

## Electronic Supplementary Information

# The advantages of nanoparticle surfactants over Janus nanoparticles on structuring liquids

You-Liang Zhu,<sup>\*,†</sup> Dapeng Wang,<sup>‡,¶</sup> Jun-Lei Guan,<sup>‡,¶</sup> Zhao-Yan Sun,<sup>\*,‡,¶</sup> and  
Zhongyuan Lu<sup>\*,†</sup>

<sup>†</sup>*State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry,  
Jilin University, Changchun 130012, China*

<sup>‡</sup>*State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied  
Chemistry, Chinese Academy of Sciences, Changchun 130022, China*

<sup>¶</sup>*University of Science and Technology of China, Hefei, 230026, China*

E-mail: youliangzhu@jlu.edu.cn; zysun@ciac.ac.cn; luzhy@jlu.edu.cn

# (Section 1) Models, parameters, and the illustration of droplet deformation

The simulations in this study are all performed on the NVIDIA GTX 1080 Ti GPU by GALAMOST. GALAMOST is a highly optimized molecular dynamics simulation package on GPU computation to have a high performance and aim to study the soft matters and polymers with tailored coarse-grained models and methods. Specifically, the computational efficiency for such as a NP surfactant system with 179,600 beads can reach 980 time steps per a second. The models with parameters for Janus NPs, polymer-grafted NPs, and NP surfactants are depicted as following.

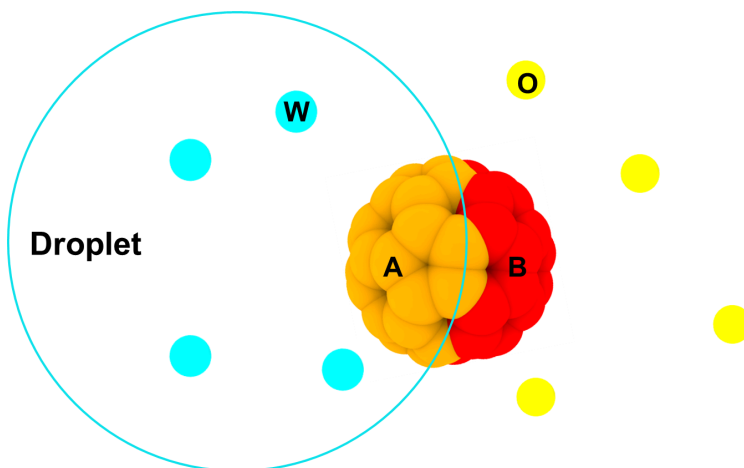


Figure S1: Model of Janus NPs.

Table S1: The non-bonded interaction parameter  $\varepsilon$  in the unit of  $k_B T$  for Janus NPs.

$\varepsilon$	A	B	W	O
A	0.1	0.1	1.5	0.1
B		0.1	0.1	1.5
W			1.5	0.5
O				1.5

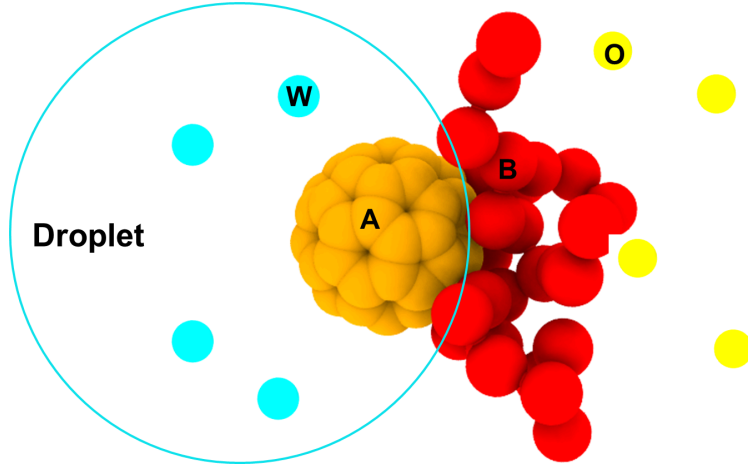


Figure S2: Model of polymer-grafted NPs.

Table S2: The non-bonded interaction parameter  $\varepsilon$  in the unit of  $k_B T$  for polymer-grafted NPs.

$\varepsilon$	A	B	W	O
A	0.1	0.5	1.5	0.1
B		1.5	0.1	1.5
W			1.5	0.5
O				1.5

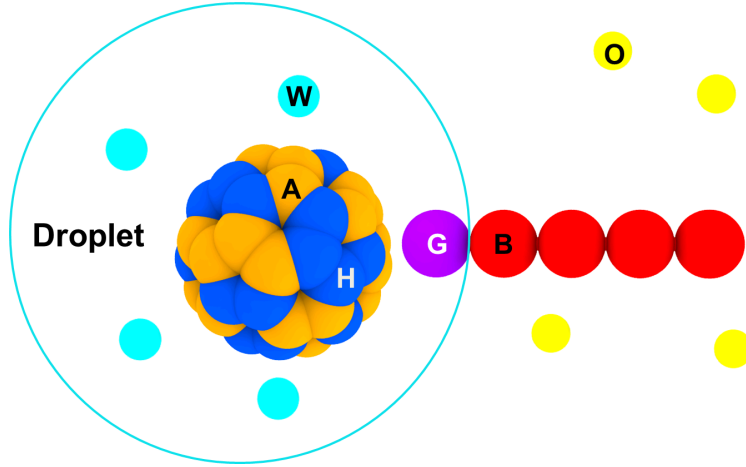


Figure S3: Model of NP surfactants.

Table S3: The non-bonded interaction parameter  $\varepsilon$  in the unit of  $k_B T$  for NP surfactants.

$\varepsilon$	A	H	G	B	W	O
A	0.1	0.1	1.5	0.5	1.5	0.5
H		0.1	$E_{host-guest}$	0.5	1.5	0.5
G			1.5	0.5	1.5	0.5
B				1.5	0.5	1.5
W					1.5	0.5
O						1.5

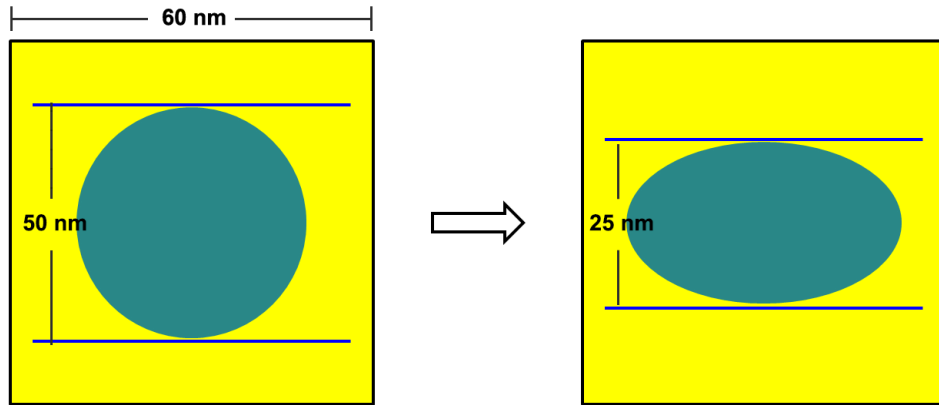


Figure S4: Illustration of deforming a droplet of liquid  $W$  suspended in another liquid  $O$ . The simulation box is  $60 \text{ nm} \times 60 \text{ nm} \times 60 \text{ nm}$ . To mimic the deformation of the droplet achieved by an electric field in experiments, two virtual planes with a repulsive Weeks-Chandler-Andersen potential that sandwich the droplet are moved closely at a constant speed ( $9 \text{ nm}/\mu\text{s}$ ) in relative direction to the distance of  $25 \text{ nm}$ .

## (Section 2) The calculation of host-guest energies

The host-guest energies between carboxylate (A) and amine (B) groups were calculated as the energy difference between the host-guest complex and two separated groups, by the following equation,

$$E_{\text{host-guest}} = E_A + E_B - E_{AB}. \quad (1)$$

The configurations of the carboxylate and amine groups, and carboxylate-amine complex were optimized by Density Functional Theory (DFT) method. Then the host-guest energies were calculated by considering the solvation condition as water in DFT. The DFT calculations employ the gradient corrected (GGA) correlation functional of Perdew and Wang (PW91) with the double numerical plus (DNP) polarization basis set, where the convergence threshold parameters for the optimization were set as  $2.7 \times 10^{-4}$  eV (energy), 0.05 eV/Å (gradient), and 0.005 Å (displacement). The calculations were all carried out using the Dmol3 module in Materials Studio 7.0 (Accelrys inc., San Diego).

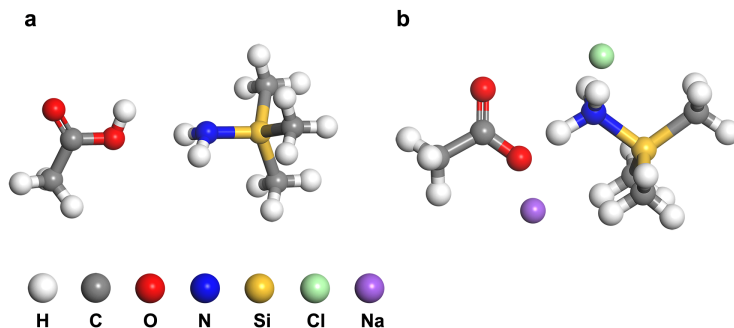


Figure S5: The equilibrium configurations of carboxylate-amine complex with (a) no ionization and (b) complete ionization. The calculated host-guest energies with no ionization and complete ionization are 3.15 and 13.39  $k_B T$ , respectively. The host-guest energies are thereby in the range of 3.15 - 13.39  $k_B T$  for partial ionization.