Electronic Supplementary Material (ESI) for Faraday Discussions.

Numerical analysis of Pickering emulsion stability: insights from ABMD simulations Supplemental Information

François Sicard* and Alberto Striolo

Department of Chemical Engineering, University College London, Torrington Place, London WC1E 7JE, United Kingdom

E-mail: francois.sicard@free.fr

Droplet characteristic

We consider nanoparticle (NP) types and concentrations that are expected to be (1) strongly effective at preventing droplet coalescence, and (2) maintain the shape of the droplet spherical. As described in prior work,[S1] the first criterion can be related to the interfacial area per NP, $\mathscr{A}_{NP}$. The NPs are not expected to be strongly effective at preventing droplets coalescence when $\mathscr{A}_{NP}$ is larger than 30 R_c^2, independently on whether water or decane droplets are considered. Considering the values for $\mathscr{A}_{NP}$ reported in Table 2 in the main text, water droplets stabilized with 144 NPs have an interfacial area per NP $\mathscr{A}_{NP} > 30\ R_c^2$. These systems do not show high stability, as quantitatively shown in Fig. S1 where we follow the temporal evolution of the radius of gyration, R_{GYR}, of one water droplet stabilized with 144 spherical NPs of type 55JP. The temporal evolutions of R_{GYR} are shifted arbitrarily along the ordinate axis for clarity. In both pulling and ABMD simulations, R_{GYR} remains constant as the distance between the two droplets decreases. The departure from the plateau

indicates the merging of the two droplets. This merging happens without significant increase of R_{GYR}, indicating that the resistance to coalescence provided by the NPs is minimal.

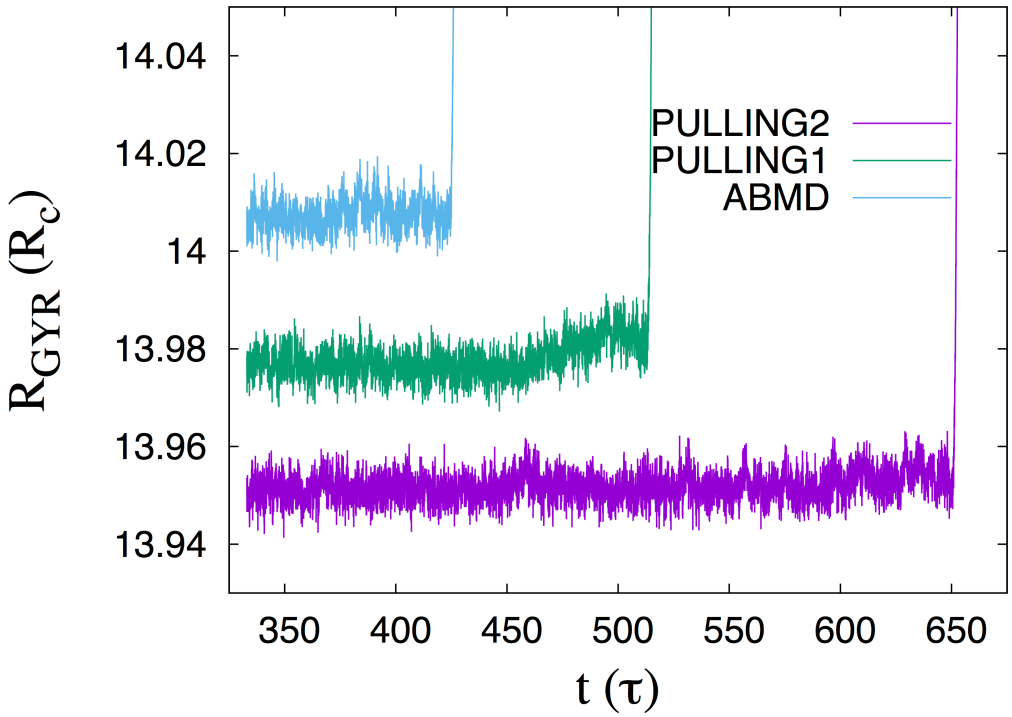

Figure S1: Temporal evolution of the radius of gyration, R_{GYR}, of one incoming droplet during pulling and ABMD simulations. The temporal evolutions of R_{GYR} are shifted arbitrarily along the ordinate axis for clarity. We use the notation: Pulling1 $\left(v_P = 0.001\ R_C/\text{time step},\ k_P = 5000\ k_BT/R_C^2\right)$, Pulling2 $\left(v_P = 0.0005\ R_C/\text{time step},\ k_P = 5000\ k_BT/R_C^2\right)$, and ABMD $\left(\alpha = 1000\ k_BT/R_C^2,\ S_{target} = 39\ R_C\right)$.

The NPs can affect the shape of the droplet at small interfacial area per NP, $\mathscr{A}_{NP}$, because the system tries to keep the NP contact angles θ_C as close as possible to their equilibrium value (cf. evolution of the contact angle θ_C in Table 2 in the main text). In Fig. S2 we compare water droplets stabilized with either 144 spherical NPs (left panel) or 170 spherical NPs (right panel) of type 55JP. Visual inspection demonstrates the alteration of the droplet shape when 170 NPs are used. In correspondence to the changes described in Fig. S2, the changes in relative shape anisotropy, reported in Table 2 in the main text, are of one order of magnitude of difference.

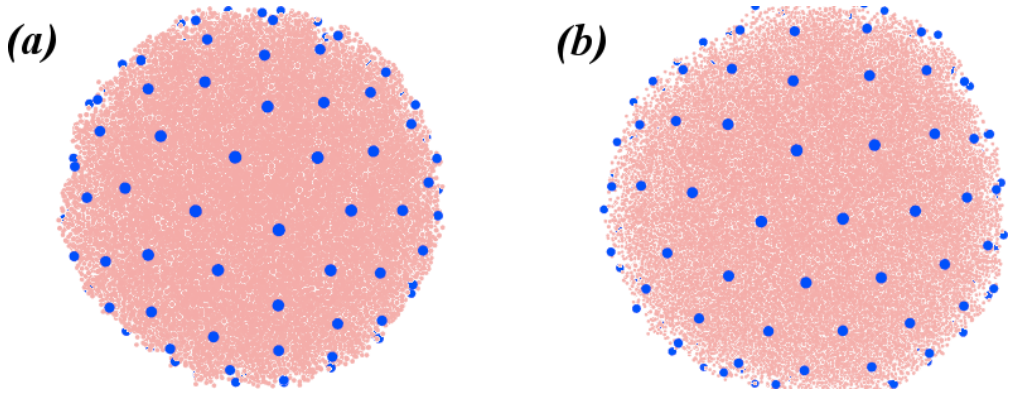

Figure S2: Simulation snapshots representing one water droplet stabilized with either 144 (panel a) or 170 spherical NPs (panel b) of type 55JP. We show the positions of the NP centers (blue points), but not he NPs for clarity.

Water droplets stabilized by homogeneous NPs

We considered the ability of homogeneous (HP) NPs to stabilize Pickering emulsions. As we explained in the main text, due to the homogeneous distribution of polar and apolar beads on the NP surface, one homogeneous NP can adsorb simultaneously on two interfaces yielding the same contact angle on both droplets. The results obtained during the present coalescence simulations are consistent with pulling simulations reported previously.[S1] In both pulling and ABMD simulations the last step of the coalescence mechanism differs from the one observed with spherical Janus NPs. In Fig. S3 we show detailed sequence of simulation snapshots representing typical collision processes of two water droplets in decane solvent. The droplets are stabilized by 160 spherical NPs of type 75HP (contact angle $\theta_c = 101.7 \pm 3.5$). The results are obtained with ABMD simulations. The key point is the interaction between the incoming NP and the second droplet. Indeed, the coalescence process requires only the contact of one NP to induce the merging of the two water droplets.

Coalescence mechanism for ellipsoidal NPs

We show in Fig. S4 detailed sequences of simulation snapshots representing typical coalescence processes of two water droplets stabilized with either 160 spherical NPs of type 60JP

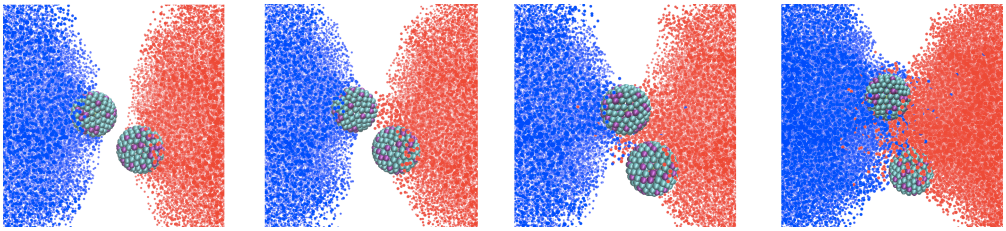

Figure S3: Detailed sequence of simulation snapshots representing typical coalescence process of two water droplets (red or blue) in decane solvent. The droplets are stabilized with 160 spherical NPs of type 75HP. The results are obtained using ABMD simulations. Green and purple spheres represent polar and apolar beads, respectively. The distance between the two droplets decreases from left to right. The coalescence process only requires the contact of one NP to induce the merging of the two water droplets.

(left panel) or 160 ellipsoidal NPs of type 70JP (right panel). The results are obtained using ABMD simulations. When the droplets are stabilized by ellipsoidal NPs, the coalescence process does not require the contact of two NPs from the two merging droplets. This is due to the longitudinal orientation of the ellipsoidal NP with respect to the interface, as explained in the main text.

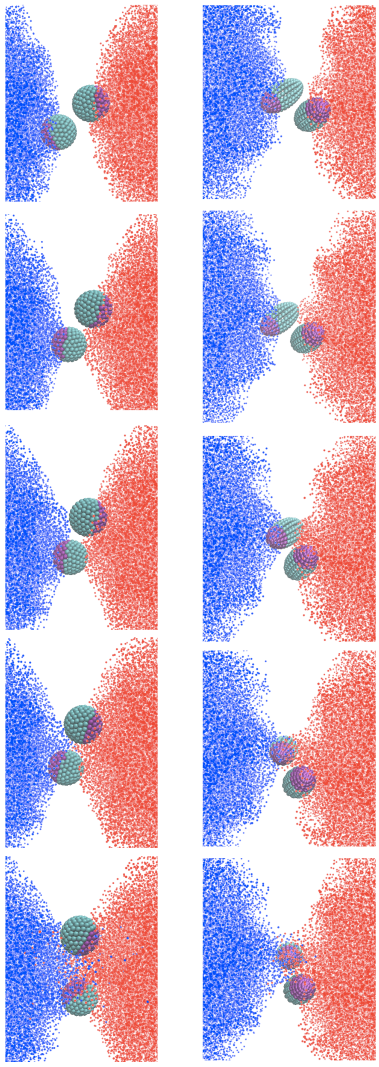

Figure S4: Detailed sequences of simulation snapshots representing typical coalescence process of two water droplets (red or blue) in decane solvent. The droplets are stabilized with either 160 spherical NPs of type 60JP (left panel) or 160 ellipsoidal NPs of type 70JP (right panel). The results are obtained using ABMD simulations. Green and purple spheres represent polar and apolar beads, respectively. The distance between the two droplets decreases from top to bottom. When the droplets are stabilized by ellipsoidal NPs (right panel), the coalescence process only requires the contact of one NP to bridge the two interfaces ans to induce the merging of the two water droplets.

References

[S1] H. Fan and A. Striolo, *Mechanistic study of droplets coalescence in Pickering emulsions*. Soft Matter 2012, **8**, 9533-9538.