Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for:

Self-Assembly of Mono- and Poly-Dispersed Nanoparticles on Emulsion Droplets: Antagonistic vs. Synergistic Effects as a Function of Particle Size

Abeer Khedr and Alberto Striolo*

Chemical Engineering Department, University College London, United Kingdom

* Corresponding Author: a.striolo@ucl.ac.uk

Additional Results

Figure S1 shows a schematic representation of the three-phase contact angle of an adsorbed NP at the water-oil interface. We provide the equations relating the contact angle to the geometric distribution of the NP surface area across the interface.

In Figure S2, we report simulation snapshots representative of the arrangement of small NPs on the droplet surface after 65 μs of simulations. The results are for low and high surface coverage in left and right panels, respectively.

In Figure S3, we reproduce simulation snapshots for three-dimensional flocs of small NPs formed on the droplet surface. Flocs composed by increasing number of NPs are shown from top to bottom as obtained when $a_{\mathrm{NP-NP}} = 1\ \mathrm{k_B T/r_c}$.

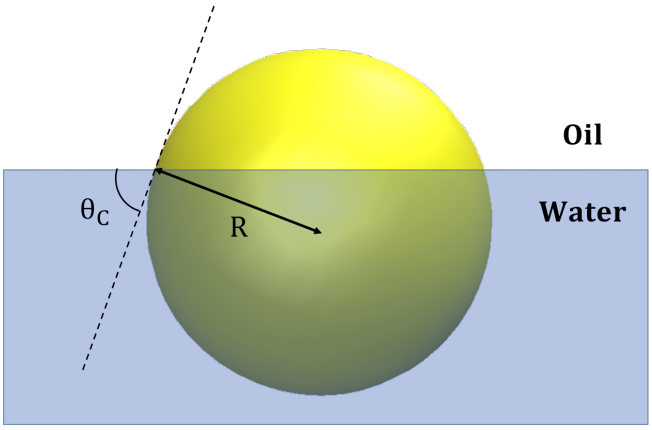
In Figure S4, we reproduce simulation snapshots representative of the arrangement of large NPs on the droplet surface after 65 μs of simulations. The results are for three increasing surface coverages from left to right panels, respectively.

In Figure S5, we provide simulation snapshots for 3D flocs of large NPs obtained when $a_{\mathrm{NP-NP}} = 1\ \mathrm{k_B T/r_c}$.

In Table S1, we provide the difference in the total energy of selected simulated systems due to the adsorption of either small or large NPs on an oil droplet dispersed in water.

In Figures S6, S7 and S8, we provide details regarding the arrangement of small and large NPs on the oil droplet as obtained after 403 μs of simulations starting the simulations from the three different initial configurations shown in Figure 4 of the main text.

In Figure S9, we provide two simulation snapshots to highlight the mechanism by which a small cluster of small NPs adsorbs from the bulk water to the oil droplet surface. This simulation was started from initial configuration (c) shown in Figure 4 of the main text.



$$A_w = 2\pi R^2[1 - \cos(180 - \theta_C)]$$

$$\frac{A_w}{A_{NP}} = \frac{2\pi R^2[1 - \cos(180 - \theta_C)]}{4\pi R^2}$$

$$\theta_C = 180 - \arccos\left(1 - \frac{2A_w}{A_{NP}}\right)$$

Figure S1. Schematic representation of the three-phase contact angle of a NP adsorbed at the water/oil interface. On the right, we provide equations used to calculate the contact angle as a function of the area of the NP immersed in water (A_w) and the total NP surface area (A_{NP}).

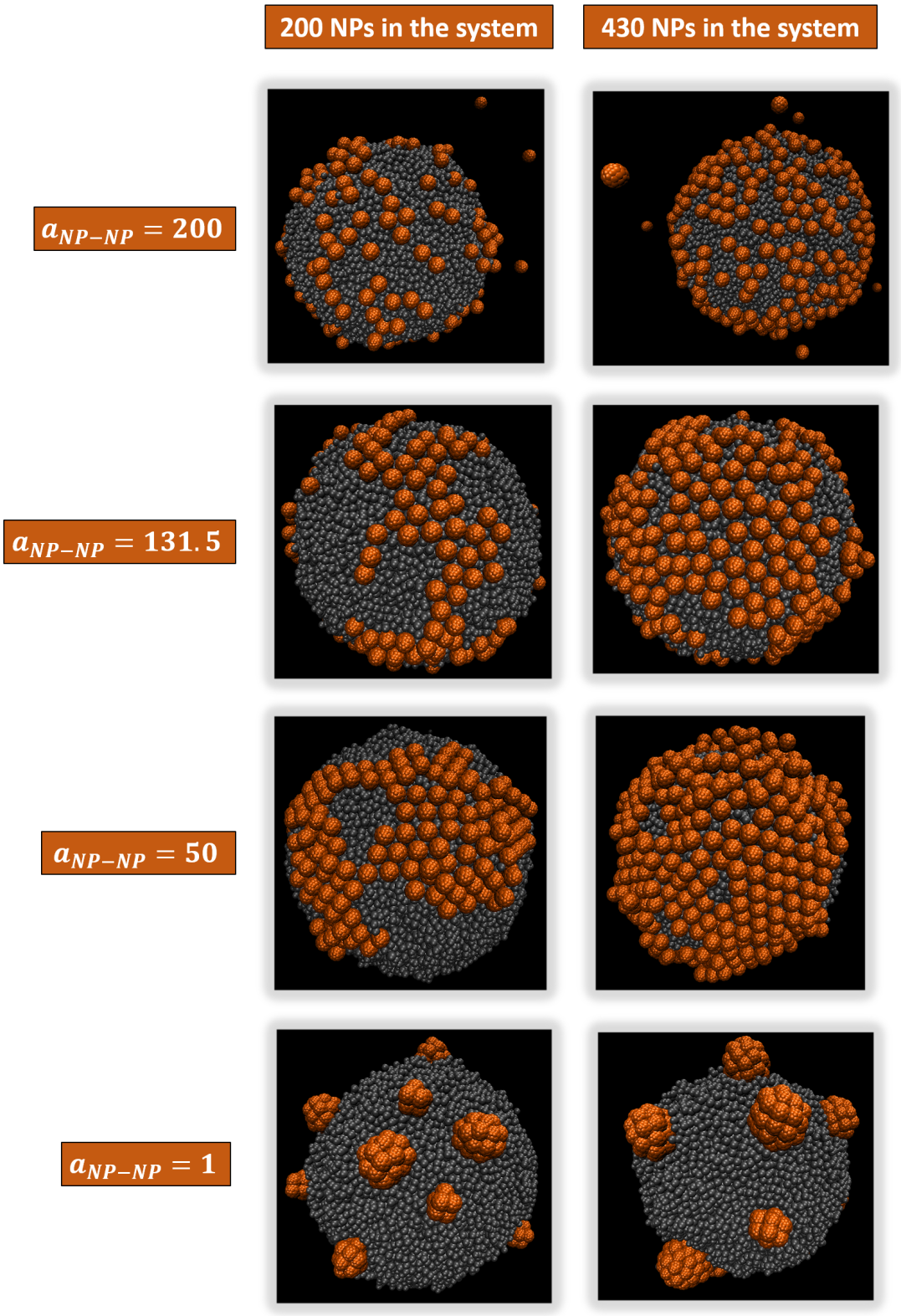


Figure S2. Representative simulation snapshots illustrating the arrangement of 200 (left) and 430 (right) small NPs on the oil droplet when $a_{\mathrm{NP-NP}}$ is equal to 200, 131.5, 50 and 1 $\mathrm{k_BT/r_c}$ from top to bottom, respectively. Snapshots were taken after 65 μs of simulations.

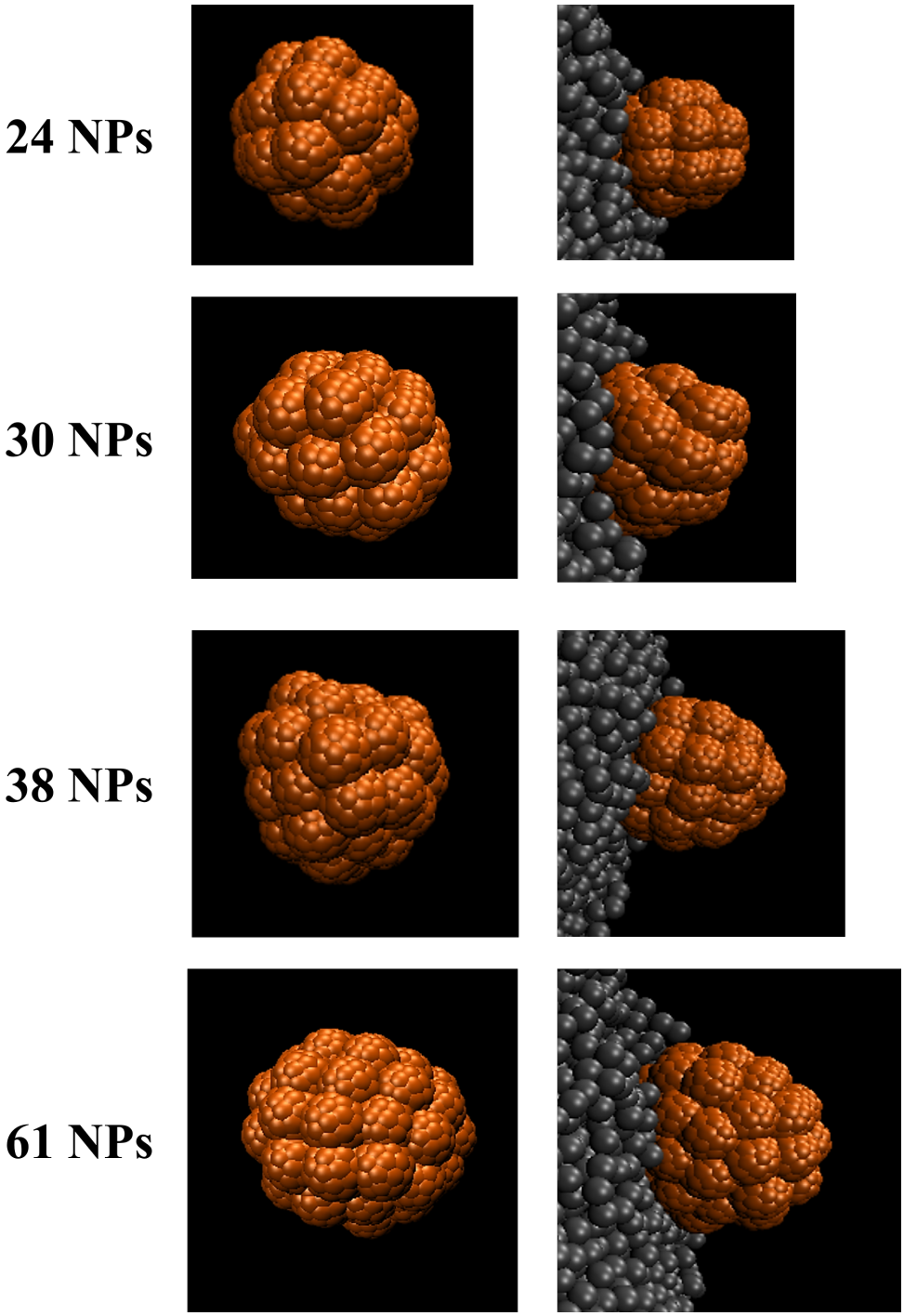


Figure S3. Representative snapshots illustrating the structure of 3D flocs formed by small NPs on the droplet surface when $a_{\mathrm{NP-NP}}$ = 1 $\mathrm{k_B T/r_c}$. Snapshots were taken after 65 μs for flocs with different NPs densities. Top (left) and side (right) views are provided. From top to bottom, the results are for flocs composed of the number of NPs indicated in the left.

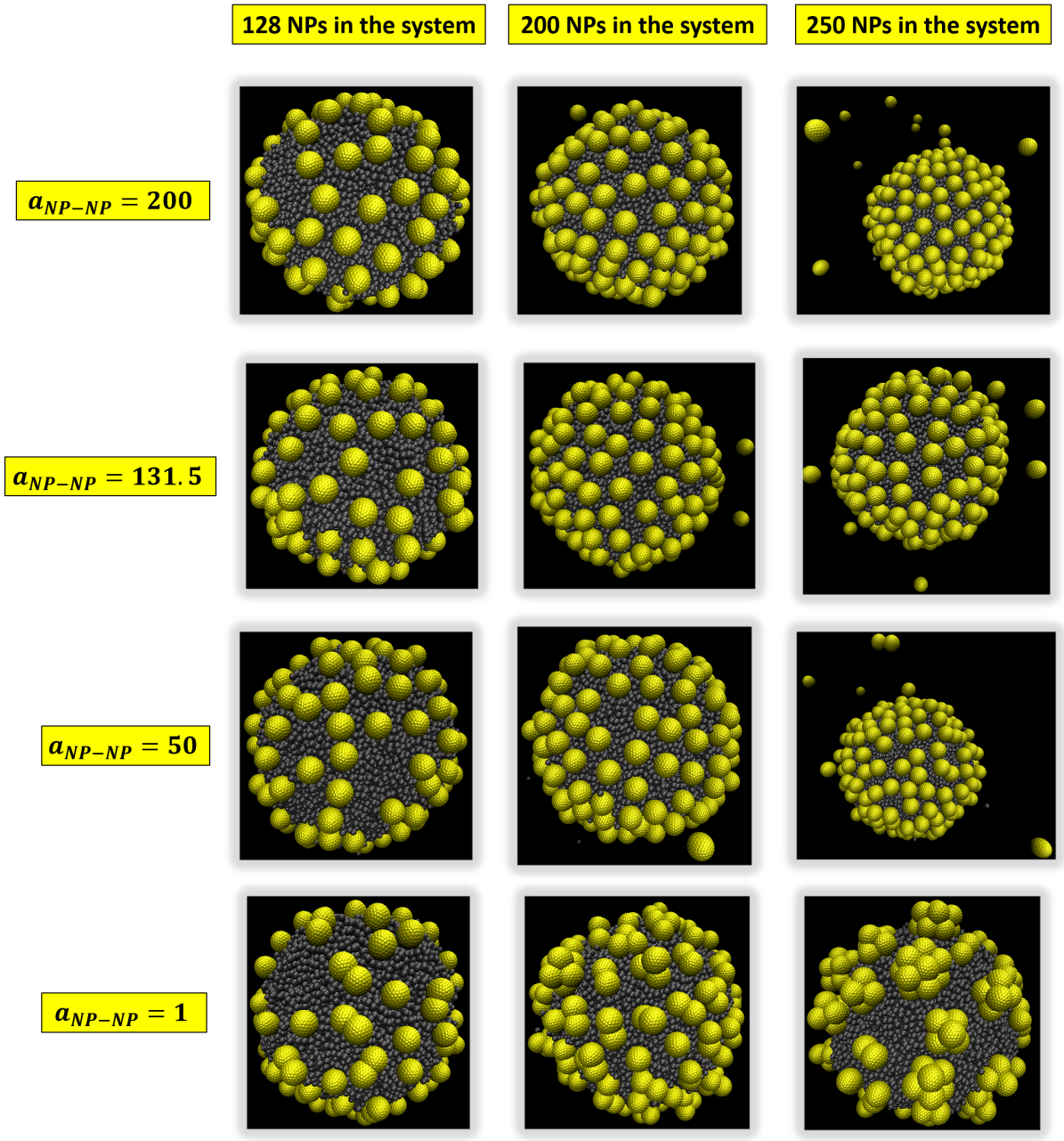


Figure S4. Representative simulation snapshots illustrating the arrangement of 128 (left), 200 (middle) and 250 (right) large NPs on the oil droplet when $a_{\mathrm{NP-NP}}$ is equal to 200, 131.5, 50 and 1 $k_B T/r_c$ from top to bottom, respectively. Snapshots were taken after 65 μs of simulations.

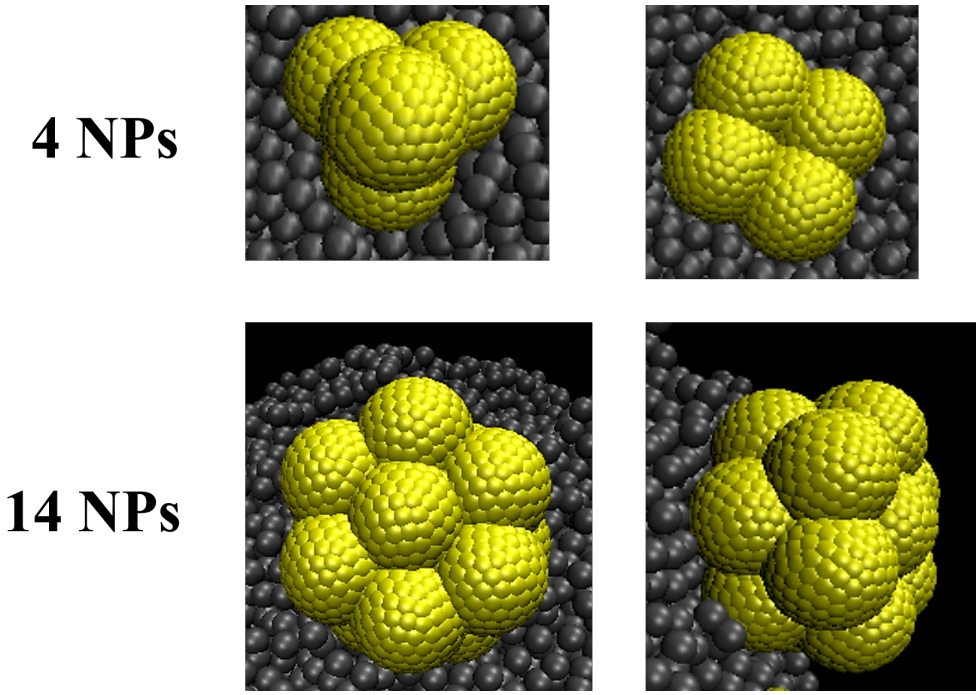


Figure S5. Representative snapshots illustrating the structure of 3D flocs formed by large NPs on the droplet surface when a_{NP-NP} = 1 k_BT/r_c. Snapshots were taken after 65 μs for flocs with different NPs densities. Top (left) and side (right) views are provided. The floc in the top panels is formed by 4 NPs, that in the bottom panels are formed by 14 NPs.

Table S1. Estimated changes in total energy of the simulated systems due to the adsorption of 200 or 430 mono-dispersed small NPs, or that of 128, 200 or 250 large NPs on an oil droplet dispersed in water. The differences in the total energy are averaged over 10^6 simulation steps, which is equivalent to 5.45 μs.

	Small NPs		**Large NPs**		
	200 NPs	430 NPs	128 NPs	200 NPs	250 NPs
ΔE in k_BT	-1.42 ± 0.007	-2.88 ± 0.02	-3.3 ± 0.007	-4.74 ± 0.005	-3.35 ± 0.01

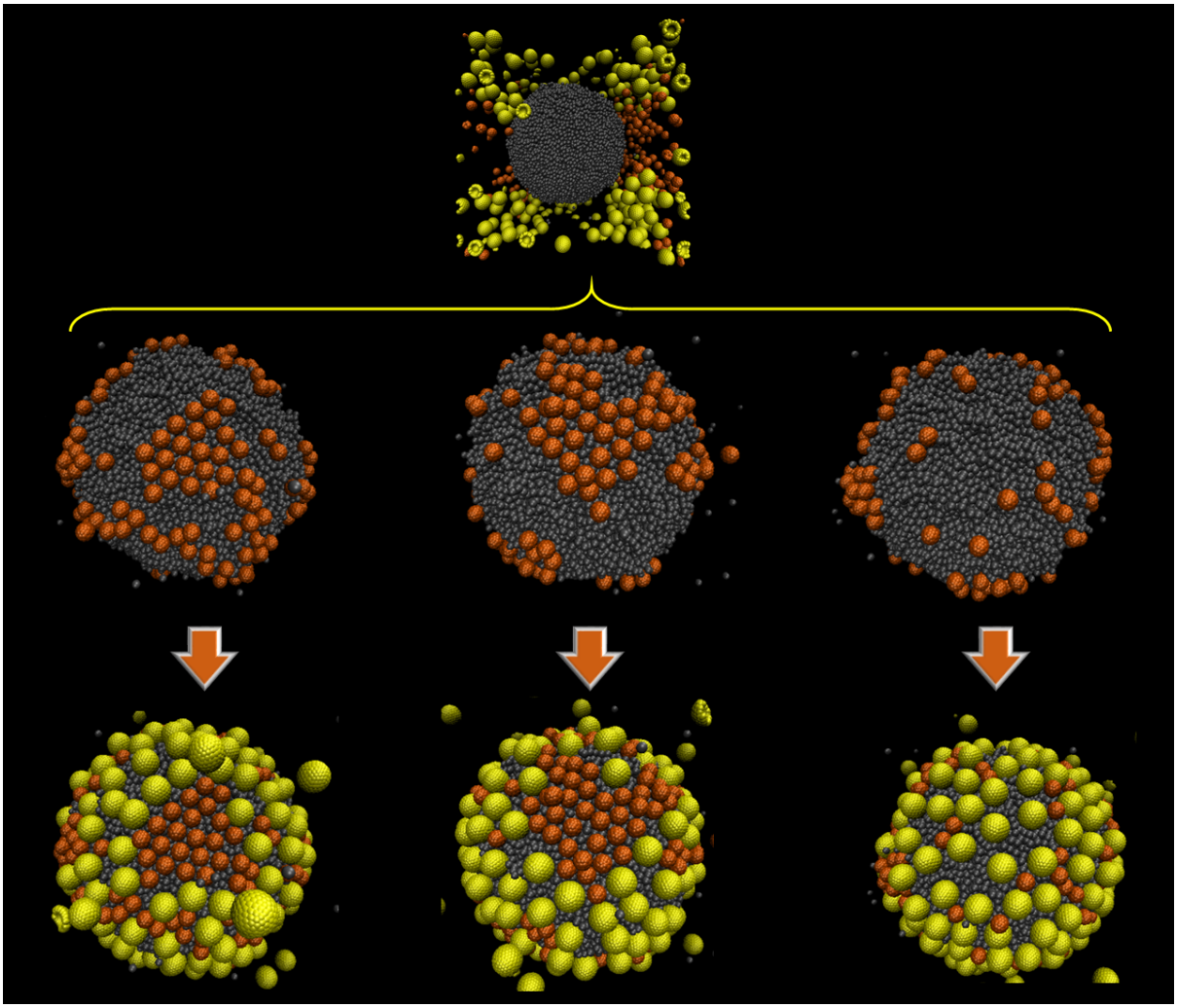


Figure S6. Arrangement of a mixture of small and large NPs, 200 NPs each, after 403 µs (bottom) when starting with an initial configuration where both NPs were dispersed in bulk water (top). Arrangement of only small NPs on the droplet is shown in the middle panels. Snapshots from three different angles are provided.

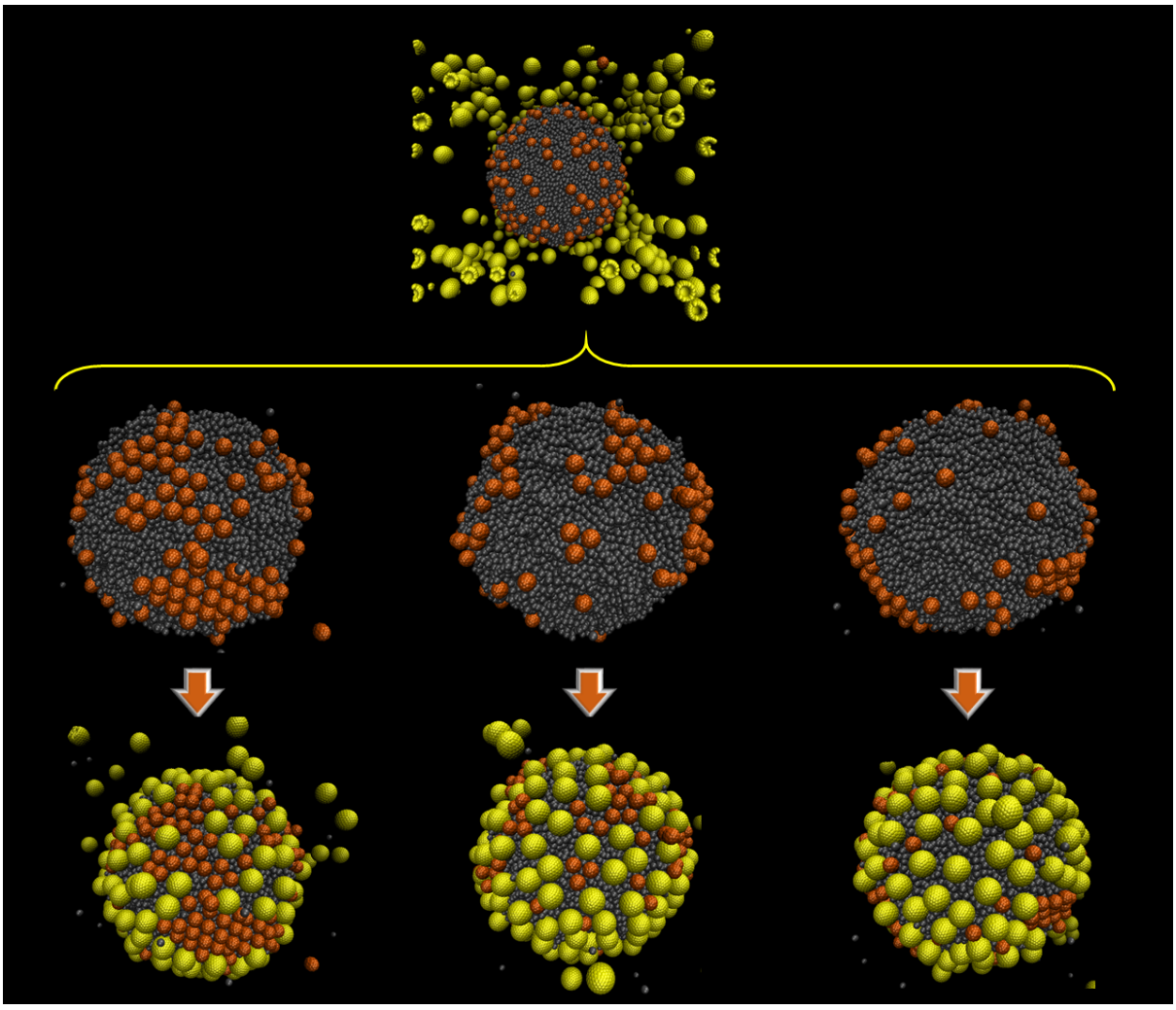


Figure S7. Arrangement of a mixture of small and large NPs, 200 NPs each, after 403 μs (bottom) when starting with an initial configuration (top) of the small NPs adsorbed on the droplet surface while the large NPs were in the bulk. Arrangement of only small NPs on the droplet is shown in the middle panels. Snapshots from three different angles are provided.

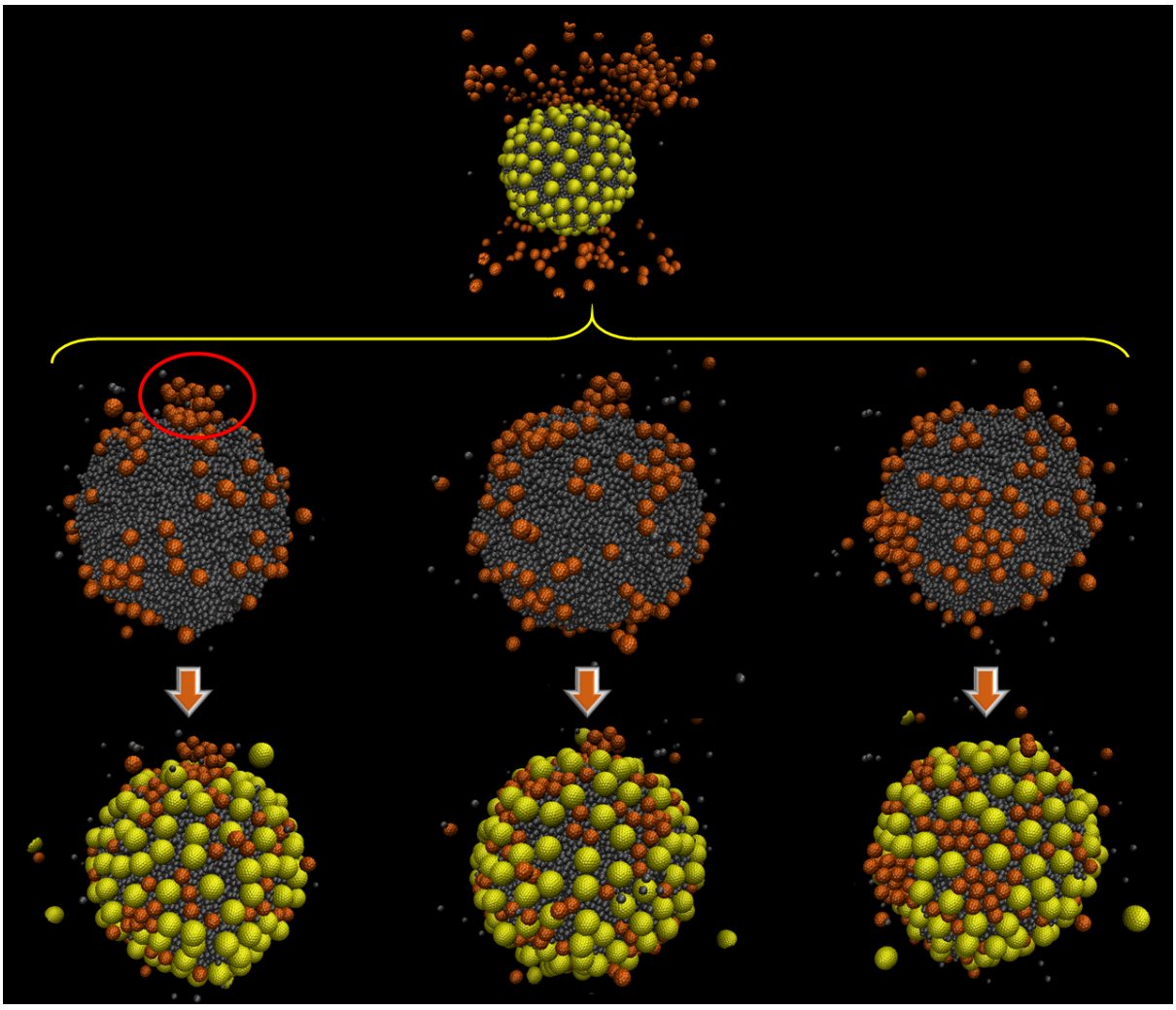


Figure S8. Arrangement of a mixture of small and large NPs, 200 NPs each, after 403 µs (bottom), when starting with an initial configuration (top) with the large NPs adsorbed on the droplet surface while the small NPs were in the bulk fluid. Arrangement of only small NPs on the droplet is shown in the middle panels. Snapshots from three different angles are provided. The circle highlights a cluster of small NPs adsorbed on the droplet.

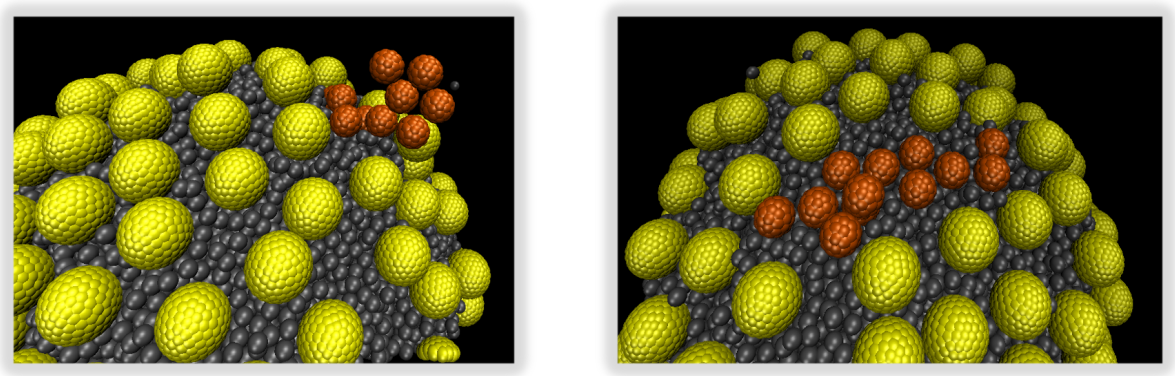


Figure S9. A cluster of small NPs diffuses to the droplet surface by pushing the large NPs. Snapshots are taken from our simulations after 8.2 (left) and 8.7 μs (right), illustrating how the cluster of small NPs makes room among the large NPs on the droplet surface.