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Decoupling film thickness and interface permeability effects on the mass transfer between microbubbles

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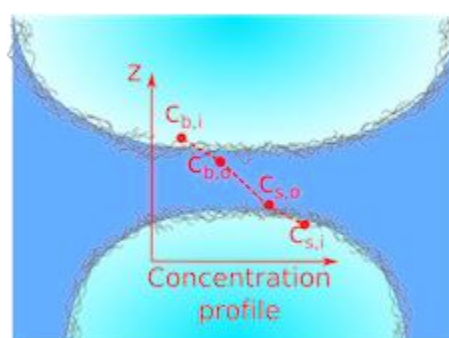
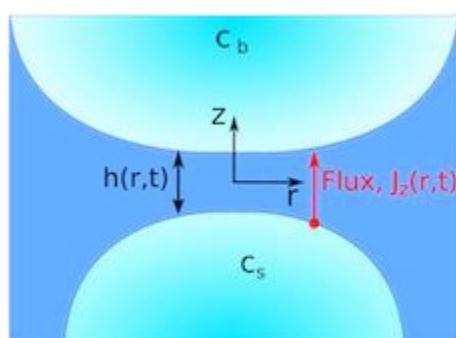
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Abstract

Hypothesis

The role of interfacial coatings in gas transport dynamics in foam coarsening is often difficult to quantify. The complexity of foam coarsening measurements or gas transport measurements between a bubble and air-water interface requires assumptions about the liquid thin film thickness profile in order to explore the effects of interfacial coatings on gas transport. It should be possible to independently quantify the effects from changes in film thickness and interfacial permeability by using both atomic force microscopy and optical microscopy to obtain time snapshots of this dynamic process.

Experiments

We measure the mass transfer between the same nitrogen microbubbles pairs in an aqueous solution using two methods simultaneously. First, we quantify the bubble volume changes with time via microscopy and second, we use Atomic Force Microscopy to measure the film thickness and mass transfer resistances using a model for the gas transport.

Findings

Modelling of the interface deformation, surface forces and mass transfer across the thin film agrees with independent measurements of changes in bubble size. We demonstrate that an anionic surfactant does not provide a barrier to mass transfer, but does enhance mass transfer above the critical micelle concentration. In contrast, a polymer monolayer at the interface does restrict mass transfer.

KEYWORDS: Colloids, Interfaces, Bubbles, Mass Transfer, Thin Films, Soft matter, Atomic Force Microscopy, Ostwald ripening

Introduction

Microbubbles are used in a wide range of applications in the biomedical, food, cosmetics, petroleum and chemical industries[1-5]. Microbubble size controls the stability and rheological behavior of foams[2]; and their efficacy as ultrasound image contrast agents, oxygen carriers, therapeutic gases or drug delivery systems[3, 6]. However, microbubbles in solution can shrink or grow over time depending upon their local environment due to Ostwald ripening. Much of the ability to control the storage, stability and size distribution of microbubble suspensions relies on a well-developed understanding of their individual and collective dynamics[6-10]. For a single spherical bubble, Epstein and Plesset[11] first formulated the theory describing its dissolution via gas diffusion into an infinite medium, driven by the difference between the gas concentration at the bubbles surface and in the bulk phase. In polydisperse foams, Ostwald ripening is driven by the Laplace pressure differential giving rise to a concentration gradient between bubbles of different sizes[10, 12-15]. Theories to describe Ostwald ripening in foams focus on the changes in bubble size distributions in foams with inter-bubble gas diffusion, *i.e.* foam coarsening, as well as characterizing how single bubble and foam stability is affected by the permeability of coatings of lipids, surfactants or polymers[7, 15-17]. In addition to the presence of surface active species, foam stability is challenging to measure due to the dependence of bubble size on the dynamics of gas transfer between bubbles and hydrodynamic drainage of the foam films[18, 19].

Single bubble measurements by Borden and others[7, 8, 20] have confirmed the Epstein-Plesset model in the presence and absence of surface-active coatings. One of the earliest advances to study transport between two air-water interfaces was the diminishing bubble method first used by Princen[21] and others[17, 22, 23]. A constant film thickness is assumed between a single bubble and a flat air-water interface to monitor gas transfer from the bubble. Measurements of foams have included methods from micro-gravity measurements[24, 25] to tracking individual bubbles in the foam[26]. More recent models have incorporated detail on the effect of surface-active species on gas transport, but still focus on predictions of bubble size distribution, often requiring simplifying assumptions of transport through the nanometer thick films between individual bubbles[15, 17]. A limitation of foam coarsening studies is that a film permeability is typically inferred by assuming a constant film thickness and then fitting a surface coating permeability[18, 27], or vice versa. In addition, foam studies are limited to situations where the surface-active components are at sufficient concentration to give a stable foam. Thus, simultaneously quantifying the gas transport between micro-bubbles with a sensitivity to the variation in the film thickness and

the permeability of surface-active coatings as a function of surface coverage remains a considerable challenge.

We report the direct measurement of gas transfer between two adjacent nitrogen microbubbles separated by an aqueous film of thicknesses as small as 15 nm using Atomic Force Microscopy (AFM). AFM allows the direct measurement of interaction forces between colliding drops or bubbles in the presence of surfactants, polymers and salt solutions[28-32]. Here we compare the gas flow rates between the same microbubble pair determined using two methods simultaneously, by changes in bubble size captured using optical microscopy and by calculating the interfacial gas flux between the bubbles based on an AFM force measurement. We use equilibrium force measurements between two deformable bubbles in combination with well-developed theory coupling surface forces with bubble deformation[28-30, 33] to quantify both the variation in film thickness and gas flux between the two gas-water interfaces. In addition, the effect of gas-water interfacial properties on mass transfer is examined by the addition of either anionic surfactant sodium dodecylsulfate (SDS) or poly(N,N-diallyl-N,N-dimethylammonium chloride) (PDADMAC).

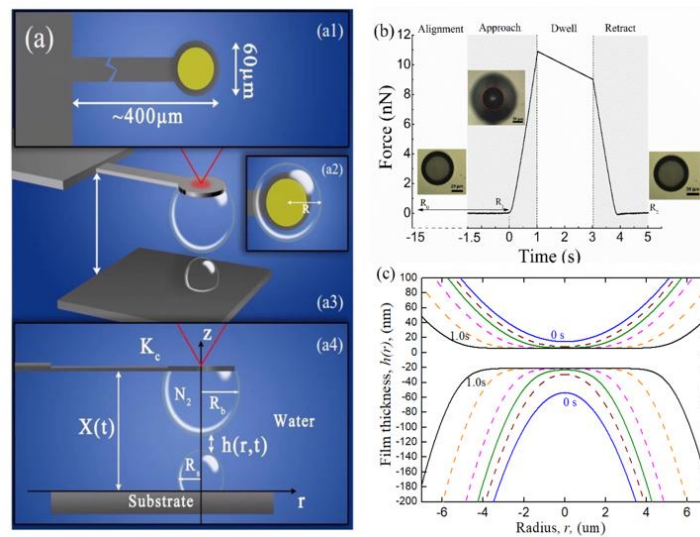


Figure. 1. (a) AFM force measurement geometry between a small bubble immobilized on a hydrophobic substrate, radius R_s , and a big bubble, radius R_b , anchored on a custom-made AFM cantilever with a gold patch. Force is measured with a thin liquid film $h(r, t)$ between them, as a function of piezo travel, $X(t)$. (b) Interaction force between two nitrogen bubbles (radii 132 and 56 μm) in 1 mM of NaNO_3 at a velocity of 0.5 $\mu\text{m/s}$ with a 2 s dwell, applied at $t = 1.0$ s, the red dash line is the edge of the small bubble during force curve measurement. (c) Interfacial profiles, $h(r)$, from the model calculation for force curve in (b) at time steps from 0 to 1 s.

Materials and Methods

Materials

Sodium nitrate, NaNO_3 , and sodium dodecylsulfate (SDS) were purchased from Sigma Aldrich, Australia and used as received. Polydiallyldimethylammonium chloride (PDADMAC) of average molecular weight 200-350KDa (Sigma Aldrich, Australia) was purified using dialyse with a cellulose acetate membrane of 10KDa pore size (Sigma Aldrich, Australia) against Milli-Q water (Millipore, Sigma Aldrich, Australia) for 2 days, replacing the water twice daily. Once cleaned, the dialysed solution was placed in 50mL polypropylene centrifuge tubes (Sigma Aldrich, Australia), frozen at -80°C (ThermoFisher, Australia) and freeze-dried in a cryo-vacuum (Christ Alpha 1-2 LD, John Morris, Australia) until fully desiccated, requiring 2-3 days. For glassware cleaning sodium hydroxide (Chem-Supply, Australia), 78 % Nitric acid (Sigma Aldrich, Australia) and Labware Detergent Concentrate (AJAX, ThermoFisher, Australia) were used. All glassware and glass rounds were washed by soaking in AJAX detergent for 1 hour, 10 % nitric acid solution for 1 hour, and 10 %wt sodium hydroxide solution for one hour.

AFM measurements

We have developed a new method using AFM to measure the transport between bubbles. Briefly, a bubble in a 1 mM NaNO_3 solution was picked from up a population of nitrogen bubbles and immobilized on a custom-made rectangular cantilever using the circular gold pattern at one end, shown in the AFM schematic in Fig. 1(a). The larger bubble was then positioned over a smaller bubble immobilized on the substrate (see supporting material). The equilibrium interaction forces were measured as the two bubbles were brought together then held at a constant position using the dwell function for 2 – 12 s (Fig. 1(b)). The bubble dimensions were obtained via an inverted optical microscope and used to calculate the bubble volume change based on a truncated sphere geometry. This process was repeated approximately 100–150 times for each bubble pair where the radii change over several hours (Fig. S1). For different bubble pairs, the addition of surfactant and polymer was achieved through solution exchange.

Experiments were performed on an Asylum MFP-3D-BIO AFM (Santa Barbara, CA) mounted on an inverted optical microscope. After sparging nitrogen bubbles through milli-Q water for 20 minutes, the saturated water was added to the AFM fluid cell. A gentle vacuum (-0.2 bar) was then applied for 1-5 seconds to generate a population of bubbles with radii from tens to hundreds of microns. A bubble of ~ 130 μm radius was picked up using a custom-made rectangular cantilever with the approximate dimensions $480\text{ }\mu\text{m} \times 50\text{ }\mu\text{m} \times 2\text{ }\mu\text{m}$ and a circular gold pattern at one end[31] (Fig. 1(a)). The gold pattern was made

hydrophobic by exposure to an alkane thiol solution following the procedure outlined in [31]. The cantilever spring constant measured, using the thermal method [34] [2], ranged from 0.09 to 0.14 N/m. The equilibrium interaction forces between the bigger bubble and an immobilized smaller bubble of $\sim 90\ \mu\text{m}$ radius on the glass substrate were recorded by driving the two bubbles together at a constant velocity of $0.5\ \mu\text{m/s}$ over a distance of $1\ \mu\text{m}$ and then holding the bubbles together using the dwell function of the MFP3D at a constant position for 2 – 12 s (Fig. 1(b)). For each independent force curve measurement, the cantilever with the larger bubble attached was moved directly over the top of the smaller bubble prior to measurement and moved away after the measurement to capture video microscopy images of the bubbles before and after the force curve measurement. The recorded time taken for alignment of the two bubbles varied between 5 – 15 s.

The bubble radii (Fig. 1(a)) and the contact radii of the smaller bubble were obtained using an image extraction code in MATLAB. The contact radii of the larger bubble was set by the dimension of the cantilever gold disk. These radii were used to calculate the volume of the bubbles based on the geometry of a truncated sphere. The change in volume of the bubbles and the total time of the measurements, both from alignment and force curve acquisition, are used to calculate the total flowrate of gas from the small to the large bubble.

The same bubble pair was used to take a series of sequential, but independent force curve and bubble size measurements approximately 100–150 times over a period of 6 – 7 hours. During this period the small bubble radius decreased in size, for example from 90.4 to $41.5\ \mu\text{m}$, whilst the bigger bubble radius increased in size, for example from 130.0 to $152.7\ \mu\text{m}$ (Fig. S1). A number of bubble pairs were studied for each solution condition.

Surfactant and polymer with 1mM NaNO_3 solutions were added to the fluid cell through fluid exchange by using two microinjection pumps in push-pull configuration with a nitrogen bubble remaining on the cantilever tip. Bubbles were given 30 min and 2h for full adsorption of surfactants and polymer respectively to the gas/water interface. Experiments with surfactants were repeated 5-6 times on a number of bubble pairs.

Transport Model Between Bubbles

The theory used to predict mass transport between two adjacent bubbles is based on the approaches of Epstein and Plesset [11] and Borden [7], with and without surfactant present. We consider the mass transfer from a smaller bubble (radius R_s) to a bigger bubble (radius R_b), separated by a film thickness, $h(r)$ as shown in Fig. 1(a). The bubbles are

assumed to be in alignment and deformed axi-symmetrically. The molar flux of gas J at the bubble surface is given by $J = -D\nabla c \cdot \mathbf{n}$, where D is the gas diffusivity in water, c is the gas concentration and $\mathbf{n}$ is the unit surface normal. Assuming that the film separating the bubbles is of thickness $h \ll R_s$, and that the molar flux of gas, J , leaving the smaller bubble surface enters the bigger bubble surface, the flux across the film occurs in the z -direction only:

$$J_z(r, t) = -\frac{D}{h(r)+2\Omega_s D} (c_s - c_b). \quad (1)$$

Here c_s and c_b are the concentration of N_2 at the interfaces of the small and big bubbles in equilibrium with the pressure in the bubbles, respectively, and Ω_s is the shell resistance due to the presence of surface active species at each interface. The gas concentration inside a bubble is related to the bubble pressure via Henry's law. By accounting for the Laplace pressure of each bubble, the one dimensional flux between the bubbles in Eq (1) can be described as a simple function of measurable quantities as:

$$J_z(r, t) = -\frac{2\sigma H D}{h(r)+2\Omega_s D} \left(\frac{1}{R_s} - \frac{1}{R_b} \right) \quad (2)$$

where H is the molar Henry's law constant, and σ is the surface tension of the interface. The molar flux during the interaction can be calculated if the thickness of the aqueous film $h(r)$ separating the two bubbles is known. We use the Chan–Dagastine–White model[28, 29, 33] to calculate the film thickness, $h(r)$, from the forces and cantilever displacements measured by AFM, accounting for the presence of surface forces between the bubbles, and interfacial deformation. The volumetric flow rate is then determined by integrating the one dimensional flux over the region between the bubbles using the film thickness profiles according to $Q = 2\pi V_0 \int_0^{\bar{R}} J_z(r) r dr$, where V_0 is the molar volume. The integration limit, $\bar{R}$, is set to R_s . The approximation of one-dimensional flux is not valid for large r , away from the thin film region, however we show below that the result is not sensitive to choice of $\bar{R}$ due to the overwhelming contribution to the flow rate within and near the thin film region. Further details of how Q was calculated over the AFM force curve time frame are included in the supporting material. Surface tension and contact angles of the bubbles were independently measured for a comparison of experimental data of the AFM measurable quantities with theoretical calculations. Table S1 shows all the parameter values and their uncertainties used for predicting gas transfer in this study where the propagation error in the AFM transport model are discussed in the supporting material[30, 35, 36].

Results and Discussion

A bubble in a 1 mM NaNO_3 solution, picked from up a population of nitrogen bubbles, was immobilized on a custom-made rectangular cantilever using the circular gold pattern at one end[30], shown in the AFM schematic in Fig. 1(a). The larger bubble was then positioned over a smaller bubble immobilized on the substrate. The equilibrium interaction forces were measured as a function of time as the two bubbles were brought together then held at a constant position using the dwell function for a range of times (2 – 12 s). An example force curve is shown in Fig. 1(b). The bubble dimensions were obtained before and after the force curve via an inverted optical microscope and used to calculate the bubble volume change based on a truncated sphere geometry.

The total gas flowrate from the small to large bubble can also be calculated from the AFM force curve. An example equilibrium force-time curve between two bubbles with dwell time of 2 s measured with 1mM NaNO_3 is shown in Fig. 1(b). The total interaction time is 5s, where $t=0$ has denotes the beginning of the interaction period. The bubbles were stable against coalescence, due to the electrical double layer (EDL) repulsion between the bubbles, previously observed in AFM measurements[30] as well as electrokinetic[37, 38] measurements. The interaction force decreased during the dwell period, indicating an increase in separation between the two deformed bubble surfaces due to mass transfer from the smaller to the bigger bubble. Quantification of the mass transport between the bubbles requires an interfacial transport model described above in detail.

Fig. 1(c) depicts calculations of the film thickness between the two bubbles corresponding to the force measurement shown in Fig. 1(b) for six-time steps. The film approaches a constant film thickness in the radial center as the disjoining pressure within the film approaches the Laplace pressure inside the bubbles. In this instance, the central limiting film thickness is 23 nm, where the specific value is dependent on both the disjoining pressure, surface tension and the bubble radii[28, 29]. The disjoining pressure is dependent on the surface force between the bubbles, here due to EDL and van der Waals forces. A 1.0 mM NaNO_3 solution was used to ensure a well-defined ionic strength in calculating the EDL forces. The radial dimensions for most of the time profiles make detailed film thickness information inaccessible by interferometry, which is why the AFM measurement and analysis is required[31]. Reflective interference contrast microscopy has been used in AFM for a

single bubble and a flat plate, but two bubbles of this size still remains a considerable challenge[39, 40].

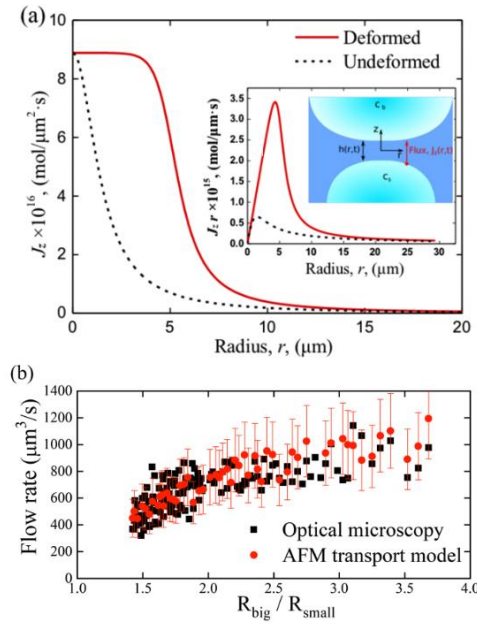


Figure 2. (a) Molar flux J_z as a function of radius for the interfacial profile at $t = 1$ s shown in Fig. (1c). The molar flux result for the deformed interfaces (red line) compared that for two spherical non-deformed interfaces (black dashed line) at the same separation. inset: The contribution of the molar flux $J_z r$ to the overall mass transfer for the two cases and a transport model schematic. (b) The gas transfer flow rate during an AFM measurement between two nitrogen microbubbles based on changes in bubble size from optical microscopy (black squares) and using the AFM force curve data and transport model (red circles) in 1 mM NaNO_3 .

Prior to calculating the total flow between the bubbles, using the film profiles one can explore the impact of the bubble deformation on the variation of the molar flux J_z with radius r . The molar flux is shown in Fig. 2(a) for the bubbles in Fig 1(b) at $t = 1$ s as well as for two undeformed bubbles at the same separation at $r = 0$. In contrast to the undeformed interfaces, the molar flux for the deformable interfaces remains constant over the thin film region ($r \lesssim 5 \mu\text{m}$) and decreases thereafter. The total flow rate is calculated via integration where the integrand is the product of the molar flux with radius, $J_z r$, shown in the inset of Fig 2(a). For the deformed bubbles, the quantity $J_z r$ increases and then decreases with radius. This is a result of the deformed region with a nearly constant film thickness, meaning that $J_z r$ grows with the increase in r . Outside this region the film thickness h increases faster than r , causing $J_z r$ to decrease rapidly. Thus, the choice of the outer limit $\bar{R}$ in the flow rate integral introduces negligible error in the calculation. Further details of the flow rate calculation can

be found in the supporting material, but it is clear that the deformability of the air-water interfaces greatly enhances the sensitivity of the mass transfer measurements, in the same way that the deformability increases the sensitivity of force measurements[41].

Fig. 2(b) shows the flow rate between two bubbles as a function of bubble radii ratio measured two different ways over the course of hours, in a 1 mM NaNO₃ aqueous solution assuming zero shell resistance ($\Omega_s=0$). The black squares correspond to the flow rate calculated based on the change in bubble radii measured via optical microscopy before and after the AFM force measurement. For a subset of these measurements, the flow rate was also calculated using the transport model described above and the corresponding AFM force curve for that bubble radius ratio (red circles). Excellent agreement between optical microscopy and AFM calculation is found using parameter values within the range of experimental tolerance (Table. S1), the force calibration uncertainty and the difference in initial bubble separation, h_0 , from each measurement during alignment period. The flow rate increases with increasing radii ratio due to a larger Laplace pressure difference between the bubbles, which drives gas transfer. However, as the bubble size difference increases the interaction area decreases, causing the flow rate to plateau at large radii ratios.

The trend of flow rate against radii ratio of the measured bubble pairs and the excellent agreement between the two methods is also observed for a bubble pair with 4 mM SDS, using a shell resistance $\Omega_s = 0$ (Fig. 3(a)). The film thickness for this bubble pair is 5-7 nm smaller than surfactant free data in Fig 2(b), due to the EDL screening from the higher ionic strength. The measured gas transfer is lower due to the presence of SDS at the interface despite the negligible shell resistance and decreased film thickness, because of the decrease in surface tension and consequently Laplace pressure, the main driving force for gas transfer. This behaviour demonstrates the importance of the interplay between disjoining pressure, film thickness and Laplace pressure in quantifying the mass transfer rate or shell resistance. Based on surface tension data, the surface excess of SDS at the critical micelle concentration, 8 mM, was calculated to be 2.69 mol/m² with a surface area per molecule of 62 nm² (Table S1). Thus, the interface is dominated by gas-liquid contact and no significant barrier to transport is present. Interestingly, when applying the same parameters to measurements of a bubble pair with 12 mM SDS, the experimental data is generally 10% higher than the model predicts (Fig. 3(b)), due to the enhanced solubility (diffusivity) of the gas. A correction factor ϕ of 1.3 was determined through iteration of the AFM calculation until agreement with optical microscopy data was achieved, attributed to the presence of SDS micelles in solution which may act as hydrophobic carriers for facilitated diffusion[13, 42, 43]. Kwan and

Borden[13] found that the solubility of SF_6 was enhanced by 1.5 times in a 10 mM SDS solution.

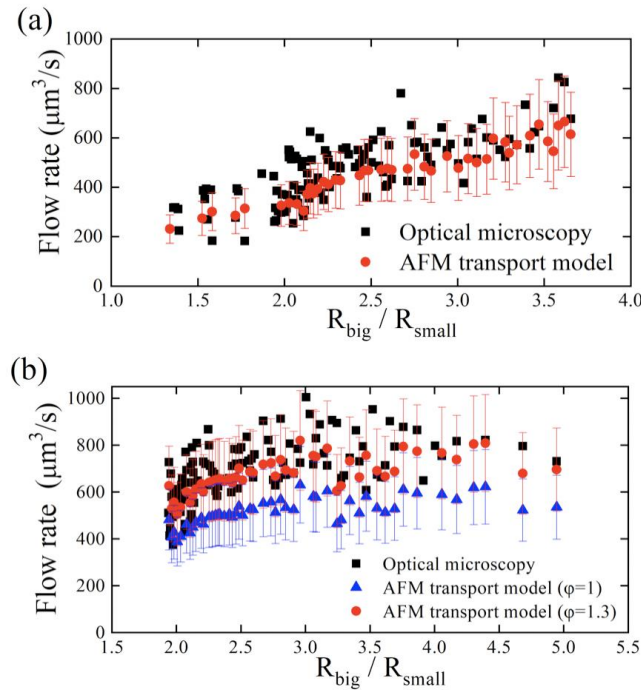


Figure 3. The gas transfer flow rate during an AFM measurement between two nitrogen microbubbles in 1 mM NaNO_3 solution and (a) with 4 mM SDS based on changes in bubble size from optical microscopy (black squares) and from using the AFM force curve data and transport model (red circles), (b) with 12 mM SDS based on changes in bubble size from optical microscopy (black squares), from using the AFM force curve data and transport model (blue triangles) and from using a correct factor φ of 1.3 for enhanced solubility of nitrogen (red circles).

For nitrogen bubbles in the presence of 10 mg/L PDADMAC, the parameter Ω_s , determined from the fit of the model to the data, is the only unknown in the system. As shown in Fig. 4, the AFM analysis shows excellent agreement with optical microscopy data with a fitted shell resistance $\Omega_s = 0.20 \pm 0.06$ s/cm. Compared to the flow rate calculated with negligible resistance ($\Omega_s = 0$ s/cm), there is significant reduction in the measured gas transfer. Therefore, the PDADMAC layer imparts a barrier to gas transfer. This behaviour is described using the validated model without invoking interfacial rheological effects. It is worth noting that there is little experimental data of the shell resistance of monolayers at gas-liquid interface lower than 1 s/cm[23, 44-46].

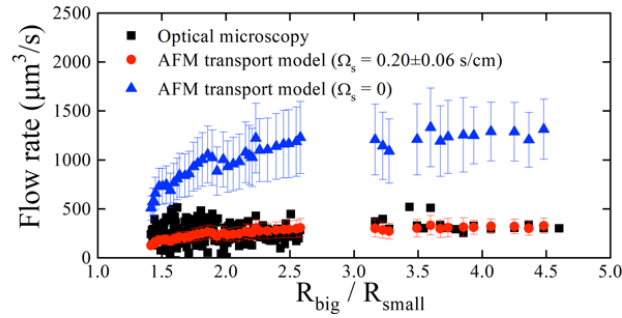


Figure 4. The gas transfer flow rate during an AFM measurement between two nitrogen microbubbles based on changes in bubble size from optical microscopy (black squares) in 1 mM NaNO_3 and 10 mg/L PDADMAC, using the AFM force curve data and transport model with no shell resistance, $\Omega_s = 0$ (blue triangles) and with resistance to gas permeation through the PDADMAC monolayer, $\Omega_s = 0.20 \pm 0.06$ s/cm (red circles).

Conclusions

We have quantified gas transfer between two adjacent microbubbles separated by a thin film, far less than 100 nm, with and without surface active species. In contrast to either diminishing bubble[21, 23] or foam coarsening studies[27, 44, 47], we can quantify and decouple the effects of film thickness and interface resistance on the transport between bubbles. The observation that SDS does not provide a barrier to transport addresses an outstanding question in the foam coarsening literature[18]. Further, the observation that SDS increases the solubility (or diffusivity) above the CMC adds another data point in a set of observations with varied results[13, 42]. In addition, the observations of small shell resistances, in this case with PDADMAC, demonstrate the potential to examine systems that may not form single bubbles or stable foams over long times.

Acknowledgements

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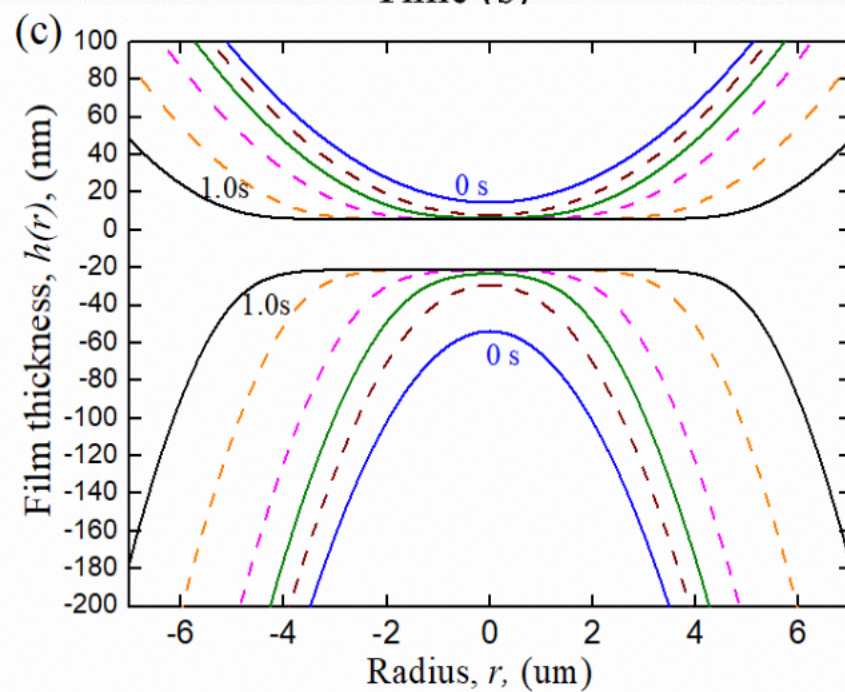
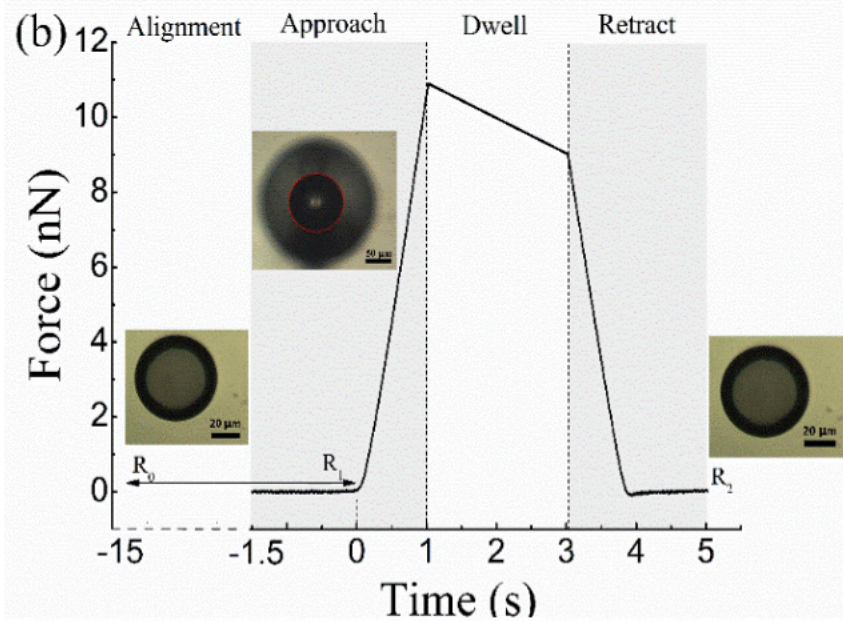
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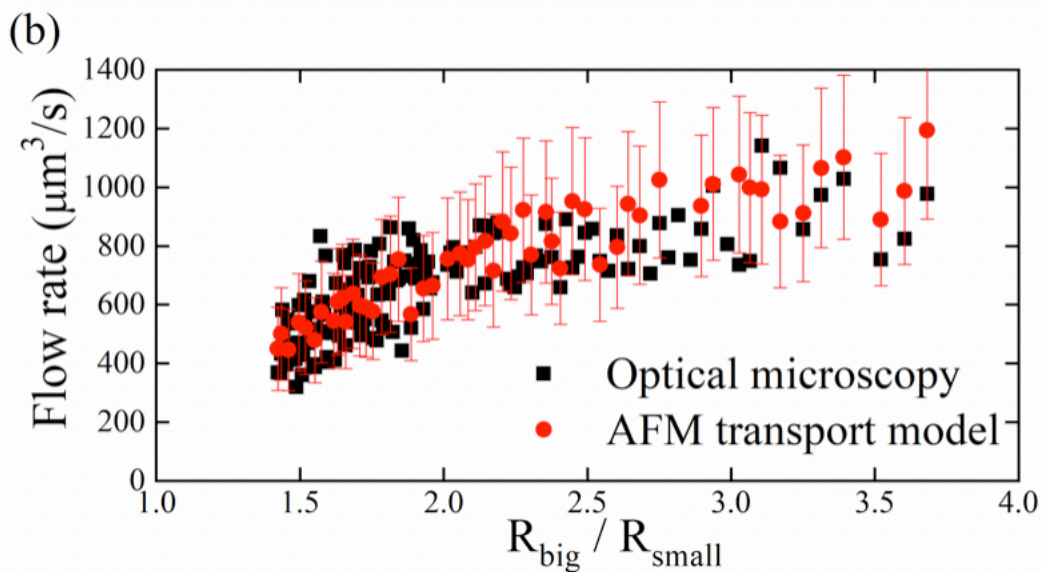
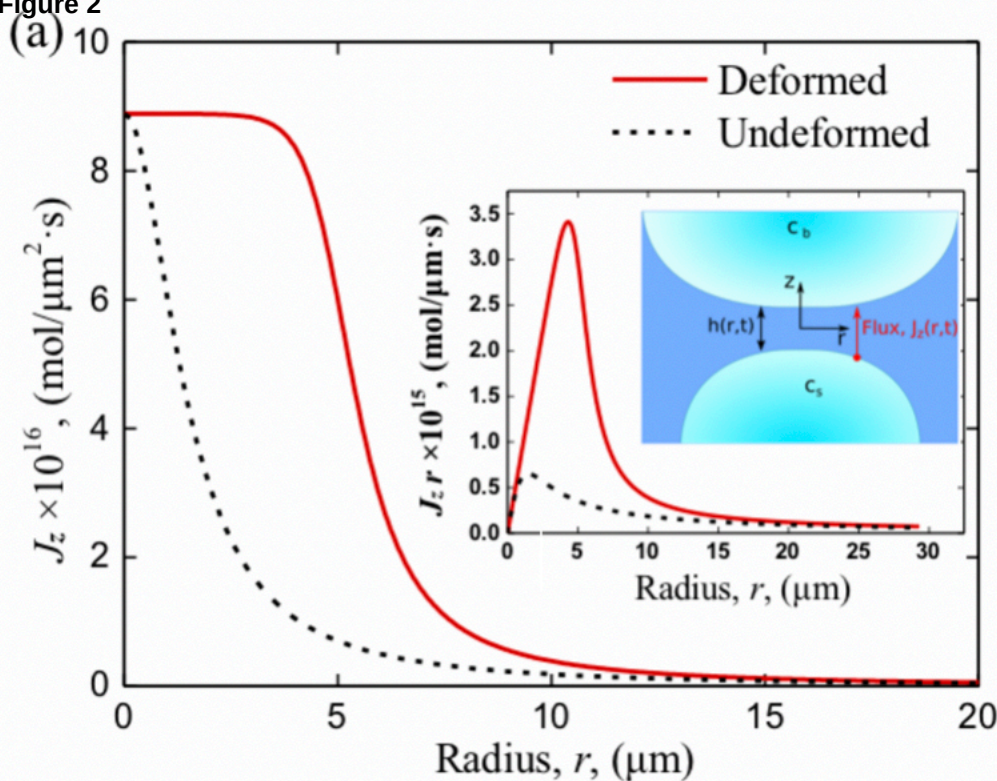
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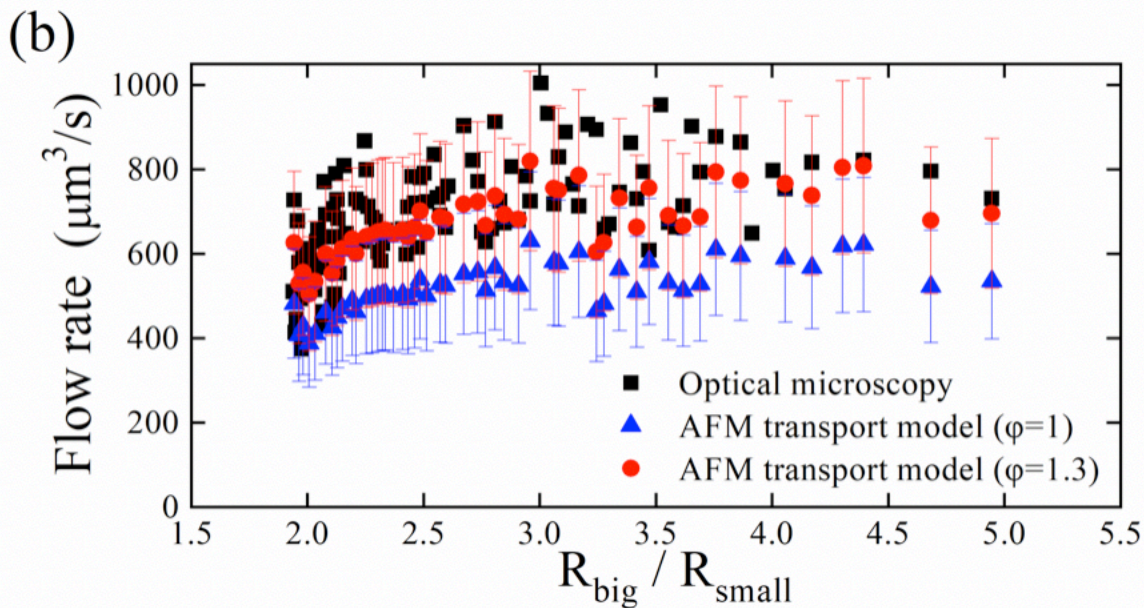
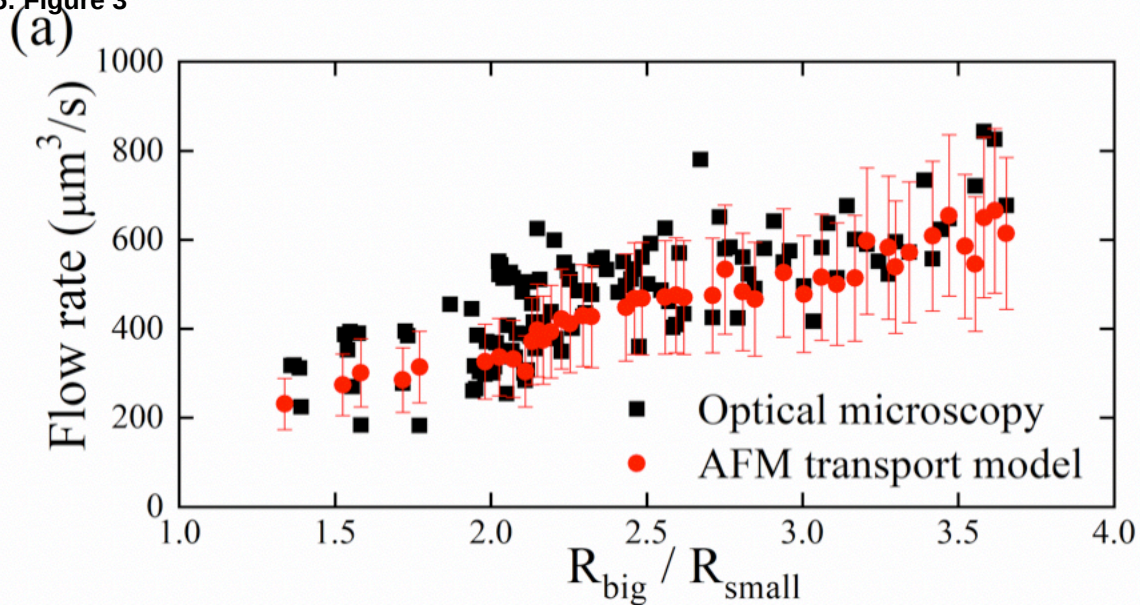
Figure 1 consists of four panels labeled (a), (a1), (a2), (a3), and (a4). Panel (a) is a top view of a microfluidic device showing a channel with a diameter of $60\mu\text{m}$ and a length of $\sim 400\mu\text{m}$. Panel (a1) is a schematic of the microfluidic device showing a channel with a diameter of $60\mu\text{m}$ and a length of $\sim 400\mu\text{m}$. Panel (a2) is a schematic of the microfluidic device showing a channel with a diameter of $60\mu\text{m}$ and a length of $\sim 400\mu\text{m}$. Panel (a3) is a schematic of the microfluidic device showing a channel with a diameter of $60\mu\text{m}$ and a length of $\sim 400\mu\text{m}$. Panel (a4) is a schematic of the microfluidic device showing a channel with a diameter of $60\mu\text{m}$ and a length of $\sim 400\mu\text{m}$.



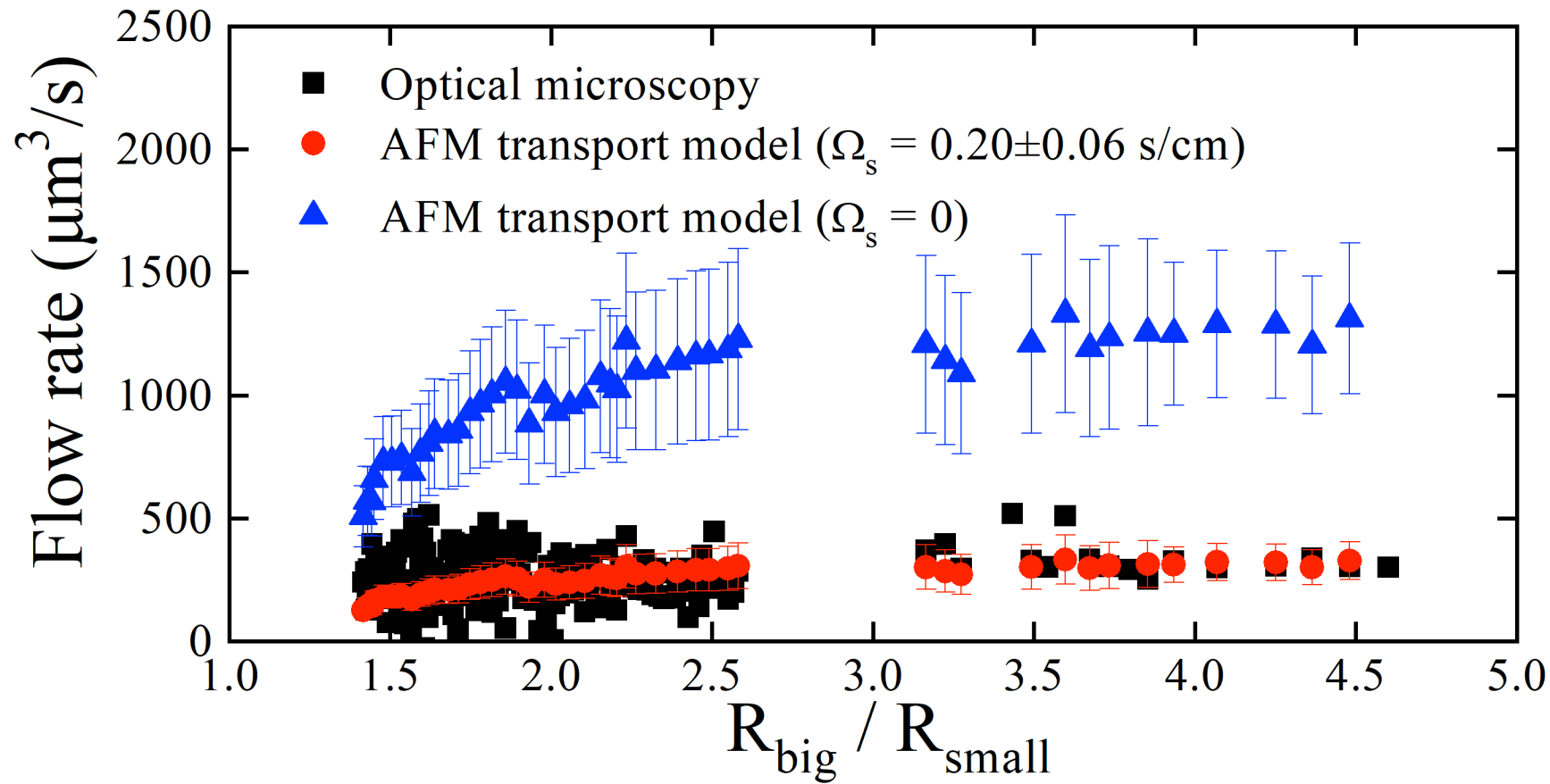
5: Figure 2



5: Figure 3



5: Figure 4



Supporting Material for

Decoupling film thickness and interface permeability effects on the mass transfer between microbubbles

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Contents

<i>Materials and Methods</i>	1
<i>Theoretical Modelling</i>	3
<i>Calculation of Flow Rate Between Bubbles</i>	5
<i>Details Experimental Error</i>	7
<i>References</i>	8

Materials and Methods

Details of the AFM measurement

A bubble in a 1 mM NaNO₃ solution was picked from up a population of nitrogen bubbles and immobilized on a custom-made rectangular cantilever using the circular gold pattern at one end, shown in the AFM schematic in Fig. 1(a). The larger bubble was then positioned over a smaller bubble immobilized on the substrate (see supporting materials). The

equilibrium interaction forces were measured as the two bubbles were brought together then held at a constant position using the dwell function for 2 – 12 s (Fig. 1(b)). The bubble dimensions were obtained via an inverted optical microscope and used to calculate the bubble volume change based on a truncated sphere geometry. This process was repeated approximately 100–150 times for each bubble pair where the radii change over several hours (Fig. S1). For different bubble pairs, the addition of surfactant and polymer was achieved through solution exchange.

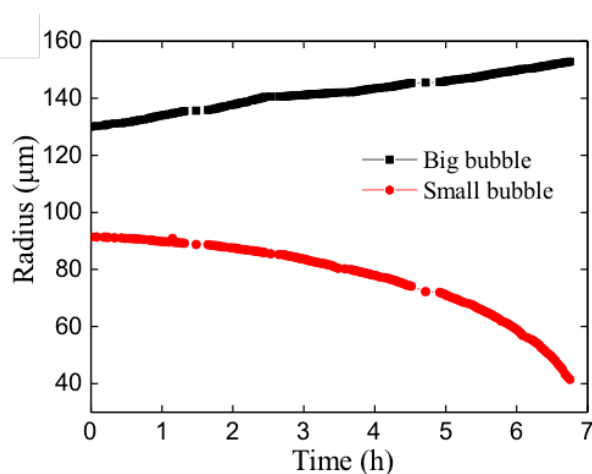


Figure S1. An example of how the radius of small and big bubble change as function of time due to their flux during a series of force curve measurements.

Experiments were performed on an Asylum MFP-3D-BIO AFM (Santa Barbara, CA) mounted on an inverted optical microscope. After sparging nitrogen bubbles through milli-Q water for 20 minutes, the saturated water was added to the AFM fluid cell. A gentle vacuum (-0.2 bar) was then applied for 1-5 seconds to generate a population of bubbles with radii from tens to hundreds of microns. A bubble of ~ 130 μm radius was picked up using a custom-made rectangular cantilever with the approximate dimensions $480\mu\text{m} \times 50\mu\text{m} \times 2\mu\text{m}$ and a circular gold pattern at one end[1] (Fig. 1(a)). The gold pattern was made hydrophobic by exposure to an alkane thiol solution following the procure outlined in[1]. The cantilever spring constant measured, using the thermal method[2] [2], ranged from 0.09 to 0.14 N/m. The equilibrium interaction forces between the bigger bubble and an immobilized smaller bubble of ~ 90 μm

radius on the glass substrate were recorded by driving the two bubbles together at a constant velocity of $0.5 \mu\text{m/s}$ over a distance of $1 \mu\text{m}$ and then holding the bubbles together using the dwell function of the MFP3D at a constant position for $2 - 12 \text{ s}$ (Fig. 1(b)). For each independent force curve measurement, the cantilever with the larger bubble attached was moved directly over the top of the smaller bubble prior to measurement and moved away after the measurement to capture video microscopy images of the bubbles before and after the force curve measurement. The recorded time taken for alignment of the two bubbles varied between $5 - 15 \text{ s}$.

The bubble radii (Fig. 1(a)) and the contact radii of the smaller bubble were obtained using an image extraction code in MATLAB. The contact radii of the larger bubble was set by the dimension of the cantilever gold disk. These radii were used to calculate the volume of the bubbles based on the geometry of a truncated sphere. The change in volume of the bubbles and the total time of the measurements, both from alignment and force curve acquisition, are used to calculate the total flowrate of gas from the small to the large bubble.

The same bubble pair was used to take a series of sequential, but independent force curve and bubble size measurements over a period of $6 - 7$ hours approximately $100-150$ times. During which the small bubble radius decreased, for example from 90.4 to $41.5 \mu\text{m}$ while the bigger bubble radius increased, for example, from 130.0 to $152.7 \mu\text{m}$ (Fig. S1). A number of bubble pairs were studied for each solution condition.

Surfactant and polymer with 1mM NaNO_3 solutions were added to the fluid cell through fluid exchange by using two microinjection pumps in push-pull configuration with a nitrogen bubble remaining on the cantilever tip. Bubbles were given 30 min and 2h for full adsorption of surfactants and polymer respectively to the gas/water interface. Experiments with surfactants were repeated $5-6$ times on a number of bubble pairs.

Theoretical Modelling

Details of the calculation of the flow rate between bubbles from AFM measurements

The theory used to predict mass transport between two adjacent bubbles is based on the approach of Epstein and Plesset for a bubble in the absence of surface-active material[3], and

the work of Borden for a stabilised bubble[4-6]. We consider the mass transfer from a smaller bubble (radius R_s) to a bigger bubble (radius R_b), separated by a film thickness, h . The bubbles are assumed to be in alignment and deformed axi-symmetrically. The molar flux of gas J at the bubble surface is given by $J = -D\nabla c \cdot \mathbf{n}$, where D is the gas diffusivity in water, c is the gas concentration and $\mathbf{n}$ is the unit surface normal. Assuming that the film separating the bubbles is of thickness $h \ll R_s$, and that the flux leaving the smaller bubble enters the bigger bubble, the flux across the film occurs in the z -direction only:

$$J_z(r, t) = -\frac{D}{h(r)+2\Omega_s D} (c_s - c_b). \quad (\text{S1})$$

Here c_s and c_b are the concentration of N_2 at the interfaces of the small and big bubbles in equilibrium with the pressure in the bubbles, respectively, and Ω_s is the shell resistance due to the presence of surface active species at each interface. The gas concentration inside a bubble is related to the bubble pressure via Henry's law, $c_i = HP_i$, where H is the molar Henry's law constant. The internal pressure of each bubble, $P_i = P_\infty + 2\sigma/R_i$, is expressed using the ambient pressure P_∞ and the Laplace pressure arising from the surface tension σ . Combining Eq. 1 with Henry's law gives the molar flux in the form $J_z(r) = -[2\sigma H D / (h(r) + 2\Omega_s D)](1/R_s - 1/R_b)$. The molar flux during the interaction can be calculated if the thickness of the aqueous film $h(r)$ separating the two bubbles is known.

We use Chan–Dagastine–White (CDW) model[7-9] to calculate the film thickness from the forces and cantilever displacements measured by AFM, accounting for the presence of surface forces between the bubbles, and interfacial deformation (see supporting materials). The volumetric flow rate is then determined from calculated film thickness profiles using $Q = 2\pi V_0 \int_0^{\bar{R}} J_z(r) r dr$, where V_0 is the molar volume. The integration limit, $\bar{R}$, is set to R_s . The approximation of one-dimensional flux is not valid for large r , away from the thin film region, however we show below that the result is not sensitive to choice of $\bar{R}$ due to the overwhelming contribution to the flow rate within and near the thin film region. Further details of how Q was calculated over the AFM force curve time frame are included in the supporting materials. Interfacial tension and contact angles of the bubbles were independently measured for a comparison of experimental data of the AFM measurable quantities with theoretical calculations. Table S1 shows all the parameter values and their uncertainties used for predicting

gas transfer in this study where the propagation error in the AFM transport model are discussed in the supporting materials[10-12].

Details of the calculation of the thickness of the aqueous film $h(r)$

To calculate the thickness of the aqueous film $h(r)$ separating the two bubbles during the force curve measurements we use the Chan–Dagastine–White (CDW) model[7-9]. This model can be used to calculate the film thickness from the forces and cantilever displacements measured by AFM, accounting for both the presence of both surface forces between the bubbles and interfacial deformation. The force between two interacting microbubbles is described by

$$F = 2\pi \int_0^\infty \Pi(h)rdr \quad (S2)$$

where $\Pi(h) = -\frac{\partial E(h)}{\partial h}$ is the disjoining pressure and $E(h)$ is the interaction energy between the drops due to EDL and vdW forces. The EDL interaction energy is calculated assuming a weak overlap model with a larger surface potential and the vdW interaction energy is defined with the Hamaker function, $A(h)$, calculated using Lifshitz theory and the dielectric spectra for water from[13] [6]. A 1.0 mM NaNO₃ solution was used to ensure a well-defined ionic strength in calculating the EDL forces.

The augmented Young-Laplace equation describes the bubble deformation arising from the disjoining pressure in the film and the Laplace pressure inside the bubbles:

$$\frac{\sigma}{2r} \frac{\partial}{\partial r} \left(r \frac{\partial h}{\partial r} \right) = \frac{2\sigma}{R} - \Pi(h) \quad (S3)$$

The CDW model combines Eqs. (S1) & (S3) with appropriate boundary conditions to fit the AFM force measurements, enabling calculation of the film thickness $h(r)$ during the interaction.

Calculation of Flow Rate Between Bubbles

During alignment, before bringing the bubbles into close separation, the initial separation distance h_0 between the two bubbles is less than 1 μm . The time to align the bubbles took between 5 – 15 s, and mass transfer must be accounted for during this period. The total mass flow occurring during alignment is estimated by assuming no bubble deformation, applying the CDW model to determine separation distance h_0 , and calculating the volumetric

flow rate, Q . The flow rate during the alignment period is added to the flow rate during interaction, for example from $t = 0$ to 5 sec in Fig. 1(b), to calculate the total gas flow rate for the measurement. This flow rate can then be compared to the flow rate calculated by the bubble volume changes from optical microscopy. The mass transported during alignment is in the range 15-50% of the total mass transfer over the entire measurement. Thus, most of the transport occurs when the drops are at nanometre separations during the dwell, but all gas transport between the bubbles must be accounted for in order to compare the AFM data to the optical microscopy data.

A series of experiments without close interaction between two clean N_2 bubbles were done for calibrating the gas transfer during alignment period. Before each measurement, a force curve without dwell (shown in Fig. S2(a)) was measured to determine the initial starting separation distance h_0 and the initial film profile at the beginning of interaction $h_{initial}(r, 0)$ ($t = 0$ s) between the two bubbles. Following this, the bubble attached to the cantilever tip was moved parallel to the surface away from the bottom bubble to enable accurate measurement of the bottom bubble size, then moved back again into alignment with the small bubble. The top bubble was then held in place for 15 seconds and then moved away to again allow accurate measurement.

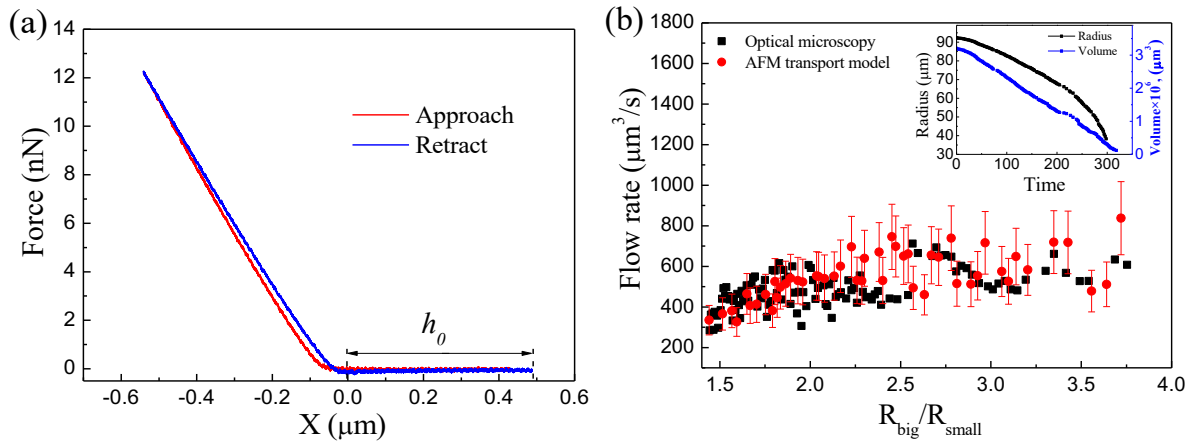


Figure S2. (a) $F(t)$ against cantilever displacement $X(t)$, where the initial separation distance h_0 is ~ 0.49 μm. (b) The comparison the flow rate of gas transfer during an AFM measurement between two N_2 microbubbles in 1 mM $NaNO_3$ solution based on both changes in bubble size from video microscopy (black squares) and using the AFM force curve data and transport model (red circles) without the small separation interaction period. Insert: the radius and volume of small bubble decreased as function of time due to its flux out after each measurement.

The images of the small bubble on the substrate were taken and recorded continuously 4 times per second during the whole course of a bubble ripening experiment. R_0 and R_1 are the radii of the small bubble before and after one measurement with no interaction force, respectively. The experimental gas transfer from small bubble to big bubble without interaction force was considered to be equal to the volume reduction of the small bubble, due to its radius change being more sensitive to the gas transfer than big bubble. The theoretical gas transfer without interaction forces was calculated by using the transport model with the film thickness profile between the two bubbles $h_{alignment}(r, 0) = h_{initial}(r, 0) + h_0$. For N_2 bubbles in the absence of impurities, the resistance to gas permeability due to interface Ω_s was assumed to be 0. Excellent agreement between experiment and theory with the gas transport model is found (Fig. S2(b)) using parameter values within the range of experimental tolerance.

The flux and integrand of the flow rate integral, $J_z(r)r$, were used to calculate the instantaneous flow rate between the bubbles. The total flow rate between the bubbles must be calculated by summing over a series of time intervals of the force curve as shown in Fig. 1(b), where at each time step, the film thickness and the resulting flux, $J(r)$ change. The change in the intervening film corresponding to different time points is shown for a portion of the force curve in Fig. 1(b), from $t=0$ to $t=1$ seconds, in Fig. 1(c). The total flow rate must account for the total gas transfer including the time period for the alignment period and for the force curve.

As mentioned in the discussion of Figure 2, the interaction force decreases linearly during dwell period as the film thickness between the bubbles increases because the smaller bubble shrinks faster than the bigger bubble grows (Fig. 1(c)). In order to avoid overestimating the mass transfer due to the film thickness changing during the interaction, the approach and retract force curves were used to calculate the film thickness before and after the dwell period, respectively. A range of dwell times were studied to vary the change in film thickness over the interaction period.

Details Experimental Error

Details on the uncertainty of the flow rate error bars for the AFM transport model

The error bars in Fig. 2 - 4 are based on the propagation of the uncertainties outlined in Table 1 in the AFM transport model. Propagation of the error from the surfaces potential values results in differences of the film thickness of several nanometers and has the largest impact on the error bars at larger bubble size ratios. This reflects the sensitivity of the model the bubble separation, $h(r)$. The uncertainties of the surface potential are commensurate with surface force measurements[12] and electrokinetic studies[14, 15].

Table S1. Parameters H , D_i , ζ and σ used in this work from a range of references.

Parameters	N ₂	N ₂ +4mM SDS	N ₂ +12mM SDS	N ₂ +10ppm PDADMAC
Henry's law constant H [mol/(m ³ *Pa)] [4]	$(6.4\pm0.2)\times10^{-6}$	$(6.4\pm0.2)\times10^{-6}$	$(6.4\pm0.2)\times10^{-6}$	$(6.4\pm0.2)\times10^{-6}$
Diffusivity D_i [m ² /s]	$(2.02\pm0.2)\times10^{-9}$	$(2.02\pm0.2)\times10^{-9}$	$(2.02\pm0.2)\times10^{-9}$	$(2.02\pm0.2)\times10^{-9}$
Surface potential ζ [mv]	-30±10 [12]	-60±10 [16]	-65±10 [16]	+50±10 [11]
Interfacial tension σ [mN/m]	72±1	42.5±2	37.5±2	71.5±2
Surface Excess [mol/m ²]	-		2.69	-

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