Supplementary Materials

Ultra-long lifetime water bubbles stabilized by negative pressure generated between micro particles

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Part 1 | Derivations of Equation (1) and (2)

As shown in paper *Ultra-long lifetime water bubbles stabilized by negative pressure generated between micro particles* Figure 3a, which is in two dimensions, we can get the geometric relationship of curvature radius ρ and bar radius r (Figure A1(a)):

$$d/2 = \rho\cos(\theta+\phi) = r(1-\cos\theta) \Rightarrow \rho = r\cdot\frac{(1-\cos\theta)}{\cos(\theta+\phi)} \tag{1}$$

where d is the span of water between two cylindrical bars.

It's also obvious the thickness of bubble film is relative with bar radius and the angle θ.

$$\frac{t}{2} = r\sin\theta \Rightarrow \theta = \arcsin\left(\frac{t}{2r}\right) \tag{2}$$

Based on Laplace Equation we can get the negative pressure caused by concave water film among microscale particles:

$$p = \frac{\gamma}{\rho} = \frac{\gamma}{r}\frac{\cos(\theta+\phi)}{(1-\cos\theta)} \tag{3}$$

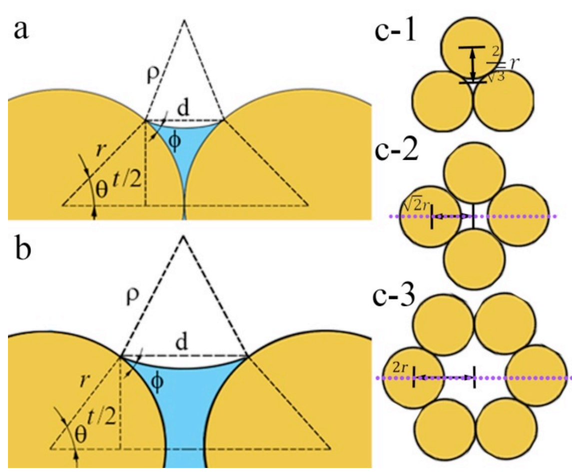

Figure A1. Schematic illustration of bubble with various holes. a, Cross section of two cylinders contact with each other. b, Cross section of two close cylinders but not contact with each other. c, Next we consider true three dimension case (Figure A1). At first we imagine all particles are touched with other particles in “three particles pattern” tightly as shown in paper *Ultra-long lifetime water bubbles stabilized by negative pressure generated between micro particles s* Figure 3b the most upper line. Using the symmetry, we can find the largest negative pressure produced must go along with certain curves connecting corresponding points on the particles and the other point at the center of concave water film. Look down at the “three particles pattern” case (Figure A1(c-1)), we can modify the relationship of curvature radius ρ and sphere radius r as:

$$d/2 = \rho\cos(\theta+\phi) = \frac{r}{\sin 60^\circ} - r\cos\theta \Rightarrow \rho = r\cdot\frac{(2/\sqrt{3}-\cos\theta)}{\cos(\theta+\varphi)} \tag{4}$$

And the corresponding negative pressure is:

$$p = \frac{\gamma}{\rho} = \frac{\cos(\theta+\phi)}{(2/\sqrt{3}-\cos\theta)}\frac{\gamma}{r} \tag{5}$$

For the hole as illustrated in Figure A1(c-2), the relationships update as:

$$d/2 = \rho\cos(\theta+\phi) = \frac{r}{\sin 45^\circ} - r\cos\theta \Rightarrow \rho = r\cdot\frac{(\sqrt{2}-\cos\theta)}{\cos(\theta+\phi)} \tag{6}$$

And the corresponding negative pressure is:

$$p = \frac{\gamma}{\rho} = \frac{\cos(\theta+\phi)}{(\sqrt{2}-\cos\theta)}\frac{\gamma}{r} \tag{7}$$

For the hole as illustrated in Figure A1(c-3), the relationships update as:

$$d/2 = \rho\cos(\theta+\phi) = 2r - r\cos\theta \Rightarrow \rho = r\cdot\frac{(2-\cos\theta)}{\cos(\theta+\phi)} \tag{8}$$

And the corresponding negative pressure is:

$$p = \frac{\gamma}{\rho} = \frac{\cos(\theta+\phi)}{(2-\cos\theta)}\frac{\gamma}{r} \tag{9}$$

For holes with diameters of *n* times of the particle size, the relationships update as:

$$d/2 = \rho\cos(\theta+\phi) = n \cdot r - r\cos\theta \Rightarrow \rho = r \cdot \frac{(n-\cos\theta)}{\cos(\theta+\phi)} \tag{10}$$

And the corresponding negative pressure is:

$$p = \frac{\gamma}{\rho} = \frac{\gamma}{r}\frac{\cos(\theta+\phi)}{(n-\cos\theta)} \tag{11}$$

We can also estimate the maximum height of a bubble by considering how far up water can be pumped by the generated negative pressure induced by the densely-assembled particles in the bubble water film.

$$p = \rho g H_{\max} \tag{12}$$

Plug in Eq(11) the expression for pressure *p*, we can obtain the estimate of the maximum height of the ultra-long lifetime stable bubbles.

$$H_{\max} = \frac{l_c^2}{r}\frac{\cos(\theta+\phi)}{n-\cos\theta} \quad \text{with} \quad \theta = \arcsin\frac{t}{2r} \tag{13}$$

where $l_c = (\gamma/\rho g)^{1/2}$ ($\approx$ 2.7mm for water) is the capillary length.

Part 2 | Measure Advancing and Receding Contact Angles on Individual Particles

In our experiment, we use atomic force microscope (AFM, Ntegra Prima or NT-MDT, see Fig A2-a) to measure microsphere particles' advancing and receding contact angles [1]. To measure particle's advancing contact angle, the microsphere particle is glued to the end of AFM cantilever. Then it is moved towards a liquid droplet center from top. When the particle touches the air-liquid surface, a particle-liquid-air three-phase contact (TPC) is formed and the capillary force pulls the microsphere into the drop (see Fig A2-b). The deflection of the AFM cantilever gives the external force on the particle, while the position of the cantilever tip gives the particle position. We can plot the exterinal force v.s. particle position curve (see Fig A2-d) and find the distance between the particle jump-in liquid droplet point and the zero-force point on the curve. Neglecting the weight of the microsphere particle and its buoyancy, the advancing contact angle can be calculated using simple geometric relation [1]:

$$\cos\theta_A = \frac{D_A - R}{R} \tag{13}$$

where R is the radius of the microsphere, D_A is distance between the jump-in point and the zero-force point, θ_A is the micro sphere's advancing contact angle.

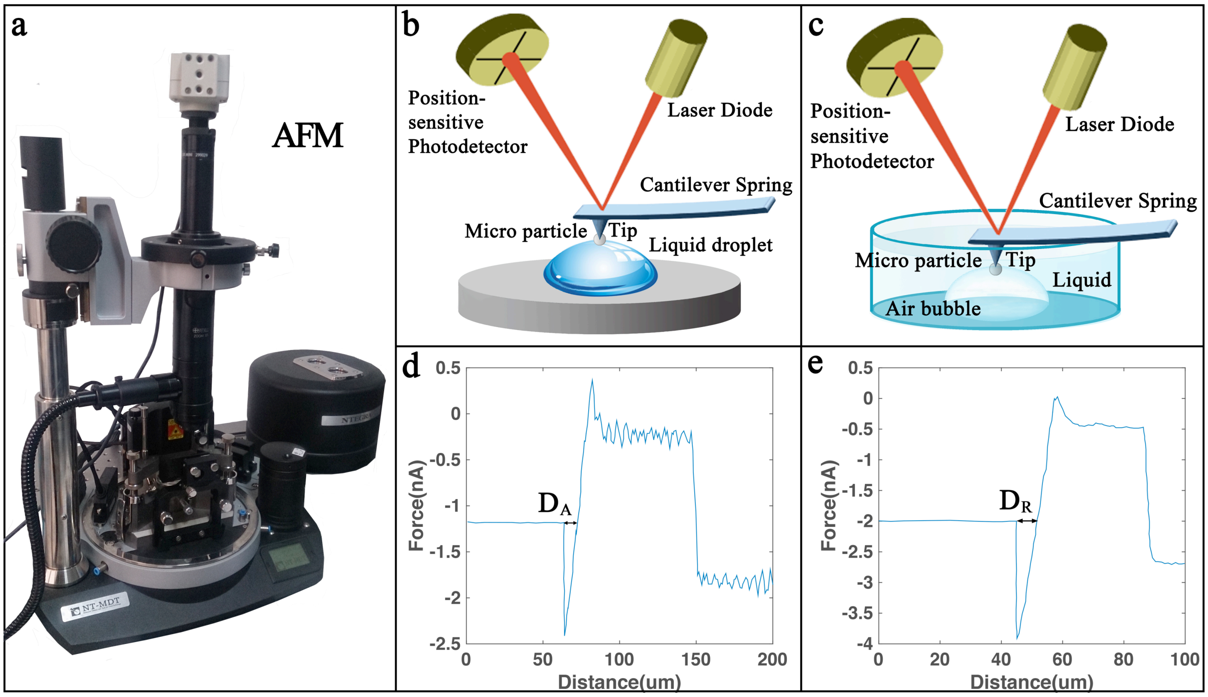

Figure A2. Atomic force microscope (AFM) tensiometry method to measure advancing and receding contact angles of micro particles in liquids. a, Photo of Ntegra Prima (or NT-MDT) AFM. **b**, Microsphere particle is glued to the end of AFM cantilever tip, and drops into the liquid droplet from top. **c**, Microsphere particle is glued to the end of AFM cantilever tip, and drops into the air bubble top in the liquid. **d**, External force v.s. particle position curve in the advancing contact angle measurement. **e**, External force v.s. particle position curve in the receding contact angle measurement.

Similarly, we can also measure microsphere particle's receding contact angle using AFM. The microsphere particle is still glued to the end of AFM cantilever. We pour some liquid into a container and blow one big bubble at the bottom of container. After that we slowly dip microsphere particle into the bubble inside from bubble top dome center and a particle-liquid-air three-phase contact (TPC) is formed (see Fig A2-c). At the same time, the deflection of the AFM cantilever gives the external force on the particle, while the position of the cantilever gives the particle position. We can plot the external force v.s. particle position curve (see Fig A2-e) and find the distance between the particle jump-in bubble point and the zero-force point on the curve.

Neglecting the weight of the microsphere particle and its buoyancy, the receding contact angle can be calculated using simple geometric relation [1]:

$$\cos\theta_R = \frac{R - D_R}{R} \tag{13}$$

where R is the radius of the microsphere, D_R is distance between the jump-in point and the zero-force point, θ_R is the micro sphere's receding contact angle.

Part 3 | Description of Supplementary Movie

In the movie, we at first scattered hydrophilic PMMA spherical particles with suitable density onto the surface of water contained in a big vessel. (Particles' diameters distribute from 300 μm to 600 μm average contact angle 47.84° ± 6.42° and average density 1.19g/mL). Next, we slowly and constantly pipe some air into the water through an injector in Movie 1. The air rose up to the water surface and plumped up a bubble. The more air is piped, the bigger the bubble will be blown up. What must be sure is that all the surface of bubble should be covered with particles. If we stop piping air into water now, then this bubble can stay quite long time (usually over one month).

However, if we continue piping air into the bubble (as shown in Movie 2) and there will appear some large area on the bubble film without densely assembled particles coatings (since Movie 2 time 01:34). This area is called circle hole of the particles layer in the paper. Once the circle hole grows to be certain large, bubble will break up (Movie 2 time 01:39).

REFERENCES

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