

Supplementary Information for: Molecular Dynamics Study of Nanoparticles and Non-Ionic Surfactant at an Oil/Water Interface

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In this supplementary section we give further details on the method of constrained molecular dynamics (CMD) and our application of this technique to evaluate the free energy profiles of (1) the transfer of a nanoparticle (NP) from bulk oil to bulk water across an oil/water interface, and (2) the dimerization of two NPs at an oil/water interface. We also elaborate on our mean field approach to evaluating the interactions involving the solid nanoparticles. Also discussed is the method used to evaluate the oil/water interface removed by an interfacially localized NP, and calculating the interfacial concentration of surfactants. Finally, we show additional snapshots of systems studied in the main text.

1 Evaluation of Free Energy Profiles

Thermodynamic Integration and Constrained Molecular Dynamics

For an isobaric-isothermal system (NPT ensemble) undergoing motion along the reaction coordinate ξ , the Gibbs free energy, G , can be given in relation to the probability density function $P(\xi)$ ¹,

$$G(\xi) = -k_B T \ln P(\xi) \quad (1)$$

where k_B is the Boltzmann constant. This implies that evaluation of $G(\xi)$ is simply a case of determining the probability density along the reaction coordinate, $P(\xi)$. Assuming the ergodic hypothesis enables sampling of these probabilities through sampling a simulation over time. However the above equation also suggests that a small rise in free energy corresponds to an exponential drop in the probability density. Hence, an equilibrium simulation is unlikely to sample over regions of high free energy in any practically achievable timescale. The method of thermodynamic integration (TI) aims to sample over the complete reaction coordinate by recognizing that the change in free energy in going between states ξ_0 and ξ_1 can be given through,

$$G(\xi_1) - G(\xi_0) = \int_{\xi_0}^{\xi_1} \frac{dG}{d\xi} d\xi \quad (2)$$

The key to using this relation is through equating the right hand side with a measurable quantity. First we acknowledge that,

$$\frac{dG}{d\xi} = \left\langle \frac{\partial \mathcal{H}}{\partial \xi} \right\rangle_{\xi} \quad (3)$$

where \mathcal{H} is the Hamiltonian of the system. The angle brackets imply ensemble averaging while the subscript ξ is used to

indicate that the sampling is carried out at a single point of the free energy profile. When ξ is simply one of the cartesian coordinate components of one of the particles, for example the z coordinate of the NP, z_{NP} , in the case of a NP going across an oil/water interface, it can be easily shown that

$$\frac{dG}{dz_{\text{NP}}} = \left\langle \frac{\partial \mathcal{H}}{\partial z_{\text{NP}}} \right\rangle_{z_{\text{NP}}} = \left\langle \frac{\partial U}{\partial z_{\text{NP}}} \right\rangle_{z_{\text{NP}}} = -\langle F_{\text{NP}} \rangle_{z_{\text{NP}}} \quad (4)$$

where U is the potential energy of the system, and F_{NP} is the z component of the mechanical force acting on the NP.

However, ξ is generally a collective coordinate involving the positions of many particles in the system, and $-dG/d\xi$ the mean force acting on ξ . Usually a set of generalized coordinates are needed to define ξ , and the equation for $\langle \partial \mathcal{H} / \partial \xi \rangle_{\xi}$ becomes more complex. Fortunately, it can be shown rigorously that¹

$$\left\langle \frac{\partial \mathcal{H}}{\partial \xi} \right\rangle_{\xi} = \left\langle \frac{\partial U}{\partial \xi} - k_B T \frac{\partial \ln |J|}{\partial \xi} \right\rangle_{\xi} \quad (5)$$

where $|J|$ is the determinant of the Jacobian matrix for transforming from a cartesian coordinate system to those of the generalized coordinates.

For the second type of free energy calculation we carry out, i.e. the dimerization free energy of two NPs, the generalized coordinates are of polar form. This would suggest that the above equation must be followed to evaluate the correct $\langle \partial \mathcal{H} / \partial \xi \rangle_{\xi}$. However, in practice, the logarithmic term in the above equation is negligible and can be omitted without significant loss in accuracy.

In the CMD method a supplementary force is added to the systems to counterbalance the natural tendency of ξ to change

value; this additional force is termed the force of constraint. The mean force of constraint \bar{F}_{cons} can be shown to be approximately equal to the derivative of free energy

$$-\langle F_{\text{cons}} \rangle \approx \langle \partial \mathcal{H} / \partial \xi \rangle_{\xi} = \frac{dG}{d\xi} \quad (6)$$

where the approximation results from the previously described omission of the log term in $\langle \partial \mathcal{H} / \partial \xi \rangle_{\xi}$. The ensemble averaged force of constraint values $\langle F_{\text{cons}} \rangle$ are determined for different values of ξ going from ξ_0 to ξ_1 . This is done by application of a biasing potential which constrains ξ during a simulation, giving the name constrained molecular dynamics. Once the average force of constraint values have been determined, these can be integrated to obtain the final free energy function. For a thorough review on this subject we refer the reader to the book 'Free Energy Calculations' edited by Chipot and Pohorille¹.

Evaluation of Transfer Free Energy Profiles

To determine the transfer free energy profile of the 10.0 Å radius nanoparticle (NP) going from bulk oil to bulk water, the constrained molecular dynamics technique described above was used. The reaction coordinate ξ is taken as the distance from the oil/water interface to the NP (called η in the main text). η is constrained in simulations by application of stiff harmonic constraint potential,

$$U(z_{\text{NP}}; z_0) = \frac{1}{2} k_{\text{bias}} (z_{\text{NP}} - z_0)^2$$

where z_{NP} is the instantaneous z position of the NP center of mass, and z_0 , the value that the potential is centered on, is varied with each simulation. The z_0 values go from deep in the oil phase to deep in the water phase. The force constant of the potential is $k_{\text{bias}} = 100 \text{ kcal mol}^{-1} \text{ \AA}^{-2}$. For each simulation, the average force of constraint was determined through measurement of the instantaneous force on the NP due to the constraint potential, sampled at 200 fs intervals.

$$\bar{F}_{\text{NP}} = -\langle k_{\text{bias}} (z_{\text{NP}} - z_0) \rangle$$

The average position of the oil/water interface (which changes for each simulation but does not drift during a given simulation because the net momentum of the simulation box is zero) is calculated by evaluating the mass density profiles of the water and oil separately and finding the z coordinate where the profiles cross. For an average interfacial position of \bar{z}_{int} the value of η is simply, $\eta = z_0 - \bar{z}_{\text{int}}$.

The points of constraint, i.e. the z_0 values, are chosen such that the sections of $dG(\xi)/d\xi$ that are rapidly varying are

sampled with a higher density of z_0 values. The left panel of Figure 1 shows the force of constraint values and the resulting free energy profiles for two systems; (1) a 10.0 Å radius particle transferred across a pristine oil(heptane)/water interface, and (2) the same particle transferred across an oil/water interface with a nominal C_{12}E_3 surfactant coverage of 100 Å² per surfactant. As shown in the plot, the density of points used in the latter calculation was much higher due to the increased complexity of the system. Each point was equilibrated for 1 ns prior to data acquisition simulations of 5 ns for system 1 and 3 ns for system 2. In Figure 1 the profiles show similar transfer free energies, which is expected because the transfer free energy of a NP from bulk oil to bulk water is independent of the system composition at the oil/water interface.

Evaluation of Dimerization Free Energy Profile

The free energy profile for the dimerization of two NPs localized at an oil/water interface is evaluated in a similar manner, although the reaction coordinate in this case is the separation between the centers of mass of the two particles. The biasing potential used is

$$U(\mathbf{r}_{\text{NP}_1}, \mathbf{r}_{\text{NP}_2}; r_0) = \frac{1}{2} k_{\text{bias}} (|\mathbf{r}_{\text{NP}_1} - \mathbf{r}_{\text{NP}_2}| - r_0)^2$$

where \mathbf{r}_{NP_i} is the position vector of the i^{th} NP, and r_0 the target separation between the NPs. Again, the average force of constraint was determined through measurement of the instantaneous force between the NPs, sampled every 200 fs,

$$\bar{F}_{\text{NP-NP}} = -\langle k_{\text{bias}} (|\mathbf{r}_{\text{NP}_1} - \mathbf{r}_{\text{NP}_2}| - r_0) \rangle$$

The right hand panel of Figure 1 shows the averaged force of constraint values and the corresponding dimerization free energy profile of NPs localized at an oil/water interface. The density of points was increased in regions of variation of $dG(\xi)/d\xi$. All points represent simulations where the systems were equilibrated for 1 ns before running constrained simulations of at least 3 ns during which time the data was collected.

2 Evaluating Interactions Involving NPs

In this study the system can be thought of as comprising two types of components, the soft components: surfactant, water and heptane, and the hard component: the solid NP. Interactions between the soft components beads were described in the main text and follows a conventional form for a coarse grained treatment. On the other hand, the interactions involving the NP are treated through a mean field approximation

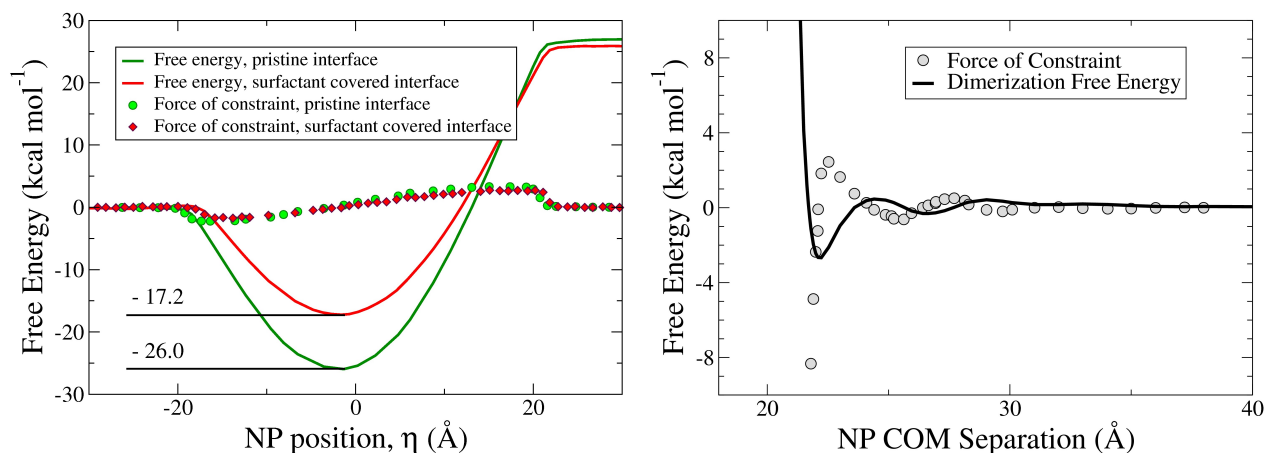


Fig. 1: Free energy profiles obtained from constrained molecular dynamics. (left) The transfer free energy profiles of a NP going from deep in oil to deep in water traversing the oil/water interface. The circles and diamonds represent the average force of constraint values obtained from simulations carried out at different constraint positions. In accordance with the theory of thermodynamic integration, the force of constraint values can be integrated with respect to η to obtain the transfer free energy profiles shown in the solid lines. (right) The same method is used to evaluate the dimerization free energy profile of two NPs equilibrated at an oil/water interface. Here the reaction coordinate is the NP center of mass separation.

which, although discussed in the main text, is a method we have developed previously and expand upon here. Here we include technical details on the continuum mean field method and provide the analytical expressions for the potential energy between a NP and a soft matter bead, as well as the potential energy expression for the interaction between two NPs.

NP-Soft Matter Interaction

In the mean field approximation, we assume the NP is made of a material of homogenous site density, in essence that its interaction sites are smeared out over the volume of the NP. Therefore, the total interaction between the solid and a soft matter atom is simply the integral of the site-site interaction over the volume of the solid.

If the site-site interaction is a simple Lennard-Jones interaction, $U_{ij} = 4\epsilon \left\{ (\sigma/d_{ij})^{12} - (\sigma/d_{ij})^6 \right\}$, the total interaction between an idealized spherical NP and a soft matter atom can be found through the integral,

$$U_{np-i}(r; R) = \int_0^R a^2 da \int_0^{2\pi} d\theta \int_0^\pi \sin\phi \rho U_{ij}(d) \quad (7)$$

where r is the distance between the center of mass of the NP and the soft matter atom. The radius of the NP, R , enters the relation through the integration limits. For a 12-6 Lennard-

Jones site-site interaction this integral evaluates explicitly to

$$U_{np-i}(r; R) = \frac{16\pi\epsilon\rho\sigma^{12}R^3P(r; R)}{45r^9(r+2R)^9} - \frac{16\pi\epsilon\rho\sigma^6R^3}{3r^3(r+2R)^3} \quad (8)$$

with $P(r; R) = (15r^6 + 90r^5R + 288r^4R^2 + 552r^3R^3 + 648r^2R^4 + 432rR^5 + 128R^6)$. In this study the site-site interaction parameters between the NP and soft matter atoms are taken from the CHARMM27 atomistic force field². As described in the main text the CA atom type ($\epsilon = 0.07 \text{ kcal mol}^{-1}$, $\sigma = 3.55 \text{ \AA}$) is chosen to represent the material of which the NP is composed, with a site density (ρ) value of 0.113 \AA^{-3} . Overall, the CA parameter results in a NP which prefers solvation in the oil phase over the water phase, although we have shown that the hydrophilicity of particles may depend on their size³.

Once the NP-soft matter atom interaction potentials are known, an additional step is needed prior to simulation because a CG representation is used for the soft matter components. For the complete derivation we refer any interested reader to the primary reference⁴.

NP-NP Interaction

The NP-NP interactions can also be evaluated through a mean field approximation, where the site-site interaction between two solid particles can be integrated to arrive at the total interaction potential. The resulting potential has an analytical

form and is a function of the separation between the two NPs, S , with parametric dependence on the radii of the particles, R . Here we specialize to the case of equal radii particles,

$$U_{\text{np-np}}(S;R) = \frac{64\pi\rho^2\varepsilon\sigma^{12}R^6P(S;R)}{4725S^7(2R+S)^8(4R+S)^7} + \frac{2\pi^2\rho^2\varepsilon\sigma^6}{3} \left[\frac{R}{2} \left(\frac{1}{4R+S} - \frac{1}{S} - \frac{4R}{(2R+S)^2} \right) + \log \frac{(2R+S)^2}{S(4R+S)} \right] \quad (9)$$

where $P(S;R) = 525S^{10} + 10500RS^9 + 93660R^2S^8 + 490560R^3S^7 + 1674456R^4S^6 + 3911712R^5S^5 + 6376832R^6S^4 + 7200256R^7S^3 + 5392384R^8S^2 + 2416640R^9S + 491520R^{10}$.

3 Determining the Properties Related to Interfacial Concentration

A Note on the Use of Nominal Interfacial Concentration

Throughout the main text we reported the nominal interfacial concentration of components which spontaneously localize at the oil/water interface. This approach is often used for interfacially spread species which do not show solubility in either of the solvent phases. However, both of the interfacially localized species we consider do show some solubility in the oil phase, and hence occasionally desorb from the interface into the heptane solvent. Nonetheless we still report concentrations using nominal concentration values because of the unambiguous and readily accessible nature of this metric. The solubility of $C_{12}E_3$ in heptane is low and only becomes noticeable when the interfacial tension of the oil/water interface becomes very low. Hence we feel the use of the nominal concentration is valid for a qualitative study although it should be kept in mind that the concentrations reported are the upper limit and the actual concentration of these species at the interface can be lower than reported.

Determining Interfacial Area Removed by NP Monolayer

Central to the hypothesis given in the main text is the removal of oil/water contact area due to the localization of NPs at the fluid interface. First we find the average position of the interface from the z coordinate value of the simulation unit cell where the mass densities of water and heptane are equal. Next a new coordinate system is introduced by $\tilde{z} = z - \bar{z}_{\text{int}}$ where \bar{z}_{int} is the average position of the interface.

The oil/water area removed is calculated by creating a histogram of the NP positions. An number N of bins are

assigned such that bin 1, 2,... N correspond to the regions $(\tilde{z}_0, \tilde{z}_1), (\tilde{z}_1, \tilde{z}_2), \dots, (\tilde{z}_{N-1}, \tilde{z}_N)$. From this histogram the interfacial area removed by the NPs can simply be calculated,

$$\frac{1}{C} \sum_{i=0}^N f(\tilde{z}_i) \pi(r^2 - \tilde{z}_i^2) \quad (10)$$

where $f(\tilde{z}_i)$ are the number of observations of NPs within the i^{th} bin, and C is the normalization constant calculated using $\sum C f(\tilde{z}_i) = N_{\text{NP}}$ where N_{NP} is the total number of NPs localized at the interface.

An example of this procedure is shown in Figure 2 for one interface. We selected a region $\pm 10 \text{ \AA}$ from $z = 0$ and used 100 bins to initialize the histogram. A trajectory using 500 frames was then used to populate the histogram.

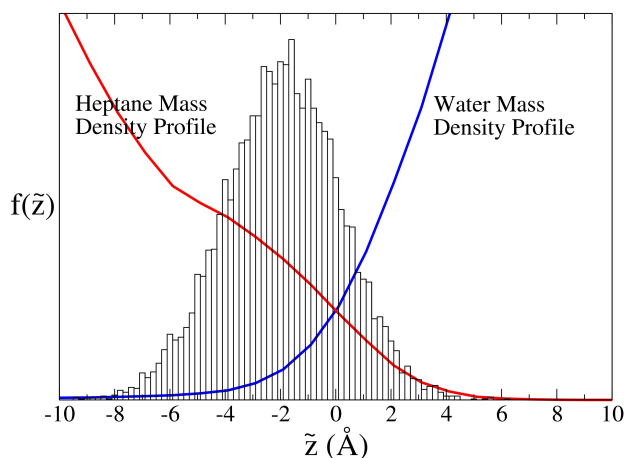


Fig. 2: Distribution of NP positions as a function of the distance from the interface \tilde{z} .

4 Representations of Simulated Systems

For the studies outlined in the main text several series of molecular dynamics simulations were carried out. These comprised NPs and surfactant at an oil/water interface. Due to space constraints some of the systems were not represented graphically in the main text. Figures 3 and 4 show snapshots of systems (A2-A5) and (B2-B5), respectively. (A1) is simply a pure oil/water interface and (B1) was shown in the main text and hence these two systems have been omitted from the snapshots.

References

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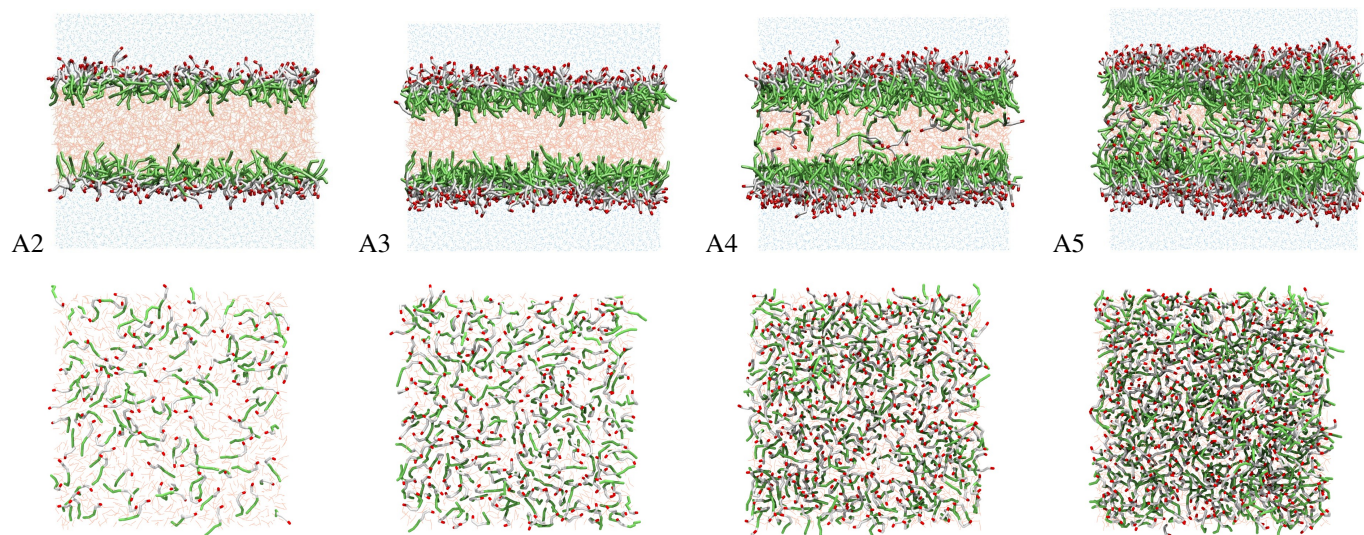


Fig. 3: Representative snapshots of Series (A) from Table 1 of the main text. The top row shows the side view while the bottom row shows top-down views. System (A1) is simply a simulation cell with two solvent blocks of oil and water and hence has been omitted. The color scheme is the same as was used in the main article.

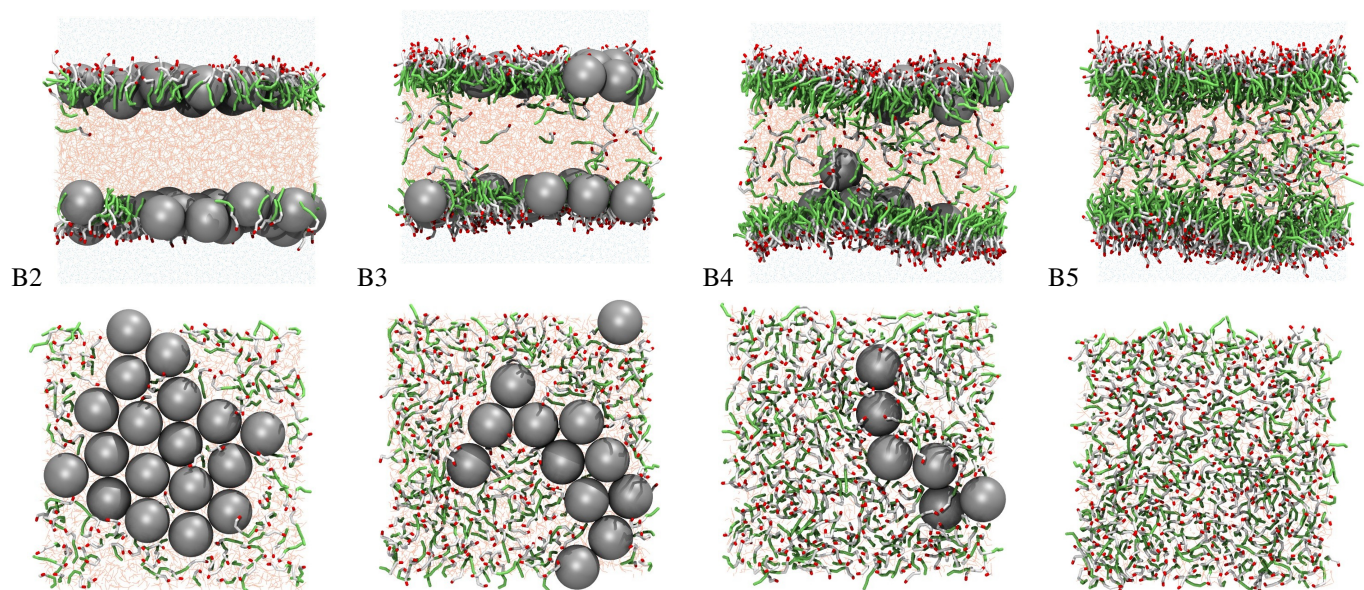


Fig. 4: Representative snapshots of series (B) from Table 1 of the main text. The top row shows the side view while the bottom row shows top-down views. System (B1) is shown in Figure 6 of the main text and therefore is not shown here. The color scheme is the same as was used in the main article.