Supporting Information

Coalescence or Bounce? How Surfactant Adsorption in Milliseconds Affects Bubble Collision

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Bubble aging time

The bubbles residing in bulk can be divided into two sub-stages: (1) Bubble growth at the capillary orifice; (2) bubble rise in bulk. The bubble surface area keeps on increasing in the first stage, but barely changes in the second stage. The evolution of the surface area in stage (1) needs to be considered in quantifying the aging time. To be more specific, the measured aging time $t_1$ for stage (1) needs to be converted to an effective aging time ($t_{\text{eff}} = 0.6 t_1$). In stage (2) the residence time $t_2$ is directly used. The overall aging time is given by: $t = t_2 + t_{\text{eff}} = t_2 + 0.6 t_1$. A detailed derivation for $t_{\text{eff}}$ is given here.

At a constant inlet flow rate $J$, the volume of the growing bubble $V(t) = J t = \frac{4}{3} \pi (r(t))^3$, where $r(t)$ is the bubble radius at time $t$. The surface area at time $t$ is,

$$A(t) = 4\pi (r(t))^2 = 4\pi \left( \frac{3V(t)}{4\pi} \right)^{\frac{2}{3}} = 4\pi \left( \frac{3J}{4\pi} \right)^{\frac{2}{3}} t^{\frac{2}{3}}$$

The effective aging time is defined as follows to represent the equilibrium time for surfactant adsorption at the surface area $A(t_1)$

$$t_{\text{eff}} = \frac{\int_{0}^{t_1} A(t)dt}{A(t_1)} = \frac{3}{2} \frac{A(t_1)}{A(t_1)} \cdot t_1 = 0.6 t_1$$

Using the above definition, the counted aging time for the pinch-off collisions is between 6.8 ms and 12.7 ms, refereed as $\sim$10 ms in the manuscript. For the rise collisions, the aging time is between 40 ms and 85 ms, referred as $\sim$50 ms in the manuscript.

Pinch-off collision: bubble bounce and coalescence

The experimental phenomenon in which the bubbles either bounce or coalesce is also observed with the pinch-off collisions. An example for bubble bounce is presented in Fig. S1a, where the slow rising bubble was hit by a bubble that was rapidly growing at the capillary orifice. In this case, the bubble deformation and bounce cannot be clearly observed, because the
Figure S1: (a) Snapshots for bubble bounce where a slowly rising bubble was pushed aside by a rapid growing one; (b) Snapshots for the bubble coalescence process. The growing bubble merge into the rising one within 0.4 ms.

The rising bubble oscillated and deformed even without collision. But there is still a clear sign indicating the interaction force between the bubbles: after colliding for more than 1 ms, the rising bubble was pushed away by the growing one. The acceleration of the rising bubble, mostly in non-vertical direction, clearly demonstrates a repulsive force between the bubbles other than the buoyancy force, indicating the immobile interface on one or both bubbles.

As a comparison, rapid coalescence is presented in Fig. S1b. Upon collision, the growing bubble at the orifice was "eaten" by the rising one within 0.4 ms. The rising bubble neither accelerated nor changed its trajectory, indicating the negligible repulsive force during their interaction. Therefore, the air-water interface on both bubbles should be mobile.

At the pinch-off case, coalescence between the bubbles happens continually and the rising bubble may engulf numerous growing bubbles before it finally leaves from collision. The probability is counted from the results whether the rising bubble left freely, or was being pushed aside and/or show a quick increase of velocity.

**Force balance**

To simulate the rising bubble and its collision with the resting bubble (Fig. S2a) or the flat surface (Fig. S2b), we need to consider the forces exerted on the bubbles. For a free rising
bubble at its terminal velocity, the buoyancy force $F_B$ is balanced by the hydrodynamic drag force $F_D$ with the relationship $F_B + F_D = 0$. Upon collision with the resting bubble or the flat air-liquid interface, the pressure builds up in the film giving rise to the film force $F_F$ that decelerates the rising bubble, accompanied by the deceleration of the surrounding liquid contributing to the added mass force $F_A$. The last two forces should be considered to obtain the force balance ($F_B + F_D + F_F + F_A = 0$). In our system, this balance is written as

$$\frac{4}{3} \pi R^3 \rho C_m \frac{dV}{dt} = \frac{4}{3} \pi R^3 \rho g - C_D \text{Re} \frac{\pi}{4} \mu R^2 V - \int_0^{r_\infty} 2\pi r pdr \quad (3)$$

In the above equation, $C_m=0.5$ is the added mass coefficient, $\rho=998$ kg/m$^3$ is the water density, $g=9.8$ m/s$^2$ is the acceleration due to gravity. $C_D$ is the drag coefficient which depends on the Reynolds number $Re = 2R\rho V/\mu$. For $C_DRe$, we use equations given by Moore$^2$ for mobile air-water interface or Schiller & Naumann$^3$ for immobile air-water interfaces. Detailed derivation and applications can be found in the review of Manica et al.$^1$ The film force $F_F$ is calculated by integration of the pressure $p$ inside the thin liquid film from the center to infinity. The pressure $p$ inside the liquid film is a complex interplay of the Laplace pressure $(2\sigma/R$, $\sigma$ is air-water interfacial tension, $R$ is the harmonic mean radius $R = 2R_1R_2/(R_1 + R_2)$ for two bubbles collision, and is the rising bubble radius for the bubble-flat surface collision, see Fig. S2b), the surface deformation, and the disjoining pressure ($\Pi$). The relationship is known as the Young-Laplace equation, for the collision between a bubble and a flat surface:

$$p = \frac{2\sigma}{R} - \frac{\sigma}{r} \frac{\partial}{\partial r} \left( r \frac{\partial h}{\partial r} \right) - \Pi \quad (4)$$

On the right hand side of the Young-Laplace equation, the Laplace pressure is directly calculated with the known bubble radius. The surface deformation depends on the pressure inside the film, including the disjoining pressure given by van der Waals and electrical double
Figure S2: (a) Schematic of the rising bubble hitting another bubble resting on the flat surface, with the symbols defined; (b) Schematic of the rising bubble hitting the flat surface, with the symbols defined. The other three schematics describe the boundary conditions at the air-water interface: (c) Immobile-immobile; (d) Immobile-mobile; (e) Mobile-mobile.
layer interactions. Therefore, a detailed treatment of the thin film evolution is achieved with the lubrication approximation. Three boundary conditions at the air-water interfaces should be considered when deriving the lubrication equations for our systems

- **Immobile-immobile boundary condition;** (Fig. S2c)

  On both surfaces, the surface velocity $U = 0$. Experimentally, this boundary condition can be achieved when sufficient amount of contamination has adsorbed on the air-water interface to inhibit the interfacial mobility. This boundary condition has been reported in various publications$^{4,5}$ and the equation describing the film flow is given by

  \[
  \frac{\partial h}{\partial t} = \frac{1}{12\mu r} \frac{\partial}{\partial r} \left( r h^3 \frac{\partial p}{\partial r} \right) \quad (5)
  \]

  With this boundary condition, the film drainage is slow and it may take seconds for the thinning liquid film to reach the critical rupture thickness of $\sim 50$ nm.

- **Immobile-mobile boundary condition** (Fig. S2d);

  The air-water interface is immobile on one side of the film, but mobile on the other side. This boundary condition is possible in our experiment because one bubble that stayed longer in bulk (i.e., the flat surface) can be immobile because of the adsorption of surface active contaminants on the surface,$^{1,5}$ whereas the rising bubble that stayed shorter in bulk might be clean and mobile. With a reasonable assumption at the mobile interface that $\partial U/\partial z = 0$, we obtained the following equation

  \[
  \frac{\partial h}{\partial t} = \frac{1}{3\mu r} \frac{\partial}{\partial r} \left( r h^3 \frac{\partial p}{\partial r} \right) \quad (6)
  \]

  The film drainage with this boundary condition is 4 times faster than the Immobile-immobile case, and may lead to a slightly faster bubble coalescence in the same magnitude. Detailed description about this model and its validation has been reported.$^1$

- **Mobile-mobile boundary condition** (Fig. S2e);
In this case, both surfaces are clean and mobile. This boundary condition can be achieved in ultraclean water or with fresh generated bubbles. The equation describing the film drainage has been derived by Davis,\(^6\) featuring by the velocity \(U\) at the interface, which is determined by the continuity of stress at the interface \(\tau_f = \mu \frac{\partial U}{\partial z} = \mu_{\text{air}} \frac{\partial U}{\partial z}\), \(\mu_{\text{air}}\) is the air viscosity. The drainage rate for this case is given by

\[
\frac{\partial h}{\partial t} = -\frac{1}{r} \frac{\partial}{\partial r} (r U h) + \frac{1}{12\mu r} \frac{\partial}{\partial r} \left( r h^3 \frac{\partial p}{\partial r} \right)
\]

(7)

where \(U\) is given by \(^6\)–\(^8\)

\[
U (r) = -\frac{1}{\mu_{\text{air}}} \int_0^\infty \Phi (r, \omega) \tau_f (\omega) d\omega
\]

(8)

\[
\Phi (r, \omega) = \frac{k}{2\pi} \sqrt{\frac{\omega}{2r}} \int_0^{\pi} \frac{\cos \alpha}{\sqrt{1 - k^2 \cos \alpha}} d\alpha
\]

\[
k^2 = \frac{2r\omega}{r^2 + \omega^2}
\]

This equation leads to the film drainage that is three or four magnitudes faster than the previous reported cases, and the bubbles may coalesce within a few milli-seconds.\(^6\),\(^9\),\(^10\)

**Air-water surface mobility (Fig. S3)**

In the above description, the surface mobility was briefly related to the surfactant adsorption onto the air-water interface. If looked in-depth, the surface mobility is determined by the fluid flow between the bubbles and the surfactant distribution at the air-water interface. Schematic illustrations are provided in Fig. S3 to explain the relation between fluid flow, surfactant distribution and surface mobility.

Without any disturbance, surfactants or surface-active contaminants should distribute evenly at the air-water interface (see Fig. S3a). The fluid flow between the bubbles
can exert a shear stress ($\tau_f$) on the interfaces, leading to the uneven distribution of surfactant on the interface (see Fig. S3), hence contributing to the surface tension gradient (Marangoni stress, $\partial\sigma/\partial r$). The competition between the shear stress and the Marangoni stress determines the mobility at the air-water interface. If the Marangoni stress is large enough to counterbalance the shear stress (Fig. S3c), the immobile boundary condition can be achieved. Otherwise, the surfactant can be swept away, resulting in the surface mobility (Fig. S3d). Therefore, the clean air-water interface should be mobile and can transition to be immobile with a sufficient amount of surfactant adsorbed onto the air-water interface.

The above description provides a qualitative and simplified discussion about surface mobility. In reality, both the shear stress and the Marangoni stress evolve continuously in the film thinning process. The dynamic competition between the stresses may lead to the dynamic evolution of surface boundary conditions. For example, an initially immobile surface can transition to mobile with the increase of fluid shear stress. In-
terestingly, according to the theoretical prediction by Chesters and Bazhlekov,\textsuperscript{11} there can be a sharp transition from immobile to mobile, which was also shown experimentally.\textsuperscript{9} With this sharp transition, it is reasonable to simplify the boundary condition into two extreme cases: either immobile or mobile.

**Initial condition**

The above equations are solved numerically using Matlab, with the initial film thickness given by:

\[ h(r, 0) = h(0, 0) + \frac{r^2}{2R} \]  

(9)

where \( h(0, 0) \) represent the initial separation between the center (apex) of the bubble and the flat surface.

**Boundary conditions**

The numerical simulation is limited within a region \( 0 < r < r_m \), with \( r_m \) similar to the bubble size. The deformation outside \( r_m \) is considered through proper boundary conditions. This method helps to greatly reduce the numerical cost compared with full solutions, while keeping the accuracy at the nanometer scale.\textsuperscript{4}

For the simulations between a rising bubble and the flat surface, both the rising bubble and the flat air-water interface can deform during the interaction. In the simulation, only the deformation of the free surface is taken into account, this simplification provides good results as discussed by Manica et al.\textsuperscript{1} The flat surface deformation in response for the overall interaction force \( F \), is described by an analytical solution \( z(r) = \frac{F}{2\pi\sigma} K_0(r/\lambda), \)\textsuperscript{1} where \( K_0(r/\lambda) \) represents the Bessel function of the second kind at order 0, \( \lambda = \sqrt{\frac{\pi}{\rho g}} \) is the capillary length.
Therefore, we can obtain the boundary condition for the flat surface where $F = F_F$:

$$z(r_m, t) = \frac{F_F}{2\pi \sigma} K_0 \left( \frac{r_m}{\lambda} \right)$$  \hspace{1cm} (10)

and boundary condition for the rising bubble.

$$z_b(r_m, t) = H(t) - \frac{r_m^2}{2R}$$  \hspace{1cm} (11)

with $H(t) = z_m(t) - R$ shown in Fig. S2b. By subtracting these two terms, the boundary condition for the film thickness at $r_m$ is given by:

$$h(r_m) = z(r_m, t) - z_b(r_m, t) = \frac{F_F}{2\pi \sigma} K_0 \left( \frac{r_m}{\lambda} \right) - H(t) + \frac{r_m^2}{2R}$$  \hspace{1cm} (12)

and the film thinning rate at $r_m$ is:

$$\frac{dh}{dt} = V + \frac{1}{2\pi \sigma} K_0 \left( \frac{r_m}{\lambda} \right) \frac{dF_F}{dt}$$  \hspace{1cm} (13)

For the bubble collision with mobile-mobile air-water interfaces, the film force is negligible ($F_F \approx 0$), then the boundary condition can be further simplified to $dh/dt = V$.

**References**


(4) Chan, D. Y. C.; Klaseboer, E.; Manica, R. Theory of non-equilibrium force measure-


