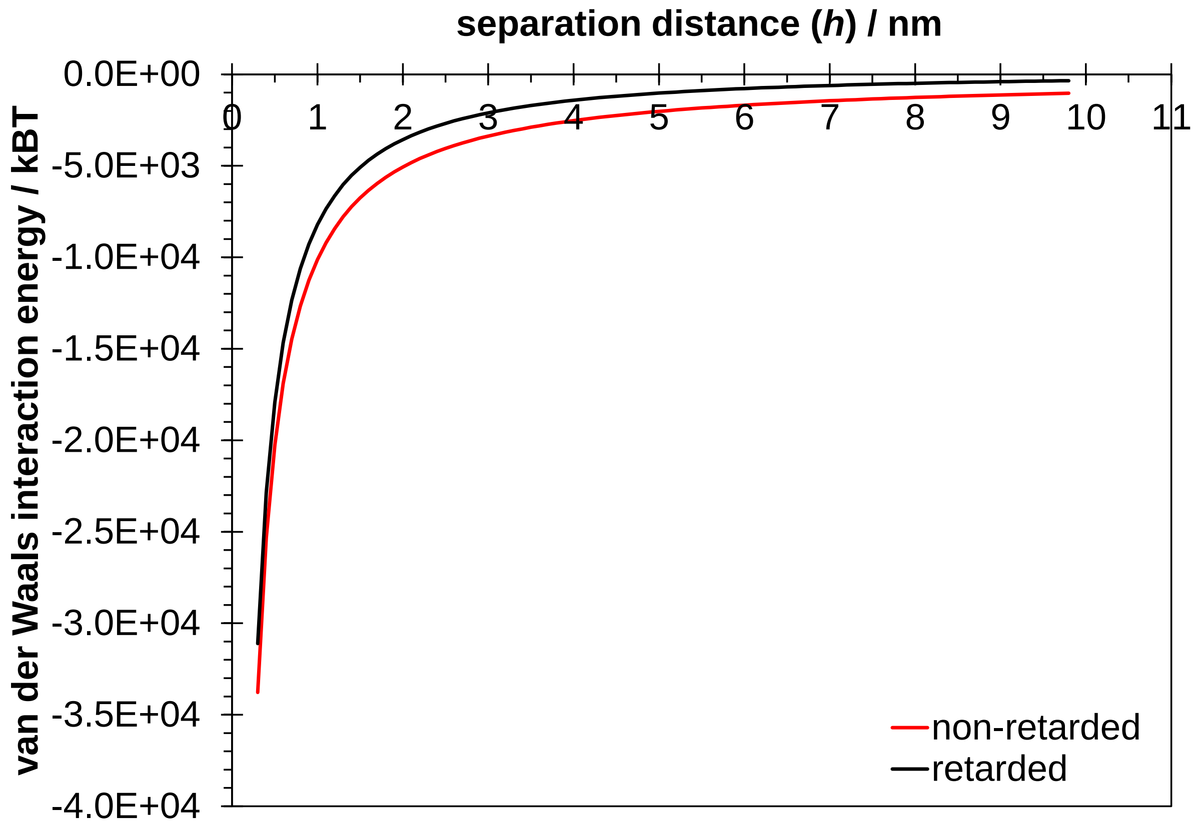

Fig. S1. Van der Waals interaction energy as a function of separating distance between two hexadecane drops with a diameter of 100 μm interacting across water. Non-retarded profile (red line) is from Eq. (2) and retarded profile (black line) is from Eq. (4) in the manuscript.

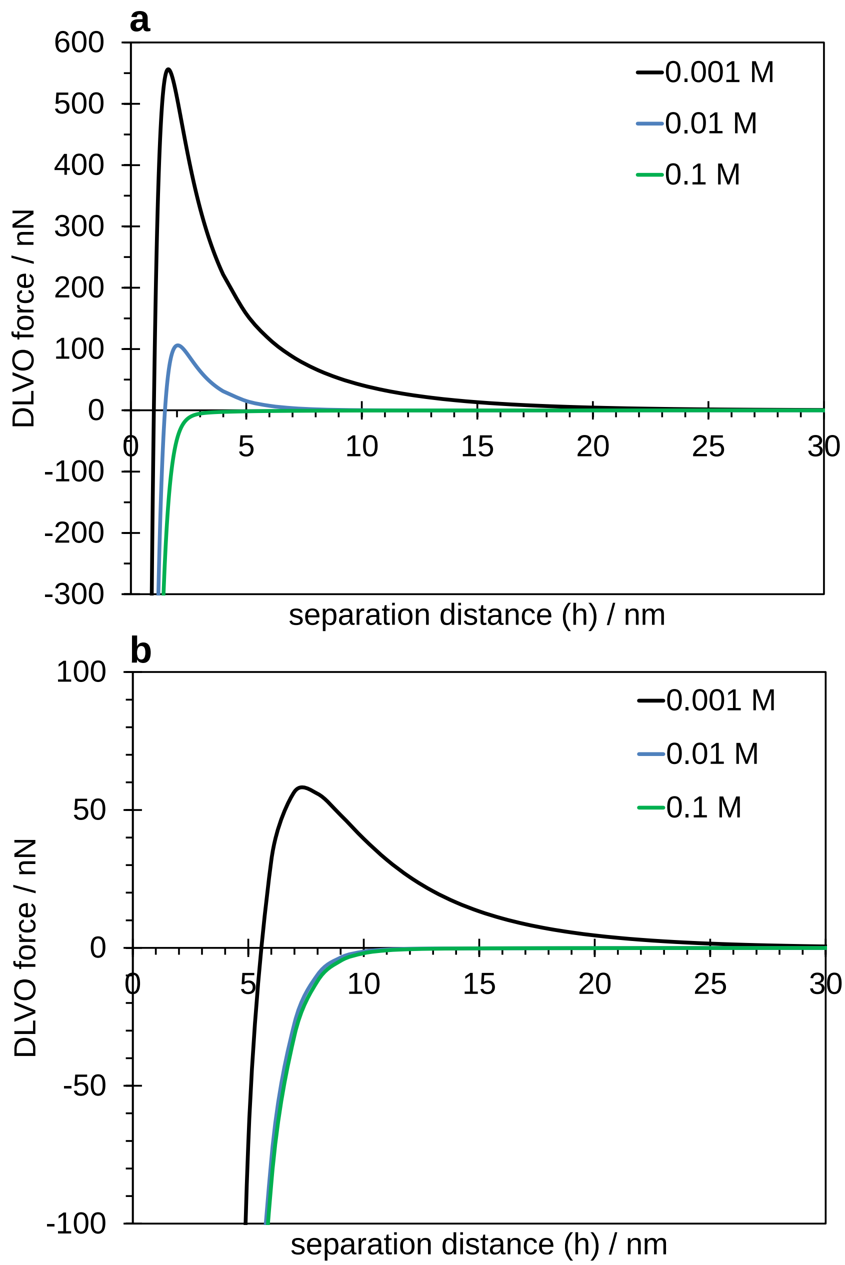

Fig. S1. Net interaction force ($f_{DLVO}(h)$) between two identical hexadecane drops (with a diameter of 100 μm) separated by *h* that are interacting through water computed from $df_{DLVO}(h) = -{d\phi_{total}(h)}/{dh}$ [2] (see below) at three different ionic strengths. (a) $D_0 = 0.3$ nm and (b) $D_0 = 1$ nm. Buoyancy ($f_b = (4/3)\pi r^3 \Delta\rho g$) and particle detachment ($f_{det} = 2\pi r \gamma_{ow} \cos^2(\theta/2)$) forces are found to be 1.2 nN and 21 nN, respectively.

- **Derivation of DLVO interaction forces for two interacting oil drops:**

Net interaction force ($f_{DLVO}(h)$) is computed from $df_{DLVO}(h) = -{d\phi_{total}(h)}/{dh}$ [2] as follows:

$$f_{DLVO}(h) = -\frac{d\phi_{total}(h)}{dh} = -\left(\frac{d\phi_{elec}(h)}{dh} + \frac{d\phi_{vdW}^{non-re}(h)}{dh} + \frac{d\phi_{hydrophobic}(h)}{dh}\right) \tag{S7}$$

$$\frac{d\phi_{elec}(h)}{dh} = -4\pi\varepsilon_0\varepsilon_r R\psi_o^2\kappa\frac{\exp(-2\kappa h)}{1-\exp(-2\kappa h)} \tag{S8}$$

$$\frac{d\phi_{vdW}^{non-re}(h)}{dh} = \frac{RH_{121}}{12h^2} \tag{S9}$$

$$\frac{d\phi_{hydrophobic}(h)}{dh} = 4\pi\gamma_{ow}R\exp\left(-{h}/{D_0}\right) \tag{S10}$$

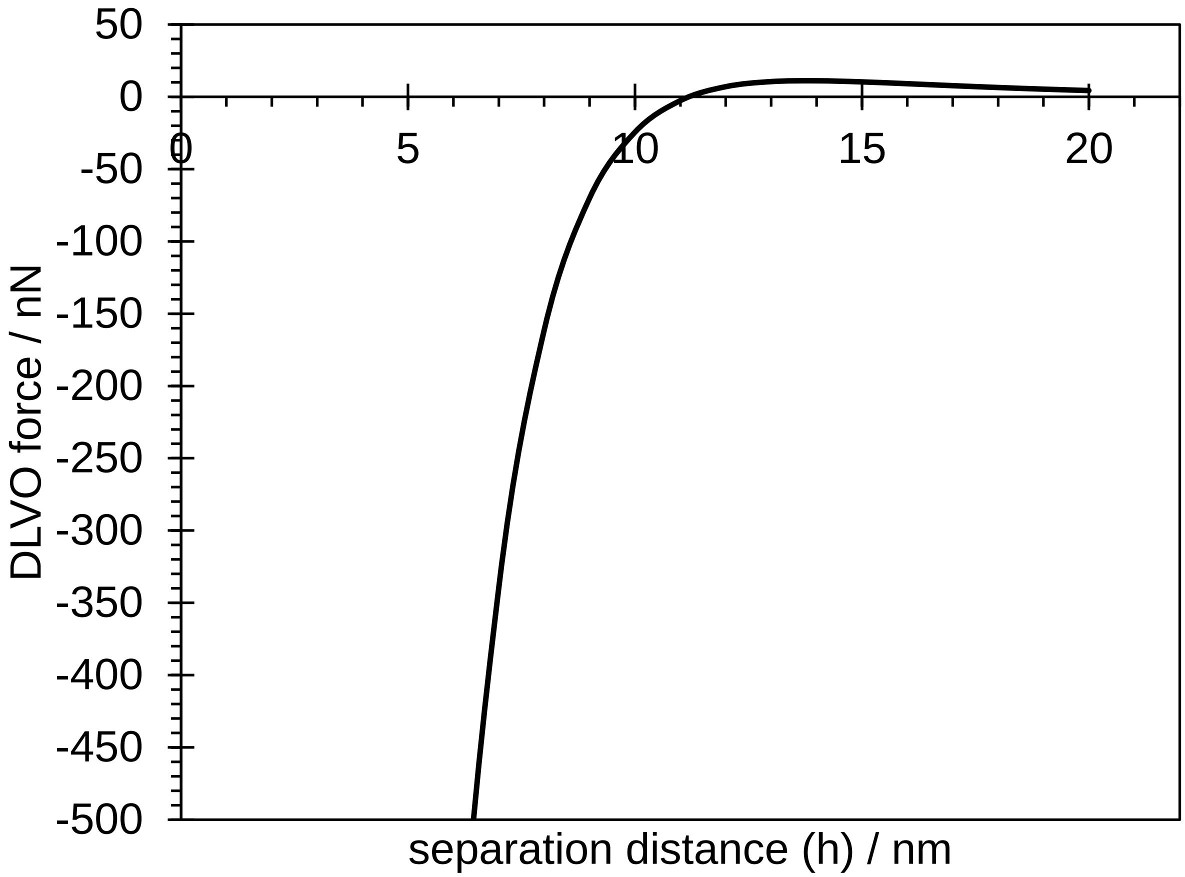

Fig. S3. DLVO forces computed from $df_{DLVO}(h) = -{d\phi_{total}(h)}/{dh}$ considering long-range ($D_0 = 1.6$ nm) hydrophobic decay length as suggested in Boyson and Pashley [4]. The profile is plotted for ionic strength of 0.001 M.

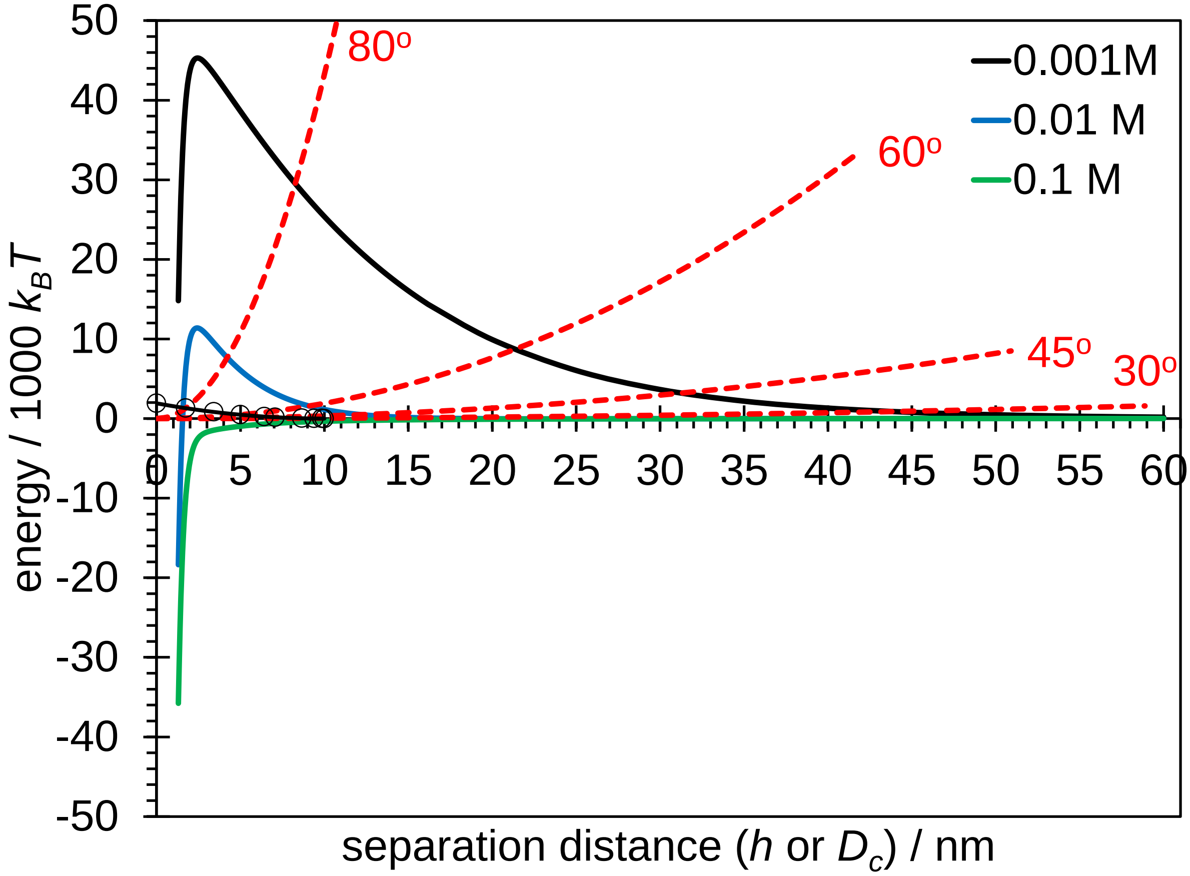

Fig. S4. Solid lines: Net interaction energy ($\phi_{total}(h)$) between two identical hexadecane drops (with a diameter of 100 µm) separated by h that are interacting through water. Computation is conducted by summation of Eqs. 1, 3, and 4 considering the retardation in van der Waals interactions at three different ionic strengths. Dashed lines: energy ($2|\Delta E|$) associated with removing bridged particles of various radii at the given contact angles from interfaces plotted against the corresponding critical separation distance, D_c. The hydrophobic decay length is $D_0 = 0.3\,\text{nm}$.

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