

Disintegration of water nanodroplet in oil: Impact of amphiphile self-assembly, surface heterogeneity, and protrusions

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Abstract Amphiphiles self-assemble around water-in-oil nanodroplets, increasing interfacial heterogeneity, reducing droplet size, and stabilizing the system through microemulsion formation. We present molecular dynamics simulations investigating how amphiphiles modulate the heterogeneity and disintegration of water nanodroplets. Utilizing network theory-based sub-ensemble analysis and curvature analysis, we characterize the amphiphile self-assembly process and the disintegration of water nanodroplets into smaller daughter droplets. We detail the microscopic mechanism of water transport from the water droplet to the oil phase, facilitated by the formation of sharp, finger-like protrusions on the droplet surface. Our results demonstrate a direct correlation between the rate of droplet disintegration and temperature-induced thermal fluctuations.

Keywords: Microemulsions, Self-assembly, Protrusions, Water Nanodroplets, Surface Heterogeneity, Network theory, Molecular Dynamics Simulations, Solvent Extraction, Chemical Separations.

I. INTRODUCTION

Water-in-oil emulsions are inherently unstable and tend to separate into water and oil over time. Amphiphiles stabilize these emulsions by forming micelles around water droplets, increasing surface heterogeneity, and breaking the droplets into smaller clusters.[1–3] Although the effects of amphiphiles on emulsions are well understood, their microscopic mechanisms remain unclear.[4, 5] Emulsions are crucial in various fields, including chemical separations, oil recovery, pharmaceuticals, and food chemistry. Understanding the structure and dynamics of water in the confinements of the nanodroplets is necessary to improve emulsion properties and controlled separations.[6–8] At elevated concentrations, amphiphiles adsorb at the nanodroplet surface and lead to the fragmentation of droplets into smaller clusters.[9] This modulation of droplet behavior is due to amphiphile effects on surface heterogeneity and the reduction of surface tension.[10]

For example, Smit et al. performed simulations to find oscillating water density on the adsorption of micelle on the water/oil interface causing a spontaneous formation of surfactant monolayer, which was related to an unexpected increase in the neutron reflectivity above critical micelle concentration.[11–13] However, the perturbations in the interfacial water structure and the formation of water protrusions have not been explored. Recently, it has been shown that increasing the concentration of amphiphiles at the water/air interface leads to enhanced

surface fluctuations and increased surface curvature. The presence of air, rather than oil, does not facilitate water transport and suppresses the formation of protrusion-type structures, which are considered in this study. It is also demonstrated that the surfactants at the water/oil interface enhance heterogeneity within the interfacial water structure and drive water transport into organic solvents through the surfactant-water dimer.[14] A similar mechanism was observed for the transport of ion pairs into the oil phase.[15] In this study, we aim to understand whether a similar mechanism might be relevant for the amphiphile driven transport of water from the water nanodroplet, leading to the formation of daughter droplets.[16]

Enhanced surface heterogeneity enables amphiphiles to break nanodroplets into tiny water clusters of various shapes and sizes.[17, 18] Importantly, the water droplets in water-in-oil emulsions range from nanometers to micrometers. For larger droplets, amphiphile self-assembly and droplet disintegration can take tens of seconds, while for nanometer-sized droplets, these processes occur much faster and can be simulated computationally.[19–22] Additionally, enhancing thermal fluctuations through heating can further accelerate the amphiphile-assisted droplet disintegration process. Therefore, in this work, we explored the microscopic mechanisms of amphiphile-induced disintegration of water-in-oil nanodroplet under different temperature conditions, with a primary focus on amphiphile self-assembly, its effects on nanodroplet curvature and surface area, surface heterogeneity, and the

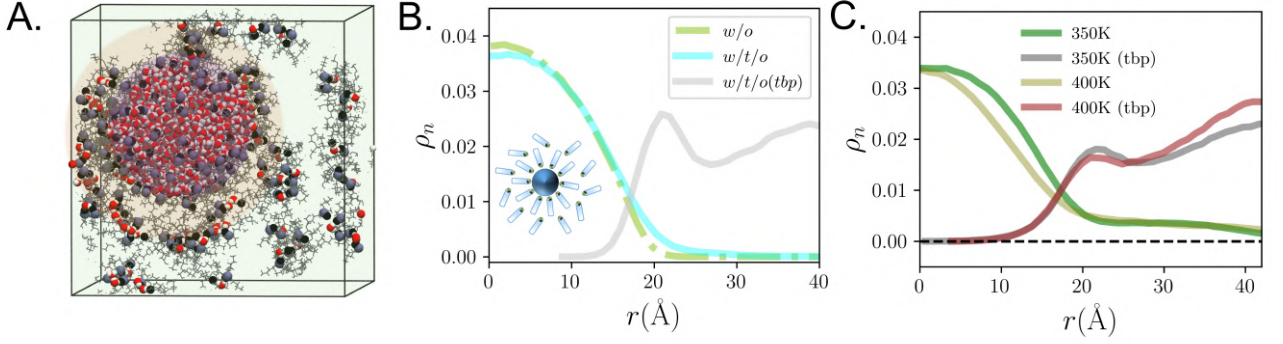


FIG. 1: (A.) A schematic illustration of the water/*tbp*/oil (w/t/o) system after 10 ns at 298 K (B.) Normalized density distributions of water (grey) and *tbp* (O=P) (blue) relative to the droplet COM present in the w/t/o system. The density of water present in the water/oil (w/o) system is plotted in orange. (C.) The density of water and *tbp* at elevated temperatures (350 and 400 K).

transport mechanism of water between the nanodroplet and oil phase.

II. RESULTS AND DISCUSSION

A. Amphiphile self-assembly

The randomly immersed amphiphile (tri-butyl phosphate (*tbp*) in this case) self-assembles around the water nanodroplet as a result of dipole-dipole interactions between the polar headgroup and water hydrogen atoms.[23, 24] To understand self-assembly of amphiphiles around water nanodroplet we first equilibrated the nanodroplet-*tbp*-hexane system for 5 ns, and plotted the density profiles of H₂O and *tbp* relative to the center of mass (COM) of the droplet (Figure 1) in a system with a water nanodroplet present in *tbp* and an oil solution (w/t/o) (Figure 1 A) relative to a droplet of pure water in the oil (w/o) system. Interestingly, within the first 10 ns, the *tbp* self-assembles around the water droplet to form a monolayer structure, with a hydrophilic head group facing the water droplet and a hydrophobic tail toward the oil phase, shown by the minima at 25 Å in the density profile of the head group (P=O atoms) of *tbp* (Figure 1 B, shown in grey color). A typical simulation snapshot showing the adsorption of *tbp* in the water droplet after 10 ns is shown in Figure 1 A. Interestingly, the H₂O density profiles show a shift in the H₂O density from the COM of the droplet to the surface of the droplet in the w/t/o system and relative droplet in the w/o system. The increased density at $r > 15$ Å in the w/t/o system arises from protrusions formed on the

water-in-oil nanodroplet surface in the presence of *tbp*. (*vide infra*) The thermal fluctuations due to increased temperature further deform the nanodroplet causing an increase in the density of extracted water ($r > 20$ Å) relative to the 298 K (Figure 1 C). The transport of water from the nanodroplet into the oil phase altered the self-assembly of *tbp*, as indicated by a decrease in the density of *tbp* molecules at the water-oil interface.

B. Nanodroplet morphology

The morphology of the intrinsic droplet surface water molecules is characterized by computing the surface curvature and areas, using the protocol described in the methodology section. The curvature and area calculations were carried out on the largest water cluster, formed primarily by the intact water molecules. Three distinct surface curvature descriptors namely, mean curvature, Gaussian curvature, and squared curvedness of the droplet were calculated.[25, 26] Figure 2 shows the distributions of instantaneous mean and Gaussian curvature of water droplet surface points at the time interval of $t = 10$ ns. The positive and negative values show the convex and concave facets of the surface, respectively. A mean curvature value of zero indicates balanced curvatures at a surface point. A Gaussian curvature nearing zero can be predominantly attributed to either κ_1 or κ_2 being zero at a specific local point on the droplet surface. The range of mean and Gaussian curvatures, from positive to negative, reflects a noticeable deformation of the nanodroplet surface, primarily due to the formation

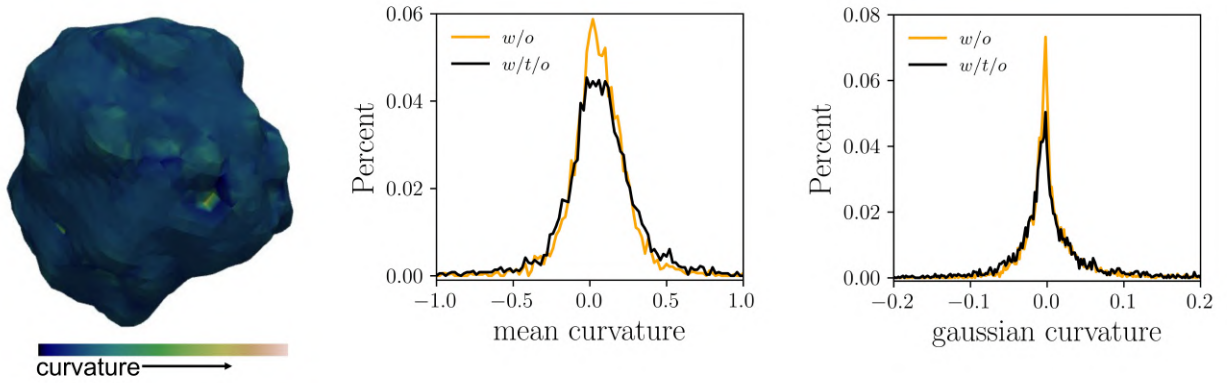


FIG. 2: Intrinsic mean and Gaussian Curvature distribution of the local points on water droplet in w/o and w/t/o systems after 10 ns of molecular dynamics simulations. The curvature analysis is performed on the largest water cluster which is separated from the extracted and dangling surface water molecules using the cluster analysis as described in the Material and Methods section.

of surface protrusions driven by the self-assembled *tbp* on the surface of the nanodroplet.

The distributions of the average mean and Gaussian curvatures of droplet surfaces collected over the 10 ns trajectory for the w/o and w/t/o systems are provided in Figure S1 A and B respectively. For a perfect sphere with radius $r = 20 \text{ \AA}$, the anticipated average Gaussian curvature, $\frac{1}{r^2}$, is projected to be 0.0025 \AA^{-2} . The droplet significantly deviates from an ideal spherical shape, as evidenced by the broad distributions of mean and Gaussian curvatures, further enhanced by the formation of surface protrusions. The distribution becomes even broader with the addition of the *tbp* to the droplet surface, which promotes surface heterogeneity and leads to an increase in surface roughness and therefore more value of the surface curvatures.

The two principle curvatures, κ_1 and κ_2 , can exhibit both positive and negative values depending on the local curvatures at a given point on the droplet surface. Therefore, the mean of these values (as in the mean curvature) may not comprehensively represent the intrinsic curvature behavior in numerous instances. To this end, we employed a new descriptor namely, squared curvedness, which is $\kappa_1^2 + \kappa_2^2$, which intrinsically possesses a positive value. This provides a relative depiction of the nanodroplet surface curvature within a w/t/o nanodroplet, as compared to the pure w/o system. The interplay between *tbp* and the water droplet prompts an increase in the cumulative surface curvedness of the droplet. Notably, the presence of the amphiphile *tbp* enhanced the surface curvedness by $\sim 1.57 \times$ compared to a pure water

droplet within 10 ns (Figure 3 A).

The impact of amphiphile on the surface morphology is further accessed by the distribution of the area of coarse-grained water droplets in the absence and presence of the amphiphile (Figure 3 B). The addition of amphiphiles increases the surface area of the water droplet (as shown by the broader distribution of the surface area and shift in the distribution maxima to a higher value), is primarily due to the formation of protruding water structures.[18, 27] This occurs because amphiphiles, disrupt the smooth spherical shape of the droplet. The hydrophilic heads interact with water molecules, while the hydrophobic tails avoid water, leading to the formation of micelle-like structures or partial solubilization at the water-oil interface. This behavior reduces surface tension and allows the development of complex surface structures, such as water fingers or buds. The protruding water structures indicate a significant alteration in the droplet's interfacial properties, highlighting the complex interplay between amphiphiles and water molecules.

We then characterized how the increase in thermal fluctuations impacts the surface morphology by quantifying the surface area of water droplets at three different temperatures (298, 350, and 400 K) in the presence of *tbp* as a function of time, as illustrated in Figure 3 C. The surface area of a pure spherical droplet with a radius of 20 \AA , calculated using the formula $A = 4\pi r^2$, was subtracted from the surface area of the triangulated droplet surface. At elevated temperatures, the self-assembled amphiphiles not only increase the roughness of the droplet surface by forming protruding structures, but also accelerate the

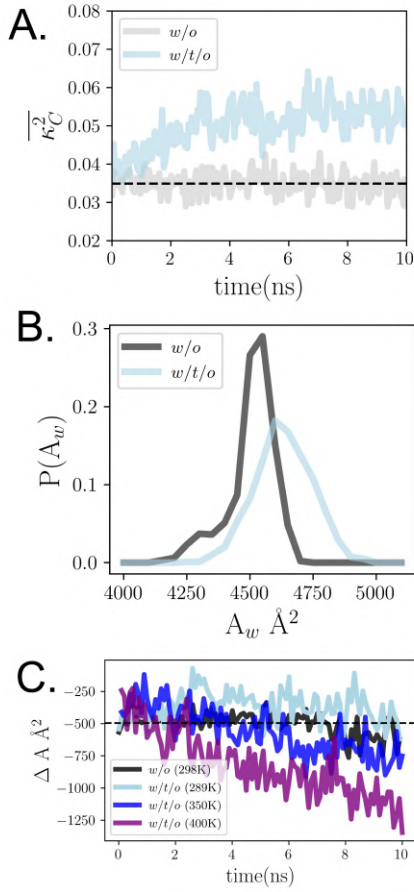


FIG. 3: (A.) The time evolution of the squared surface curviness of the water droplet in w/o and w/t/o system. The curvature analysis is performed on the largest water cluster obtained using the water H-bonding connectivity network. (B.) The probability distribution of the nanodroplet surface area in the absence and presence of amphiphiles. (C.) The time evolution of the nanodroplet surface area at different temperatures within the w/t/o system. The change in surface area ΔA of the droplet is computed by subtracting the area of the sphere $4\pi r^2$ from the area of the triangulated droplet surface.

droplet disintegration rate (vide infra). As a result, the droplets start to break into smaller clusters at a much faster rate compared to normal temperature conditions. This is also observed in the faster decay of ΔA , as shown in Figure 3. In this figure, the negative values of ΔA indicate that the triangulated mesh droplets have a surface area slightly smaller than that of a perfect sphere, due to shape heterogeneity caused by water dynamics and the amphiphiles on the surface. The deformation induced by *tbp* resulted in an increase in the droplet's surface area compared to a droplet in oil without *tbp*. The increase in system temperature further amplified shape hetero-

geneity, as evidenced by the significant reduction in nanodroplet surface area over time, as shown in Figure 3 C. This increase in surface area is related to the formation of protruding water structures and in turn possibly related to the experimentally observed enhanced reactivity on the water surfaces.[28–32]

C. Nanodroplet heterogeneity

Upon the addition of amphiphile, there was an increase in the heterogeneity of the droplet water structure, leading to more extracted and surface-dangling water molecules. To understand the evolution of perturbations in the hydrogen-bonding structure of a water droplet induced by surface-assembled *tbp*, we conducted a comprehensive cluster analysis of the hydrogen-bonding network of water. This analysis allowed us to compare the hydrogen-bonding network in the presence of *tbp* to that in a pure system without *tbp*. As shown in Figure 4, the average count of water clusters over time is depicted. The total number of water clusters, N_C , consistently remained below 20 throughout the simulation, with an average value of about 16. Adding *tbp* to the oil phase caused the water droplet to disintegrate, increasing the number of water clusters from $N_C = 20$ at $t = 0$ to $N_C = 80$ at $t = 10$ ns. Visual representations of the simulation, showing the water droplet at $t = 0$, 10, and 60 ns, are provided in Figure S 2. Increasing the temperature accentuated the heterogeneity of the nanodroplet, raising the total cluster count to 150 at 350 K (Figure S 3). A further temperature increase raised the N_C value to about 230 at 400 K. This rise in water clusters at higher temperatures is mainly due to the enhanced disintegration dynamics of the nanodroplet.

Detailed analyses of droplet topologies were conducted based on the average water connectivity (O_w coordination), as shown in Figure 4. In the intrinsic environment of the water-in-oil droplet, water interacted with nearly 2.73 adjacent water molecules. However, the introduction of *tbp* caused the water droplet to disintegrate, reducing water connectivity to $\bar{n}_{H_2O} = 2.5$ within the first 10 ns of the simulation. The increase in temperature further decreased $\bar{n}_{H_2O} = 2.15$ at 350K to ~ 1.85 at 400 K (Figure S3). Comprehensive calculations of the average H_2O coordination, associated with the most predominant water cluster (excluding extracted and dangling water molecules via cluster analysis), are shown in Figure 4. The coordination of the largest water cluster (\bar{n}_{max,H_2O})

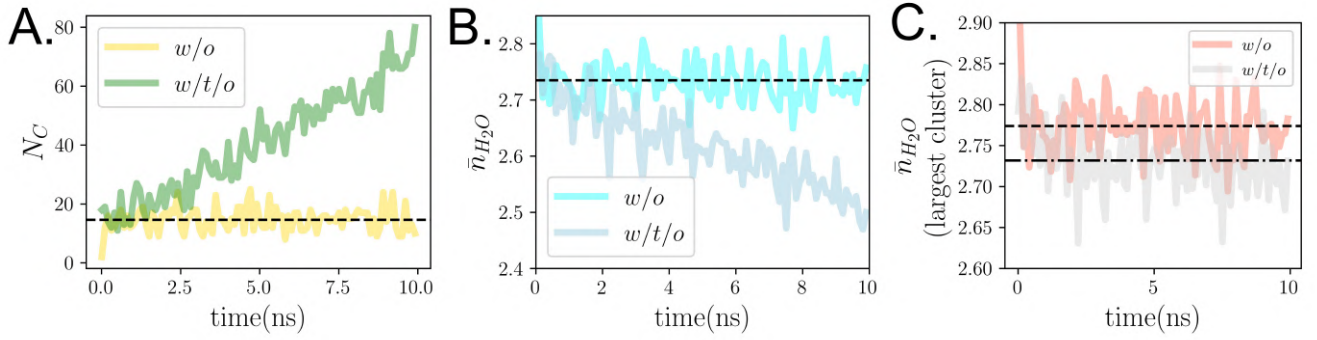


FIG. 4: Time evolution of the (A) number of water clusters (N_C), (B) average H_2O coordination (\bar{n}_{H_2O}) number and (C) the largest water-cluster coordination number (\bar{n}_{max,H_2O}) in the w/o and w/t/o systems. The mean values are represented by the dashed black lines.

evolved consistently over time. Similar trends are obtained at different temperatures (Figure S 3C). The results suggest that the time decay of disruptions within the water network (in terms of the average water coordination number) in the w/t/o system primarily arises from the dangling and extracted water molecules, while the coordination of the intact core nanodroplet remains constant, fluctuating around a stable water coordination number. Nonetheless, this average coordination number of the intact core nanodroplet (\bar{n}_{max,H_2O}) decreased both in the presence of amphiphile (Figure 4 C) and due to the action of temperature (Figure S3), due to increased heterogeneity within the hydrogen bonding network of water.

D. Protrusion driven water transport

Based on our theoretical framework, we postulated that the perturbations within the water network predominantly stem from the dangling water entities engaged in surface protrusions, thereby facilitating the transport of water from the droplet to the oil phase.[27, 33] To support this hypothesis, we presented the two-dimensional spatial density $\rho(x, y)$ distribution of the water droplet, in the systems with and without *thp*, as shown in Figure 5. The distributions show that the interaction between *thp* and the water droplet creates significant interfacial heterogeneity leading to the formation of water microchannels and protrusions of different shapes and sizes near the droplet surface. These micro-structures were responsible for driving water transport from the droplet surface to the oil phase.[14, 15] A typical simulation snapshot showing the transport of water through

the protruding structure is depicted in Figure 5 C. Importantly, these surface structures create tailored microenvironments that enhance chemical reactivity and catalysis, providing a favorable environment for liquid/liquid surface reactions.[34]

E. Kinetics of water transport

We analyzed the kinetics of water transfer from the droplet boundary to the oil phase, focusing on droplet disintegration velocities. In a system with constant parameters—particle count, volume, and temperature (where the total water entities in both oil and droplet phases, $n_o + n_d$, remain constant)—the disintegration velocity is directly proportional to the total water count in the oil phase. Notably, for this calculation, dangling water molecules at the droplet interface are considered to have moved to the oil phase. Therefore, $\frac{dn_o}{dt} \propto -n_o$, and the velocity of droplet disintegration matches the droplet formation rate $\frac{dn_o}{dt} + \frac{dn_d}{dt} = 0$, leading to $\frac{dn_o}{dt} = -n_d$. This relationship can be expressed as:

$$n_d = n_0 e^{-t/\tau} \quad (1)$$

where τ is the droplet disintegration lifetime, the time taken for the initial parent droplet to break into daughter droplets. Our initial efforts were directed towards fitting the n_d values of the droplets against time t (in nanoseconds) at temperatures 298 K and 350 K. This was achieved using a linear regression model, and a first-order decay function in alignment with Equation 1 (Figure S4).[35] However, at an elevated temperature of

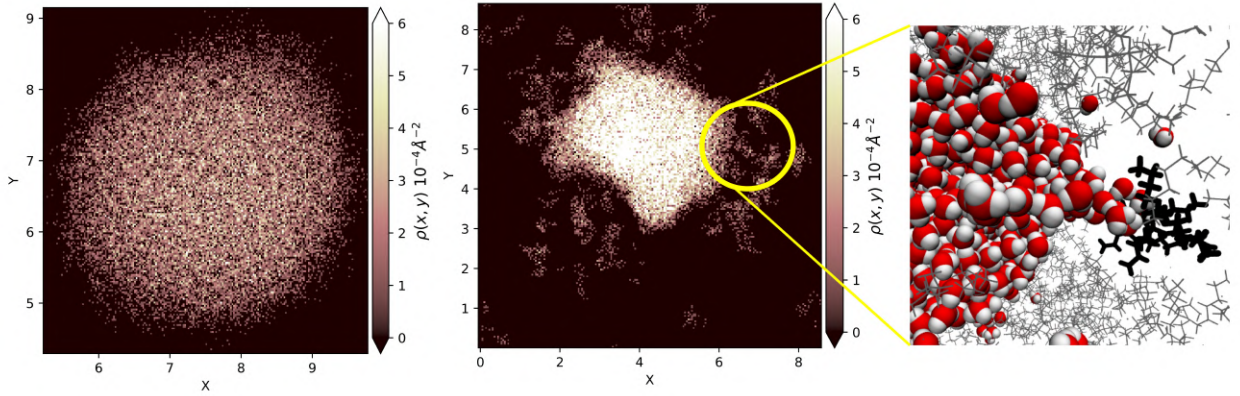


FIG. 5: Two dimensional density distribution $\rho(x, y)$ of water droplet present in w/o (left panel) and w/t/o (center panel) systems. The right panel shows a representative snapshot of water extraction by *tbp* (shown in black) through protrusions. Note that the density distributions are averaged over 100 ps after the 10 ns evolution of the molecular dynamics trajectory.

350 K, deviations from both linear and first-order decay mechanisms were observed after 10 ns. This suggests that the decay mechanism follows a more complex pathway.[36, 37] To comprehensively understand nanodroplet disintegration durations, we used a stretched exponential formulation, which typically describes complex relaxation processes,

$$n_d = n_0 e^{\left(-\frac{t}{t_0}\right)^\beta} \quad (2)$$

here, t_0 denotes the characteristic relaxation time, related to the time taken by the droplet to reach equilibrium after being disturbed by the adsorbed amphiphiles. n_0 is the initial number of H_2O in the droplet, and β is the exponent of the stretched exponential, which ranges between 0 and 1 ($0 < \beta \leq 1$). The average droplet disintegration time using this methodology is, $\tau' = \beta t_0$ (Figure S5). In the w/t/o system, we computed the average droplet disintegration rates, relaxation times, and β of the stretched component as a function of the system temperature for the first 10 ns of droplet disintegration. We found that the disintegration of the nanodroplets becomes faster and the respective rates r_0 increase linearly with temperature, from -0.82 [H_2O]/ns at 298 K to -2.21 [H_2O]/ns at 400 K (Figure 6 A). The stretched exponent β decreased linearly from ~ 1.25 at 298 K to ~ 0.12 at 400 K. The relaxation times t_0 of the water nanodroplet increase with temperature, mainly due to the increase in instantaneous rates of droplet disintegration and formation relative to the droplet at 298 K. The average lifetime of the droplet decreases from around 1004.73 ns at 298 K to around 441.2 ns at 400 K (Figure 6 B), using the

first order decay formula (Equation 1). Using Equation 2, τ' is obtained to be 837.84 ns at 298 K and 150.55 ns at 400 K, clearly demonstrating the effect of temperature on droplet disintegration, with higher temperatures leading to significantly shorter nanodroplet disintegration times (Figure S 5). In future studies, we will investigate whether the relaxation of water nanodroplets under various physicochemical conditions follows a stretched exponential trend and assess the universality of this relaxation behavior.

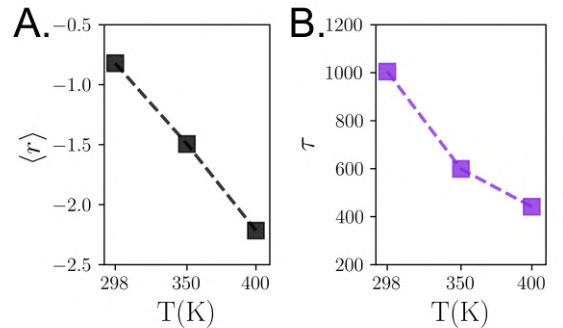


FIG. 6: (A) The average droplet disintegration rate ($\langle r \rangle$) ([H_2O]/ns) and (B) droplet lifetime (in ns) as a function of system temperature. The droplet disintegration rate became faster and the average droplet lifetime decreased with an increase in temperature.

III. CONCLUSIONS

In this study, we have presented the microscopic behavior of water-in-oil microemulsions and their disintegra-

tion in the presence and absence of *tbp* amphiphile. Our findings reveal that *tbp* adsorbs at the water droplet surface, forming a layered structure, which increases the surface area and curvature compared to pure nanodroplets without amphiphile. The adsorbed *tbp* enhances the surface heterogeneity of the nanodroplet, disrupting the water structure and leading to the disintegration of the nanodroplet into smaller water clusters, a process that accelerates linearly with increasing temperature. We also observed that interfacial *tbp* facilitates the transport of interfacial water to the organic phase by forming surface-specific morphological features known as protrusions. These protrusions resemble the morphologies observed in solvent extraction systems that mediate the transport of ion pairs from the aqueous to the oil phase. The insights provided by this study may assist experimentalists in understanding the microscopic behavior of water-in-oil emulsion nanodroplets and the mechanism of liquid/liquid extraction in the presence of amphiphiles.

IV. METHODOLOGY

All-atom molecular dynamics simulations were conducted using GROMACS 2018.2[38] on two periodic system compositions. The first system consisted of a 20 Å radius water droplet containing 1056 water molecules, immersed in a hexane solvent composed of 4087 hexane molecules. The second system was a 20 Å radius water droplet (1056 water molecules) surrounded by a mixture of *tbp* (450 molecules) and hexane (1854 molecules). Both systems were modeled with periodic boundary conditions to ensure the proper representation of bulk behavior. The simulations were run at three different temperatures: 298 K, 350 K, and 400 K, using the leapfrog algorithm with a 2 fs time step. Each system underwent initial energy minimization with the steepest descent algorithm, followed by 500 ps of equilibration in the NPT ensemble. Production runs were carried out in the NVT ensemble for at least 10 ns. The *tbp* and hexane were modeled with the optimized General Amber Force Fields (GAFF),[14] while water was modeled with the widely adapted TIP3P model.[39] This combination of the force field is utilized to successfully characterize the water and ion-pair transport mechanisms in w/t/o systems.[14] Further details are provided in ref. 15. Short-range nonbonded electrostatic and Lennard-Jones (LJ) interactions were calculated with a 12Å cutoff. LJ cross terms were obtained using Lorentz-Berthelot combination rules. Long-range

interactions were treated with the Particle Mesh Ewald (PME) method.

Network Analysis. Water networks were construed using distance based geometric criteria, specifically, the inter-oxygen atomic distance denoted as $r_{\text{cut}} < 3.5$ Å.[40] Utilizing this criterion, the water network adjacency matrix is formulated as:

$$\mathbf{A}_{ij} = \begin{cases} 1, & \text{if } r_{ij} < r_{\text{cut}}, \\ 0, & \text{otherwise.} \end{cases} \quad (3)$$

The adjacency matrix subsequently facilitates a comprehensive cluster and coordination interaction assessment.[41, 42] Within this framework, i and j signify water atoms. The principal water cluster included the intact water molecules encapsulated within the nanodroplet. The dangling water molecule were separated from the core nanodroplet using the cluster analysis module, named *connected – components*, within the NetworkX package.[43, 44] The vertices belonging to the largest connected component of water (bulk water) were separated from the remaining isolated or dangling water molecules. Connectivity analysis was then performed on the largest extracted connected component, representing an undissociated water nanodroplet.

Surface Curvature. To study the surface curvature, we first generated the triangulated coarse-grained mesh,[45, 46] derived from atomic coordinates of the w/o interfacial molecules using the pytim package.[47, 48] Subsequently, the connectivity information is used to compute surface curvature metrics using the PyVista package.[49] Detailed methodology is provided in ref. 50. Within the scope of this study, we used three distinct curvature descriptors, anchored in the principal curvatures κ_1 and κ_2 , the first one is the mean curvature, κ_m , which is equal to $\kappa_m = \frac{(\kappa_1 + \kappa_2)}{2}$, the second is the Gaussian curvature, denoted as κ_G , which is $\kappa_G = \kappa_1 \times \kappa_2$, and the third is the squared curvedness metric, κ_C^2 , which is obtained using $\kappa_C^2 = \kappa_1^2 + \kappa_2^2$. [51, 52]

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Conflicts of Interest

None.

Supplementary Information

Mean and Gaussian Curvature, Simulation Snapshots, Water Cluster, Water Hydrogen Bonds, Fitting Functions, Relaxation times.

Data Availability

The input files are deposited at https://github.com/KMNitesh05/nanodroplet_water_oil

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