

Arresting dissolution by interfacial rheology design

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A strategy to halt dissolution of particle-coated air bubbles in water based on interfacial rheology design is presented. Whereas previously a dense monolayer was believed to be required for such an "armored bubble" to resist dissolution, in fact engineering a 2D yield stress interface suffices to achieve such performance at submonolayer particle coverages. We use a suite of interfacial rheology techniques to characterize spherical and ellipsoidal particles at an air-water interface as a function of surface coverage. Bubbles with varying particle coverages are made and their resistance to dissolution evaluated using a microfluidic technique. Whereas a bare bubble only has a single pressure at which a given radius is stable, we find a range of pressures over which bubble dissolution is arrested for armored bubbles. The link between interfacial rheology and macroscopic dissolution of \sim 100 μ m bubbles coated with \sim 1 μm particles is presented and discussed. The generic design rationale is confirmed by using nonspherical particles, which develop significant yield stress at even lower surface coverages. Hence, it can be applied to successfully inhibit Ostwald ripening in a multitude of foam and emulsion applications.

interfacial rheology | foams | yield stress | Ostwald ripening | emulsions

T uning the interparticle interaction potential in bulk suspensions has long been a strategy to engineer the properties of colloidal suspensions. In this work, we apply this paradigm to interfacial materials, specifically particle-stabilized drops and bubbles. These systems with high interfacial area have broad applicability from food formulation and processing (1, 2), encapsulation (3, 4), ultrasound medical technologies (5), to lowweight/high-strength materials (6). One of the key challenges in using solid stabilized emulsions and foams in applications is curtailing Ostwald ripening, which causes the growth/shrinkage of large/small bubbles and increased size heterogeneity (7).

Ripening occurs due to differences in the Laplace pressure in bubbles of different radii; large bubbles grow, while small bubbles shrink. This suggests that strategies to impart a resistance to dilation or compression of the interface would retard or entirely stop Ostwald ripening. Previously, fully covered, "jammed," particle coated bubbles were shown to fully resist dissolution of this nature (8–12). When the ratio of particle size to bubble size is large (a/R > 0.1), specific faceted shapes may moreover reduce the mean curvature to zero, thereby reducing the driving force to zero (10). However, stability is also observed at much smaller a/R ratios, suggesting other factors come into play. Previous work supposed the particles do not interact with each other, but since such interactions have a major role in interfacial rheology, they can potentially contribute to bulk bubble and emulsion stability as well.

Here, we design and characterize model viscoplastic interfacial systems consisting of spherical and nonspherical particles at an air-water interface and show that these interfaces exhibit a surface coverage-dependent yield stress that in turn arrests the Ostwald ripening of submonolayer particle-coated air bubbles in water. There are three essential aspects to our approach: (*i*) establishing an adequately high-surface shear yield stress through lateral capillary attractions between particles at the air/water interface, (*ii*) being able to measure and tune that yield stress through control of the particle characteristics and the interfacial surface coverage on bubble interfaces, and (*iii*) observing and linking the interfacial properties to the capability of coated bubbles to withstand dissolution-driving forces of variable magnitudes.

Results

To develop appropriate viscoplastic interface model systems, it is necessary to increase the interfacial capillary interactions between particles. This is accomplished by synthesizing polystyrene-polyvinylpyrrolidone (PS-PVP) spheres by dispersion polymerization (diameter $2a = 820 \pm 6$ nm) (13, 14) and PS ellipsoids by mechanical stretching (aspect ratio 5.6 ± 0.6 , $2.48 \pm$ 0.15 μ m long, 0.45 \pm 0.03 μ m wide) (15, 16). Additional experimental details are provided in *SI Appendix*. For the spheres, the high-molecular weight PVP is expected to adsorb randomly onto the PS particles to impart an uncharged steric stabilization layer in bulk, which generates an undulating contact line at the air-water interface and increased lateral capillary interactions between the particles (17). Analogously, ellipsoids develop such interactions by their intrinsic shape (17–20). As described later, these particles impart a surface coverage-dependent interfacial yield stress at the air-water interface, which causes air bubbles in water to resist dissolution. The results are organized as follows: First, the water-air interfacial properties and measurement of the shear yield stress of planar monolayer interfaces are described. Next, experiments of single particle-coated air bubbles in water are presented, showing a surface coverage-dependent pressure window over which bubbles resist dissolution. The

Significance

The challenge of creating foams and emulsions with wellcontrolled size distribution and properties is encountered in many structured materials, such as food formulations and consumer care products. These products, like ice cream for example, must remain stable over long shelf lifetimes while their microstructure dictates product performance and consumer satisfaction. Despite the common use of particles to stabilize bubbles and emulsions, the cause of such stabilization is unknown. Here, we provide the link between the particles' ability to impart a resistance, or "armor," against bubble dissolution and their interfacial rheological properties. We propose a design strategy based on controlling interfacial particle interactions to arrest dissolution of small bubbles to create foam and emulsion materials with stable microstructures and controllable textures.

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measured yield stress is used to predict the bubble dissolution window, connecting the two results.

The interfacial properties of PS-PVP particles at the waterair interface are evaluated using a Langmuir ribbon trough combined with optical microscopy and oscillatory shear rheometry (Fig. 1A). The surface pressure-surface coverage isotherms show that the surface pressure rises beginning at an area fraction of $\phi \sim 0.5$, indicating the minimum coverage necessary for the particles to form a percolated network. Above $\phi \sim 0.7$ the surface pressure rises more rapidly, followed by buckling of the monolayer. This causes hysteresis in the compression-expansion curves on subsequent cycles. However, the beginning and final surface pressures reached are independent of cycle, which indicates that particle desorption from the interface is minimal and that differences in cycles are due to variations in monolayer morphology. The PS ellipsoids form a percolated network at a lower surface coverage ($\phi \sim 0.25$), as indicated by the increase in the surface pressure isotherm. The remainder of the isotherm is comparatively featureless, with the surface pressure rising to 35 mN/m and slight hysteresis (Fig. 1*B*).

An apparent compressional elastic modulus, $E_{d,app}$, can be evaluated based on the slope of the surface pressure-area curves:



Fig. 1. Optical microscopy, surface pressure isotherms, and apparent elasticity modulus of PS-PVP spheres (A) and PS ellipsoids (B) spread at an airwater interface. Images are taken during first compression at $\phi = 0.51$, 0.65, 0.73, and 0.87 for spheres and 0.12 for ellipsoids. The white arrows correspond to the direction of compression. (Scale bar, 100 μ m.)

$$E_{d,app} = \frac{d\Pi(S)}{d\ln S} \approx -\frac{\Pi_1 - \Pi_2}{\ln S_1 - \ln S_2}.$$
 [1]

Here, S_1 and S_2 refer to the interfacial area (trough area) at surface pressures Π_1 and Π_2 , respectively. In the above equation, the compressional elastic modulus is termed as apparent to indicate that the surface pressures obtained from the Wilhelmy plate in particle-laden interfaces contain information from both thermodynamic and mechanical contributions of the monolayer (21). For spheres, the maximum in $E_{d,app}$ occurs at a surface pressure of 26 mN/m independent of compression cycle, however the magnitude and area coverage where this maximum occurs increases with compression cycle due to consolidation of the particle aggregates after the initial compression. Beyond this peak the interface becomes less compressible and buckles, as verified by microscopy. Similar behavior is observed for graphene oxide sheets at air-water interfaces (3). For ellipsoids, $E_{d,app}$ steadily rises with surface coverage, and although it is larger than spheres in the intermediate surface coverage range (0.4-0.6), the maximum at the highest surface coverage is about a third smaller.

To interrogate the mechanical properties of the interface separate from the thermodynamic changes, interfacial shear rheology is performed on monolayers during first compression since the spreading of particles at a clean water-air interface mimics the case of a freshly coated particle-laden bubble. The very fact that a substantial yield stress develops makes it difficult to measure this using traditional interfacial rheology tools, as it is not possible to compress the sample into the small measurement gaps to sufficiently high surface coverages. Hence, a traditional double wall ring (DWR) interfacial setup (22) is modified with an additional cone in the center of the ring, which is translated vertically to ensure a more homogeneous compression of the interface (see SI Appendix for details). When compressing structured interfaces, the geometry of the measurement device may introduce anisotropic stress and strain states leading to spatially variable properties (21, 23, 24). By the design of the special DWR geometry, with the combined inside-outside compression, we obtain more uniform particle interfaces across the gap of the DWR and are able to reliably and reproducibly measure the interfacial rheological properties. A frequency sweep of the monolayer in the linear regime shows primarily elastic behavior over the accessible frequency range. The magnitude of the storage modulus, G', increases with surface coverage (Fig. 2A).

The yield stress of the PS-PVP interface is measured by three complementary methods-a stress ramp, amplitude sweep, and creep experiment—all of which show good agreement. In Fig. 2B, the results from the stress ramp experiments are shown, while the details from the amplitude sweep and creep experiment are given in SI Appendix. The yield stress corresponds to the stress at which the viscosity decreases sharply, which increases with surface coverage. At high stresses, subphase fluid inertia makes the apparent viscosity go up (25). Strain amplitude sweeps are also performed for ellipsoids, showing an increase in plateau modulus and the dynamic yield stress with surface coverage (see SI Appendix), in line with earlier results (18). As shown in Fig. 2C, the results from all three measurements show good consistency and an increase in the yield stress with PS-PVP surface coverage. We note that no yield stress is measured for lower surface coverages, where the particles do not form a percolated network. The yield stress of the PS ellipsoid interfaces determined from a strain amplitude sweep is slightly higher and shows an increased slope with surface coverage compared with spheres.

The magnitude and scaling of the yield stress with packing fraction is itself noteworthy. PS particle monolayers at water–air interfaces were previously measured to show a maximum yield stress of 7.7×10^{-5} Pa.m (26), an order of magnitude less than



Fig. 2. Rheological characterization of PS-PVP sphere and PS ellipsoid monolayers. (*A*) Frequency sweep ($\gamma = 0.05\%$) of PS-PVP particles showing increasing G'_s with surface coverage and primarily elastic behavior. (*B*) PS-PVP stress ramp experiments for varying surface coverage showing the collapse in viscosity at the yield stress. (*C*) PS-PVP monolayer yield stress determined from strain sweep, stress ramp, and creep compliance experiments shows consistency between methods and a yield stress that increases as $\tau_y \propto \phi^{4.4}$ (solid line). The yield stress of PS ellipsoids from strain sweep experiments is slightly higher and follows $\tau_y \propto \phi^{8.4}$ (dashed line).

the PS-PVP particles. The role of the PVP is important here: The yield stress is likely higher due to the irregular contact line pinning (increased capillary interactions) caused by the chemical and topological heterogeneity of the PVP steric stabilization layer. Although the variance in the data is too large to make an unambiguous determination of the scaling of the yield stress with area fraction, the sphere data are consistent with a scaling of $\tau_{y} \sim \phi^{4.4\pm 1}$. Reynaert et al. (26) found a scaling exponent of $\tau_y \sim \phi^7$ for the aforementioned PS particle interface. The scaling exponent for ellipsoids is even higher, at $\tau_y \sim \phi^{8.4}$, albeit over a small range of surface coverages. Recent numerical simulations of yielding in 2D have predicted a scaling exponent of 5.7 (27). Variations in scaling exponent can be attributed to differences in the fractal dimension of the particle aggregates at the interface. There is evidence that the compressive yield stress in 3D scales with the ratio of the interparticle attraction force to the square of the particle size (28, 29), and although the analogies between bulk and interfacial suspension rheology are still being explored, we expect similar effects at the interface. In conclusion, these measurements provide a solid foundation for interpreting the mechanical response of a particle-coated bubbles, which is presented next.

To mimic the behavior of particle-laden bubbles undergoing coarsening due to Ostwald ripening, we apply the microfluidic scheme developed by Taccoen et al. (12). Bubbles can be generated with a surface coverage varying between 0.2 and maximum packing, and these bubbles are then trapped in an observation chamber shaped as a dome and then subjected to different values of the ambient pressure. The initial bubble radius, R_0 , is 85 \pm $15\,\mu\text{m}$. During a typical experiment, for a given bubble surface coverage, the pressure is increased until the radius of the bubble is unchanging. This defines $\Delta P = 0$, and then the pressure in the microfluidic chamber is increased stepwise in 3 - 10-min increments to replicate the *driving force* for Ostwald ripening in a heterogeneous foam, but for only a single bubble. An example experiment for spheres is shown in Fig. 3A, and similar results for ellipsoids can be found in SI Appendix. The radius of the bubble is unchanged for the first pressure step, then decreases with an increasing rate at subsequent higher pressure steps, before crumpling at the highest applied pressure. The protocol of returning to $\Delta P = 0$ in between compression or expansion ensures the relaxation of any stress on the interface built up during prior steps.

The mechanical response of a particle-coated bubble with a yield stress interface to increased pressure is markedly different from that of an uncoated bubble. For an uncoated bubble, positive ΔP corresponds to shrinkage of the bubble, and negative

 ΔP corresponds to bubble growth. In the case of a foam or emulsion, heterogeneity in bubble or droplet size causes a Laplace pressure gradient between small and large bubbles whereby small bubbles dissolve and large ones grow. Fig. 3B shows that the bubble radius is constant over 4 min when $\Delta P = 0$, and also when $\Delta P < 15.6$ mbar for a bubble coated with PS-PVP particles at a coverage fraction of $\phi = 0.79$. Therefore, for a bubble coated with a submonolayer of PS-PVP particles exhibiting an interfacial yield stress, a pressure *window* develops within which bubbles resist dissolution. The "suit of armor" need not cover the entire interface.

Similar results are found with bubbles of varying particle surface coverages, and to quantify the mechanical stability imparted by the monolayer particle interface, we analyze the slope of the scaled radius versus time plots:

$$\frac{d(R-R_0)/R_0}{dt} = s^{-1}.$$
 [2]

This results in a bubble dissolution rate with units of s^{-1} to form a consistent basis to compare data between different experiments. In Fig. 3*C* the bubble dissolution rate for bubbles with varying PS-PVP surface coverages, or "armor," is given. Like the $\phi = 0.79$ data discussed previously, the $\phi = 0.72$ PS-PVP data also show a resistance to dissolution at positive applied pressures, however over a smaller pressure window of $\Delta P < 7.2$ mbar. Decreasing the surface coverage further, the effect is essentially removed for $\phi \le 0.69$. This indicates that the yield stress at this surface coverage is not sufficient to withstand the millibar scale pressure gradients applied. In this regime, the dissolution rate is similar to that of an uncoated air bubble. Conversely, increasing the surface coverage increases the pressure window over which bubble dissolution is arrested. For coverages $\phi > 0.79$, the bubbles resist dissolution at pressures up to about 20 mbar.

For ellipsoids, the bubble dissolution rate results are even more striking (Fig. 3D). There is a significant arrest of dissolution over a several millibar pressure window through the intermediate surface coverage regime where no resistance to dissolution was seen with spheres ($\phi = 0.42 - 0.66$). For ellipsoids, the minimum surface coverage necessary for the particles to form a network strong enough to resist dissolution is less than spheres. The likely cause of this can be inferred from the monolayer experiments, where a lower surface coverage was necessary to form a surface spanning network (Fig. 1B) and a higher yield stress was measured at a given surface coverage (Fig. 2C). However, the maximum pressure window at high surface coverages is similar for both systems at 15–20 mbar.



Fig. 3. Bubble dissolution experiments. (*A*) The pressure is varied from $\Delta P = 0$ to positive values stepwise over the course of a 50-min experiment on an armored bubble with PS-PVP $\phi = 0.79$. The black line corresponds to the setpoint pressure, and the gray line is the measured pressure. Images show the development of the bubble morphology over time. The image in between is a run chart of the bubble radius versus time (*x* axis). (Scale bar, 272 µm.) (*B*) Relative bubble radius change as a function of applied pressure. The positive points at the highest pressure are an artifact of the analysis as the bubble collapses. Adding PS-PVP spheres (C) or PS ellipsoids (*D*) to a bubble interface decreases the magnitude of the bubble dissolution rate at positive compressive pressures. The black line is data for an uncoated air bubble in water (from ref. 12). (*E*) The pressure window over which bubbles show minimal dissolution rate| < $3 \times 10^{-5} \text{ s}^{-1}$) to the first pressure where bubbles began to shrink appreciably (|dissolution rate| > $3 \times 10^{-5} \text{ s}^{-1}$). The sphere data points correspond to $\phi = 0.59$, 0.69, 0.72, 0.79, 0.85, and 0.90 from left to right, while the ellipsoid data points correspond to $\phi = 0.61$ and 0.66. The shaded region guides the eye. (*F*) Connecting the interfacial rheology and armored bubble experimental results. Black lines are model predictions using the second term in Eq. **9** and the appropriate quantities derived from the monolayer interfacial rheology characterization in Figs. 1 and 2. Columns denote the experimental pressure window, as in *E*, for PS-PVP spheres and PS ellipsoids.

The degree to which the dissolution rate is arrested scales with the surface coverage and yield stress of the interface (Fig. 3 E and F). Fig. 3E shows that the pressure window scales with the monolayer yield stress, strongly implying that the yield stress is contributing to bubble stability. This establishes the shaded region in Fig. 3E, where the yield stress is high enough and/or the pressure driving force is low enough such that a particle-coated bubble will resist dissolution. Although measurable yield stresses were determined for $\phi > 0.47$ (Fig. 2), bubbles resisted dissolution at positive experimental pressures only when $\phi \ge 0.72$ for PS-PVP spheres. Two scenarios can contribute to this result: (i) the resolution with which the pressure was changed for the $\phi = 0.59$ and 0.69 bubbles was too low to detect their dissolution resistance window, and/or (ii) there is a threshold yield stress necessary to impart mechanical stability in this pressure regime. The distinction between these two possibilities is important, however our experiments are not able to unambiguously make a conclusion due to the pressure resolution limit of ~ 1 mbar. There is a limited coverage range over which the yield stress was determined for ellipsoids, however for coverages where both the yield stress and bubble experiments were completed, the ellipsoid data and sphere data coincide (blue symbols).

Discussion

The results presented in Fig. 3*E* clearly suggest that interfacial yield stress is a crucial factor in the stability of particle-stabilized bubbles, which is notable for two reasons. First, while previous experiments on armored bubbles implied that full coverage was necessary to impart stability, this work shows that all that is required is a percolated network of particles with a sufficient yield stress. Second, this pressure window is tunable based on the surface coverage, or more specifically the magnitude of the interfacial yield stress of the material.

We connect the interfacial rheological properties to the resultant bubble dissolution resistance by considering the surface deformation energy of a deformable particle-laden bubble. Starting from the derivation of Danov et al. (30), the free energy of deformation can be written as:

$$W^{s} = 2 \int_{\text{sphere}}^{\text{deformed bubble}} \sigma(S) dS,$$
 [3]

where S is the surface area of the bubble and $\sigma(S)$ is the surface stress. Eq. **3** is valid for bubbles under both compression and expansion. For the bubble sizes here, effects of bending elasticity can be neglected (30). The surface stress is a function of the bubble surface area and has three components based on the surface tension, compressibility of the interface, and now yield:

$$\sigma(S) = \Pi(S) + \left. \frac{d\Pi(S)}{d\ln S} \right|_{S=S_0} \ln \frac{S}{S_0} + P_y \ln \frac{S}{S_0}, \qquad [4]$$

where $S_0 = 4\pi R_0^2$ is the surface area of the initial bubble and P_y is the compressive yield stress. For small deformations (where $(S - S_0)/S_0 \ll 1$), the energy of deformation reduces to:

$$W^{s} = 2\Pi(S - S_{0}) + (E_{d,app} + P_{y}) S_{0} \left[\frac{(S - S_{0})}{S_{0}}\right]^{2}.$$
 [5]

Eq. 5 can be rewritten by considering a uniform compression of the bubble to a final radius $R = R_0 - \ell$. Further simplification can be made by considering $R = R_0(1 - \epsilon)$ where $\epsilon = \ell/R_0$ is the strain. The energy of deformation reduces to:

$$W^{s} = 8\pi R_{0}^{2} \Pi \left[(1-\epsilon)^{2} - 1 \right] + 4\pi R_{0}^{2} \left(E_{d,app} + P_{y} \right) \\ \times \left[(1-\epsilon)^{2} - 1 \right]^{2}.$$
[6]

This energy is opposed by the dissolution energy induced by the Laplace pressure of the bubble, which is written as (12):

$$W^{\rm diss} = -\Delta P 4\pi R_0^2 \left(R - R_0 \right)$$
 [7]

and reduces to:

$$W^{\text{diss}} = \Delta P 4\pi R_0^3 \epsilon.$$
 [8]

By combining Eqs. 6 and 7, we observe that when ΔP overcomes the opposing forces of interfacial tension, elasticity, and yield, the bubble will shrink. This threshold can be established quantitatively and becomes:

$$\Delta P_{max} = \frac{2\Pi}{R_0 \epsilon} \left[(1-\epsilon)^2 - 1 \right] + (E_{d,app} + P_y) \\ \times \frac{\left[(1-\epsilon)^2 - 1 \right]^2}{R_0 \epsilon}$$
[9]

Eq. 9 should hold for bubbles under compression or expansion, and for the current case of compression $\Delta P_{max} > 0$ when $(R - R_0) < 0$. It suggests that at pressures $P < \Delta P_{max}$, the bubble will not shrink. The first term in Eq. 9 is negative and corresponds to the standard driving force due to Laplace pressure differences. We focus on the second term in Eq. 9, which is positive for compression, and evaluate it using data from the interfacial rheology measurements performed on monolayers discussed earlier.

Currently there is no method to measure the compressive yield stress of particle monolayers, so we are restricted to interpreting results using the measured shear yield stress. There is a significant body of literature discussing the relation between shear and compressive yield stress for bulk colloidal suspensions (31-34). Using linear elastic theory, these rheological parameters are related through the particle Poisson ratio by $P_y/\tau_y = [2(1-\nu)]/[(1-2\nu)]$ with $\nu \sim 0.3 - 0.5$. The principal physical difference between the two values is that under shear only a portion of the interparticle network bonds are broken, whereas under compression the load is distributed more homogeneously over the entire suspension. Between this work and that of Reynaert et al. (26), there are indications that scaling of the interfacial rheological data are similar to bulk systems, as discussed earlier. We can (tenuously) assume that P_y/τ_y will be similar for our 2D interfaces and be on the order 4 - 100(28, 31).

Fig. 3F presents model predictions of ΔP_{max} using experimental PS-PVP monolayer rheology results in Eq. 9, compared with experimental results of ΔP_{max} found from the armored bubble dissolution experiments. To generate model predictions at all coverages, we use smoothed data from Fig. 1A for $E_{d,app}$ and the best fit $\tau_y \propto \phi^{4.4}$ from Fig. 2F to calculate P_y . A Poisson ratio of $\nu = 0.495$, corresponding to $P_y = 101\tau_y$, and $\epsilon = 0.1$, corresponding to an $\ell = 8.5 \,\mu\text{m}$ length scale of deformation for a $R_0 = 85 \,\mu\text{m}$ bubble, are chosen. We present calculations using $E_{d,app}$ measured from compression of a pristine interface (cycle 1) and a previously stressed interface (cycle 3) and also separate the contribution from just considering the compressive yield stress. In addition, model results calculated with a yield stress 10 times greater than the experimentally measured τ_y are shown.

The agreement between the overall shape of the curves is promising, however quantitative agreement remains elusive. The difference in apparent elasticity modulus between the first and third compression causes changes in the shape of the model prediction curve with volume fraction—using the cycle 1 data peak in ΔP_{max} is around $\phi = 0.7$, while using the cycle 3 data ΔP_{max} continues to increase with coverage. Data from the armored bubble experiment indicate that compressing a particle-laden bubble is between these two regimes, with a plateau in ΔP_{max} at high coverages. This is rationalized because the interface is not truly pristine as in a first compression, since the nature of coating the bubble in the microfluidic channel can cause some particle compression and assembly at the interface. Additionally, using the Poisson ratio of PS corresponding to $P_y \approx 4\tau_y$ would obviously decrease the P_y term in Eq. 9 by a factor of 25.

Three comments are in order. First, the relationship between shear and compressive yield stress is not straightforward even for bulk suspensions, and therefore, there is a need to develop experimental methods and additional data for compressional yield stresses. Second, the effect of reduced interfacial curvature, which would attenuate the driving force for dissolution, would only be relevant at the highest coverages and would not result in the trends shown in Fig. 3*F*. Finally, these considerations are highlighted by the fact that such relationships can be leveraged to engineer specific properties in particle-stabilized emulsion and foam applications, such as the resistance to bubble dissolution emphasized here.

The resistance to bubble dissolution imparted by the bubble armor is a pressure window that appears due to our method of defining P_{eq} in the experiment as the lowest pressure where the bubble radius remained constant. Especially for the case of high surface coverage bubbles, the true P_{eq} as defined by Ward et al. (35) may be greater. We expect bubbles with an interfacial yield stress to resist both compression and, to a lesser extent, expansion. This would mean that the pressure we used to define $\Delta P = 0$ could very well be exposing the bubble to expansion. Therefore, the curves in Fig. 3C could be shifted to reflect the true zero pressure driving force, and this possibility is shown in *SI Appendix*. Regardless of the pressure used to define $\Delta P = P - P_{eq}$, the pressure window over which the armored bubble stays the same size remains the same and the analysis of Fig. 3F holds.

The results also suggest several processing considerations to exploit these effects. First, to tune the final size of the foam or emulsion, one must consider the appropriate particle size in addition to the overall yield stress. Smaller particles will stabilize smaller bubbles while keeping within the same $a/R \ll 1$ regime. Second, it is not necessary to optimize uniformity in the initial surface coverage to successfully arrest Ostwald ripening. As Fig. 3F shows, having $\phi > 0.7$ for spheres ($\phi > 0.4$ for ellipsoids) is sufficient to arrest dissolution due to millibar scale pressure gradients. Foams composed of interacting particles exhibiting a yield stress will also be more stable than their noninteracting particle counterparts since ripening will be blocked at lower coverages. This likewise decreases the importance of initial bubble size monodispersity to combat compositional ripening. For the simplified case of an uncoated bubble, initial size monodispersity is the only way to circumvent Ostwald ripening. As a pressuresurface coverage dissolution arrest window is created by a yield stress interface, an increased margin for polydispersity will be established while retaining the desired final overall bubble size distribution.

Lastly, one can tune the particle interactions to increase the interfacial yield stress and expand the pressure resistance window. We have tested this paradigm by increasing capillary interactions using surface chemistry (PS-PVP spheres) and particle anisotropy (PS ellipsoids) in place of previously studied PS spheres (21). There are other opportunities to impart strong lateral interactions between particles at interfaces, such as changing particle surface roughness, size, and/or solution conditions, and it remains of interest to explore this large parameter space. Generally, to arrest Ostwald ripening, one should engineer the system to prevent small bubbles from dissolving, using the pressure resistance window and interfacial characterization presented here.

We expect this behavior to be adaptable to alternative particle sizes, shapes, surface chemistries, and equally applicable to oil in water or water in oil emulsions as the foams studied here. Just as changing the particle interaction potential through pH, ionic

strength, or additive concentration modulates colloidal suspension rheology, similar control over the particle interactions at liquid–liquid or liquid–air interfaces controls the development and stability of 2D interfacial systems. In conclusion, by engineering the yield stress of the interface, we now have a powerful tool to control ripening in foam and emulsion systems relevant to a plethora of applications, including consumer care and food products.

Materials and Methods

Interfacial Rheology. Particles are spread at the water/air interface in a KSV Nima Langmuir ribbon trough modified with a quartz window to visualize the monolayer. A modified DWR set up on a stress-controlled Discovery HR3 rheometer (TA instruments) was used to perform interfacial shear rheometry measurements. At select surface coverages, a frequency sweep, strain

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amplitude sweep, stress ramp, or creep experiment was carried out to measure the interfacial yield stress.

Armored Bubble Compression. To mimic the behavior of particle-laden bubbles undergoing coarsening due to Ostwald ripening, we apply the microfluidic scheme developed by Taccoen et al. (12). Air bubbles with varying surface coverage particles are subjected to various pressures to mimic the driving force of Ostwald ripening using a pressure transducer/syringe system (36) (Baratron 120AD/Harvard Apparatus PHD Ultra CP).

Additional information on particle synthesis, interfacial rheology, and microbubble experiments is available in *SI Appendix*.

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