Nanoparticles Actively Fragment Armored Droplets

Supplemental Information

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MD simulation method

The Dissipative Particle Dynamics (DPD) simulation method1 was implemented within the simulation package LAMMPS.2 The procedure and the parametrisation details are fully described in prior work.3,4 The system simulated here is composed of water, oil (decane), and nanoparticles (NPs). One ”water bead” (w) represents 5 water molecules and a reduced density of one DPD bead is set to $\rho = 3$. One decane molecule is modeled as two ”oil beads” (o) connected by one harmonic spring of length $0.72 R_c$ and spring constant $350 k_B T / R_c$, where $R_c$ is the DPD cutoff distance. The initial size of the simulation box is $L_x \times L_y \times L_z \equiv 30 \times 30 \times 48 R_c^3$, where $L_i$ is the box length along the $i^{th}$ direction. Periodic boundary conditions are applied in all three directions. The NPs are modelled as hollow rigid
spheres and contain polar (p) and nonpolar (ap) DPD beads on their surface. One DPD bead was placed at the NP center for convenience, as described elsewhere. We considered spherical NP of the same volume, \( 4/3\pi a_0^3 \), where \( a_0 \) is the radius of the sphere. We imposed \( a_0 = 2R_c \approx 1.5 \text{ nm} \). All types of beads in our simulations have reduced mass of 1. We maintain the surface bead density on the NPs sufficiently high to prevent other DPD beads (either decane or water) from penetrating the NPs (which would be unphysical), as it has been explained elsewhere. To differentiate among NPs, we report the nonpolar fraction of the NP surface beads and the NP type. For example, 75HP and 50JP considered in this work indicate that 75% and 50% of the beads on the NP surface are nonpolar, and that we consider an homogeneous (HP) or Janus (JP) NP.

The interaction parameters shown in Table 1 are used here. These parameters were adjusted to reproduce selected atomistic simulation results, as explained in prior work. By tuning the interaction parameters between polar or nonpolar NP beads and the water and decane beads present in our system, it is possible to quantify the effect of surface chemistry on the structure and dynamics of NPs at water-oil interfaces. Specifically, the interaction parameters between NP polar and nonpolar beads were adjusted to ensure that NPs are able to assemble and disassemble without yielding permanent dimers at the water/oil interface. Additionally, we adjusted the interaction parameter between the centers of the NPs and the water beads to ensure that no artificial penetration of water molecules into the NPs happens, resulting from the significantly high force experienced by the water molecule during the self-fragmentation process. Importantly, we tuned the interaction parameter in such a way that it does not impact the value of the three-phase contact angle of the NPs at the interface. All simulations were carried out in the NVE ensemble. The scaled temperature was 1, equivalent to 298.73 K. The DPD time scale can be gauged by matching the self-diffusion of water. As demonstrated by Groot and Rabone, the time constant of the simulation can be calculated as \( \tau = \frac{N_mD_{\text{sim}}R_c^2}{D_{\text{water}}} \), where \( \tau \) is the DPD time constant, \( D_{\text{sim}} \) is the
simulated water self-diffusion coefficient, and $D_{\text{water}}$ is the experimental water self-diffusion coefficient. When $a_{w-w} = 131.5\ k_BT/R_c$ (cf. Tab. 1), we obtained $D_{\text{sim}} = 0.0063\ R_c^2/\tau$. For $D_{\text{water}} = 2.43 \times 10^{-3}\ cm^2/s$, we finally obtain $\tau = 7.6\ ps$.

Table 1: DPD interaction parameters expressed in $k_BT/R_c$ units. Symbols $w$, $o$, $ap$, $p$, and $c$ stand for water beads, oil beads, NP nonpolar beads, NP polar beads, and NP center beads, respectively.

|     | $w$   | $o$   | $ap$  | $p$   | $c$  |
|-----|-------|-------|-------|-------|------|
| $w$ | 131.5 | 198.5 | 178.5 | 110   | 250  |
| $o$ | 131.5 | 161.5 | 218.5 | 0     |      |
| $ap$|       | 450   | 670   | 0     |      |
| $p$ |       | 450   | 0     |       |      |
| $c$ |       |       | 450   |       |      |

System characterisation: Droplets and Nanoparticles

In our simulations, the number of water beads constituting the droplet was fixed to $N_W \approx 3500$. At the beginning of each simulation, the solvent (oil) beads were distributed within the simulation box. One water droplet of radius $\approx 7\ R_c$ was generated by replacing the oil beads with water beads within the volume of the spherical surface. A number of spherical NPs were placed randomly at the water-decane interface with their polar (nonpolar) part in the water (oil) phase to achieve the desired water-decane interfacial area per NP. Following previous work, the NPs considered in this study are spherical and of two different types: Janus and homogeneous. The emulsion systems are stabilized by a sufficiently dense layer of NPs. We considered water droplets coated with 24 spherical Janus and homogeneous nanoparticles of type $50JP$ and $75HP$, respectively. Considering the NP surface coverage, $\phi$, defined in Ref., we obtain $\phi \approx 0.9$. The initial configuration obtained was simulated for $10^6$ timesteps to relax the density of the system and the contact angle of the nanoparticles on the nanodroplet. The system pressure and the three-phase contact angles did not change
notably after 5000 simulation steps.

**Three-phase contact angle.** To estimate the three phase contact angle for the nanoparticles on the droplets we calculated the fraction of the spherical NP surface area that is wetted by water,\(^ {10}\)

\[
\theta_C = 180 - \arccos \left( 1 - \frac{2A_w}{4\pi R^2} \right),
\]

where \(A_w\) is the area of the NP surface that is wetted by water and \(R\) is the radius of the NP. The ratio \(A_w/4\pi R^2\) is obtained by dividing the number of NP surface beads (ap or p), which are wetted by water, by the total number of beads on the NP surface (192 for spherical NP). One surface bead is wet by water if a water bead is the solvent bead nearest to it. One standard deviation from the average is used to estimate the statistical uncertainty.

**Radius of gyration.** The description of the geometrical properties of complex systems by generalized parameters such as the radius of gyration or principal components of the gyration tensor has a long history in macromolecular chemistry and biophysics.\(^ {9,11,12}\) Such descriptors allow an evaluation of the overall shape of a system and reveal its symmetry. Considering, e.g., the following definition for the gyration tensor,

\[
T_{GYR} = \frac{1}{N} \begin{bmatrix}
\sum x_i^2 & \sum x_i y_i & \sum x_i z_i \\
\sum x_i y_i & \sum y_i^2 & \sum y_i z_i \\
\sum x_i z_i & \sum y_i z_i & \sum z_i^2
\end{bmatrix},
\]

where the summation is performed over \(N\) atoms and the coordinates \(x, y,\) and \(z\) are related to the geometrical center of the atoms, one can define a reference frame where \(T_{GYR}\) can be diagonalized:

\[
T_{GYR}^{\text{diag}} = \begin{bmatrix}
S_1^2 & 0 & 0 \\
0 & S_2^2 & 0 \\
0 & 0 & S_3^2
\end{bmatrix}.
\]
We follow the convention of indexing the eigenvalues according to their magnitude. We thus define the radius of gyration \( R_{GYR}^2 \equiv S_1^2 + S_2^2 + S_3^2 \) and we calculate \( R_{GYR} \) using the centers of the water beads.

**Accelerated dynamics simulations**

The *thermally-assisted* self-fragmentation of an emulsion droplet occurs on time scales that are orders of magnitude longer than those accessible to unbiased simulations. A variety of methods, referred to as *enhanced sampling techniques*,\(^{13-17}\) can be implemented to overcome this limitation. These methods are based on constrained simulations. Metadynamics (metaD)\(^ {18-21}\) and umbrella sampling (US)\(^ {22,23}\) belong to this class of methods: they enhance the sampling of the conformational space of a system along a few selected degrees of freedom, named reaction coordinates or collective variables (CVs), and reconstruct the probability distribution as a function of these CVs. These techniques are proven powerful tools to study biological\(^ {24-27}\) and chemical systems.\(^ {28-30}\) However, care should be taken to properly choose and implement the reaction coordinates.\(^ {19-21}\)

**Bare emulsion droplet.** To study the self-fragmentation of the bare droplet, we ran *standard* metaD simulations using the coordination number function, \( N_C \), described in the main text as CV. MetaD is a method based on a biasing of the potential surface. The biasing potential is dynamically placed on top of the underlying potential energy landscape to discourage the system from visiting the same points in the configurational space. The metaD time-dependent bias, \( V_{bias}(s, t) \) can have any form, but a Gaussian potential is usually implemented:\(^ {19}\)

\[
V_{bias}(s, t) = \omega \sum_{t'<t} \exp \left[ - \frac{(s(t) - s(t'))^2}{2\sigma^2} \right].
\]  

(S4)

In Eq. S4, \( \omega \) is the height of the biasing potential, \( \sigma \) is the width, \( t \) is the time, and \( s \) is the collective variable. A Gaussian-shaped potential is deposited every \( \tau_G = 40 \) ps, with
constant height \( \omega = 1.2 \) kcal/mol, and \( T = 298.73 \) K is the temperature of the simulation. In our implementation, the resolution of the recovered free-energy profile is determined by the width of the Gaussian \( \sigma = 0.2 \) along the CV. We checked that a slight change in the biasing potential deposition and height did not change significantly the results, particularly the positions of the local minimum and the saddle point, as well as the barrier height measured along the free energy profile. To further quantify the error of the reconstructed profile, we performed 3 runs of metaD and stopped the simulations when the system escaped from the local minimum energy well, when the mother and daughter droplets separate.

**Armored emulsion droplet.** To study the self-fragmentation of the armored droplets, we ran US simulations with the coordination number function, \( N_C \), described in the main text as CV. To design the US windows, it is common practice to implement one of two approaches: 1) the system is dragged using the steered dynamics\(^{23}\) or 2) the initial structures are prepared by changing the position of the CV directly followed by energy minimization.\(^{31}\) As discussed by Nishizawa,\(^ {31}\) it is possible, with these protocols, to drive the system into configurations with no reverse transition (i.e., breaking the ergodicity of the system). This can be particularly true with fluid/soft systems, where covalent bonds are not present. This shortcoming can be associated to artificial kinetic barriers between consecutive states that slow sampling of configurations during US. These effects could render the free-energy profile analysis inappropriate and/or unfeasible using a reasonable amount of computation.

To avoid these shortcomings, we used the adiabatic biased molecular dynamics (ABMD) framework, which is based on the local fluctuations of the system,\(^ {9,32-34}\) to design the US windows. ABMD is an algorithm developed to connect any two points in the conformational space of a given system. The method is based on the introduction of a biasing potential, which is a function of chosen coordinates of the system and which is zero when the system is moving toward the desired target point, while disfavoring motions in the opposite direction.
This is similar to what happens in a ratchet-and-pawl system, which undergoes random thermal fluctuations, while the pawl allows the ratchet to move only in one direction.\textsuperscript{34} In ABMD the chosen coordinate plays the role of the ratchet and the biasing potential that of the pawl. The biasing potential does not exert work to direct the system toward the target conformation; on the contrary the system moves toward the target conformation under the driving effect of the force-field alone. Within ABMD, the biasing potential is implemented as

\[
V(\rho(t)) = \begin{cases} 
\frac{\alpha}{2}(\rho(t) - \rho_m(t))^2 & \rho(t) > \rho_m(t) \\
0 & \rho(t) \leq \rho_m(t)
\end{cases}
\]

(S5)

where

\[
\rho(t) = (S(t) - S_{\text{target}})^2
\]

(S6)

is the distance along the coordinate \( S \) of the actual configuration of the system with respect to a target value \( S_{\text{target}} \), \( \alpha \) is a damping constant, and

\[
\rho_m(t) = \min_{0 \leq \tau \leq t} \rho(\tau)
\]

(S7)

is the minimum distance reached until time \( t \). The algorithm is defined by the choice of the coordinate \( S \) and of the damping constant \( \alpha \). The ABMD algorithm is routinely implemented by the biophysical community to explore free-energy paths associated to protein folding and unfolding.\textsuperscript{32,34,35} One of the unique features of this method is that the transformation connecting two points of interest in the configurational space occurs following natural fluctuations. Additionally, the algorithm minimizes the sum of the potential and kinetic energy of the particles and of the bias potential. This provides means of controlling the quality and adiabaticity of the simulation.

To reconstruct the free-energy profiles discussed in the main text, the authors generated 200 US windows, allowing sufficient overlap between adjacent windows. Upon completion of
the US simulations, the free-energy profiles were calculated from the final 15 ns of simulation time using the weighted histogram analysis method (WHAM).\textsuperscript{36} Statistical error analysis was conducted using the integrated Monte Carlo bootstrapping framework,\textsuperscript{37} implemented in WHAM, using 100 resampling trials.

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