Supporting information for:

Mechanical stability of surface nanobubbles

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1 Cavitation threshold derivations

1.1 2D Blake threshold

Before considering the surface nanobubble case, it is important to show how the 2D Blake threshold is derived, as the surface nanobubble cavitation threshold follows a similar approach (see Figure S1 (a)). The 2D Blake threshold equation for a free bubble can be

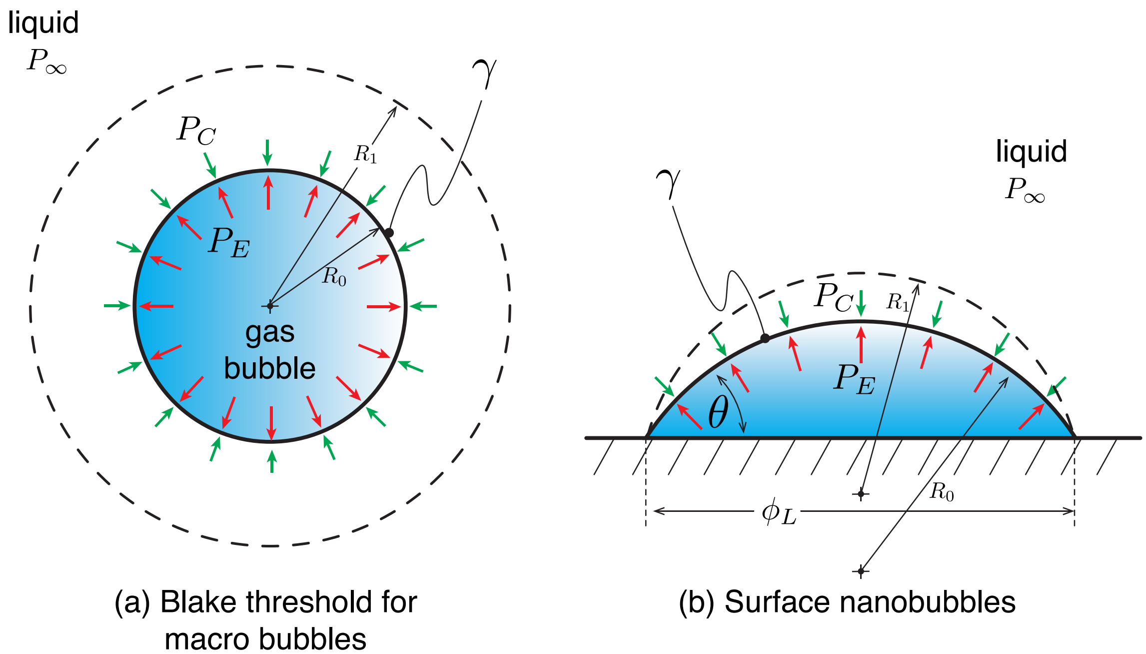

Figure S1: (a) Schematic of spherical bubble, and (b) a surface nanobubble.

obtained by considering the limit in which the pressures acting on a cylindrical bubble cannot be in mechanical equilibrium. There is an expanding pressure, P_E, which acts to grow the bubble;

$$P_E = P_g + P_v, \tag{1}$$

where P_g is the gas pressure, and P_v is the vapour pressure, inside the bubble. Assuming that the internal gas phase expansion can be expressed as a polytropic process,

$$P_{g,0}V_0^k = P_{g,1}V_1^k, \tag{2}$$

where subscripts 0 and 1 here represent the initial and final states of the polytropic process, respectively. If the initial gas pressure $P_{g,0}$ and volume V_0 are known, then the gas pressure can be calculated for any new bubble volume V_1 using Equation (2). The exponent k is a constant that depends on the thermodynamic process that occurs when the gas expands. For a 2D cylindrical bubble, the bubble size can be better expressed in terms of its cross-sectional area A, since $A \propto V$; A is a monotonic function of the bubble's radius of curvature R i.e. $A = \pi R^2$, so Equation (2) can be rewritten:

$$P_g = P_{g,0} \left(\frac{R_0}{R} \right)^{2k}. \tag{3}$$

An expanding pressure is opposed by a compressing pressure P_C, which tends to shrink the bubble[1]:

$$P_C = P_\infty + \frac{\gamma}{R}, \tag{4}$$

where P_∞ is the far-field liquid pressure, and γ is the liquid-gas surface tension. In mechanical equilibrium, these two pressures balance such that $P_E = P_C$, which is essentially a restatement of the Young-Laplace equation:

$$P_g + P_v = P_\infty + \frac{\gamma}{R}, \tag{5}$$

or by substituting in Equation (3):

$$P_\infty = P_{g,0} \left(\frac{R_0}{R} \right)^{2k} + P_v - \frac{\gamma}{R}. \tag{6}$$

If P_∞ reduces, Equation (6) indicates this typically causes the bubble to expand (an increase in R) for it to remain mechanically stable. The growth path of a 2D cylindrical bubble is illustrated in Figure S2, where P_g and γ/R of Equation (6) are plotted against R. The

[1] For spherical bubbles and droplets, the Laplace pressure component is $2\gamma/R$; however for 2D cases, the Laplace pressure component becomes γ/R as given in Equation (4).

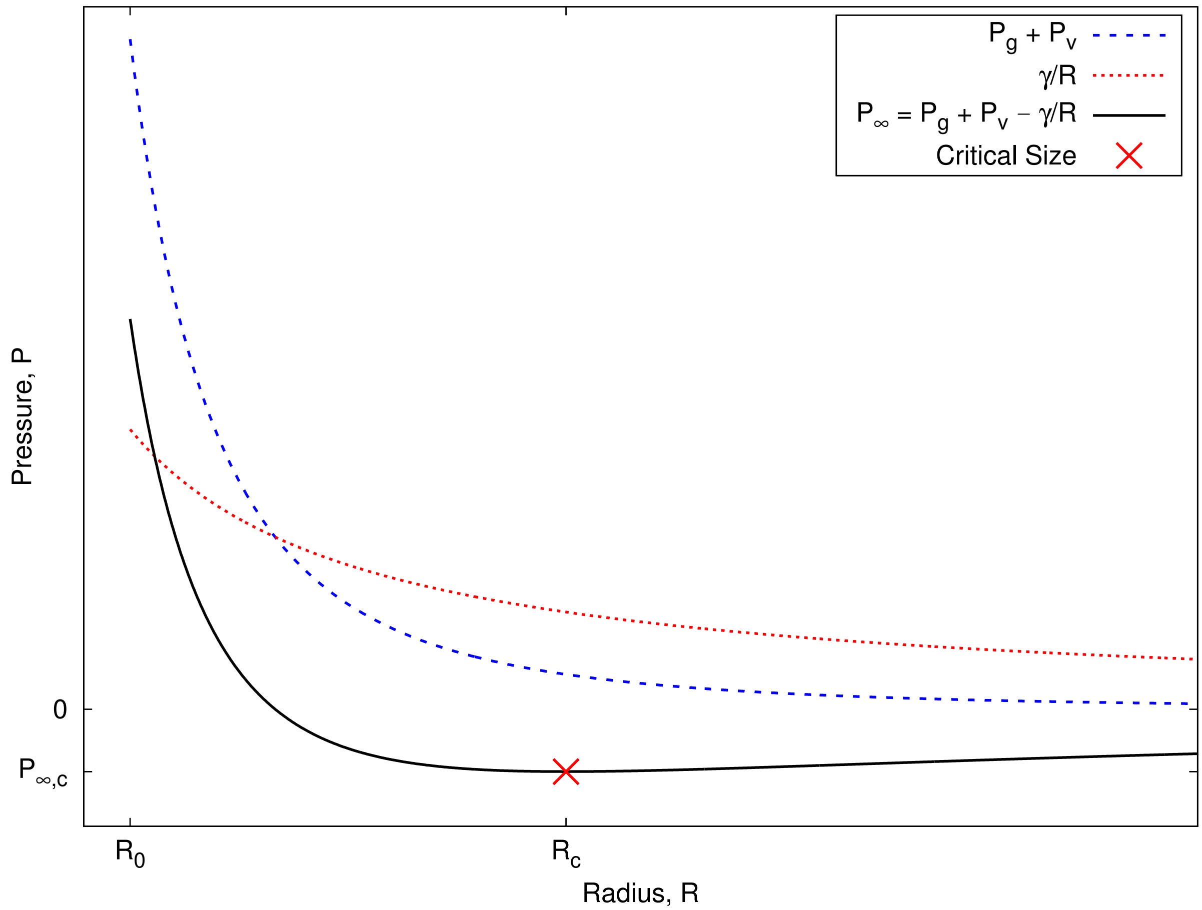

Figure S2: Threshold pressure of a simple 2D cylindrical bubble.

critical or threshold liquid pressure, $P_{\infty,c}$, is defined at the point when $P_E > P_C$ for all bubble volumes, i.e. there is no stable equilibrium size for the bubble at liquid pressure $P_{\infty,c}$ and below. The threshold pressure can be obtained by determining from Equation (6) the critical bubble size, $R = R_c$, where P_∞ is at a minimum, as can be seen in Figure S2.

Differentiating Equation (6) with respect to R yields:

$$\frac{\mathrm{d}P_\infty}{\mathrm{d}R} = -2kP_{g,0}\frac{R_0^{2k}}{R^{2k+1}} + \frac{\gamma}{R^2}, \tag{7}$$

which can be solved at the minimum to yield the critical radius:

$$R_c = \left(\frac{2kP_{g,0}R_0^{2k}}{\gamma}\right)^{\frac{1}{2k-1}}. \tag{8}$$

Substituting the critical radius, R_c, into Equation (6) for R will give the minimum possible value of P_∞ that can sustain a bubble in mechanical equilibrium:

$$P_{\infty,c} = P_v - \gamma \left(1 - \frac{1}{2k}\right) \left[\frac{\gamma}{2kR_0^{2k} P_{g,0}}\right]^{\frac{1}{2k-1}}. \tag{9}$$

1.2 2D Surface Nanobubble threshold

The 2D surface nanobubble cavitation threshold can be obtained by considering the limit in which the pressures acting on the cylindrical capped bubble cannot be in mechanical equilibrium, in a similar way to the 2D Blake threshold derived above. The internal gas and vapour pressure can be described by Equations (1) and (2) again. For a 2D bubble, the bubble size can be better expressed in terms of its cross-sectional area, A (since $A \propto V$), i.e.

$$A = \frac{1}{2} R^2 \left[2\theta - \sin 2\theta\right], \tag{10}$$

where θ is the contact angle, in radians, taken from the *gas side*. In the 2D Blake threshold case, A is a monotonic function of the bubble's radius of curvature, R, since $A = \pi R^2$. However surface nanobubbles present a non-trivial case because for contact angles $\theta < 90°$, and *pinned* lateral diameter ϕ_L, the radius of curvature R will decrease to a minimum at $\theta = 90°$, and then increase again for $\theta > 90°$: for a given R, there are two possible values of A.

Instead, A can be expressed solely as a function of θ if R is related to the pinned (constant) contact diameter for Constant Contact Radius (CCR) growth, i.e.

$$R = \frac{\phi_L}{2 \sin \theta}. \tag{11}$$

Using Equation (11) in Equation (10) gives:

$$A = \frac{1}{4}\phi_L^2 \left[\frac{\theta}{\sin^2\theta} - \frac{1}{\tan\theta}\right]. \tag{12}$$

Equation (2) can then be expressed in terms of θ:

$$P_g = P_{g,0} A_0^k \left[\frac{1}{4}\phi_L^2 \left(\frac{\theta}{\sin^2\theta} - \frac{1}{\tan\theta}\right)\right]^{-k}, \tag{13}$$

where A_0 is the original 2D bubble area, which is obtained from Equation (12) with the initial bubble contact angle θ_0.

The compressing pressures P_C are the same as in the 2D cylindrical case in Equation (4), and the equilibrium bubble shape follows the 2D Young-Laplace equation as in Equation (5). By substituting Equations (11) and (13) into Equation (5), we obtain the expression for pressure balances in a stable surface nanobubble in terms of θ:

$$P_\infty = P_v + P_{g,0} A_0^k \left[\frac{1}{4}\phi_L^2 \left(\frac{\theta}{\sin^2\theta} - \frac{1}{\tan\theta}\right)\right]^{-k} - \frac{2\gamma\sin\theta}{\phi_L}. \tag{14}$$

Interestingly, there is no effect of the surface-gas or surface-liquid interactions on the bubble pressure balance,[S1] although the substrate does play a role in keeping the contact line pinned and forcing the bubble to grow with CCR. The critical or threshold liquid pressure $P_{\infty,c}$ is defined when $P_E > P_C$ for all bubble volumes, i.e. there is no stable equilibrium size for the bubble at liquid pressure $P_{\infty,c}$ and below. The threshold pressure can be typically obtained by determining the critical bubble size where P_∞ is at a minimum from Equation (14).

Differentiating Equation (14) with respect to θ yields:

$$\frac{\mathrm{d}P_\infty}{\mathrm{d}\theta} = -kP_{g,0}\left(\frac{4A_0}{\phi_L^2}\right)^k \left(\frac{2}{\sin^2\theta} - \frac{\theta\sin 2\theta}{\sin^4\theta}\right)\left(\frac{\theta}{\sin^2\theta} - \frac{1}{\tan\theta}\right)^{-k-1} - \frac{2\gamma\cos\theta}{\phi_L}, \tag{15}$$

which can be solved to find the critical contact angle θ_c when $\mathrm{d}P_\infty/\mathrm{d}\theta = 0$, i.e.

$$-\left[\sin^2\theta_c\cos\theta_c\left(\frac{\theta_c}{\sin^2\theta_c}-\frac{1}{\tan\theta_c}\right)^{k+1}\right]^{-1}\left(1-\frac{\theta_c}{\tan\theta_c}\right)=\left(\frac{\phi_L^2}{4A_0}\right)^k\frac{\gamma}{k\phi_L P_{g,0}}. \tag{16}$$

There is no analytical solution for θ_c, and so Equation (16) needs to be solved numerically. The threshold pressure can then be determined by substituting θ_c into Equation (14), i.e.

$$P_\infty = P_v + P_{g,0}A_0^k\left[\frac{1}{4}\phi_L^2\left(\frac{\theta_c}{\sin^2\theta_c}-\frac{1}{\tan\theta_c}\right)\right]^{-k}-\frac{2\gamma\sin\theta_c}{\phi_L}. \tag{17}$$

1.3 3D Blake threshold

The 3D Blake threshold can be derived in a similar manner to the 2D case above. The bubble volume V is simply the volume of a sphere, $V = 4/3\pi R^3$, so Equation (2) can be rewritten in terms of R:

$$P_g = P_{g,0}\left(\frac{R_0}{R}\right)^{3k}. \tag{18}$$

For the 3D case, the equation for the compressing pressures P_C differs slightly from the 2D case in Equation (4), namely, the surface tension contribution is now $2\gamma/R$ so,

$$P_C = P_\infty + \frac{2\gamma}{R}. \tag{19}$$

By balancing $P_E = P_C$,

$$P_\infty = P_g + P_v - \frac{2\gamma}{R}, \tag{20}$$

and then substituting in Equation (18) yields:

$$P_\infty = P_{g,0}\left(\frac{R_0}{R}\right)^{3k} + P_v - \frac{2\gamma}{R}. \tag{21}$$

Differentiating Equation (21) with respect to R gives:

$$\frac{\mathrm{d}P_\infty}{\mathrm{d}R} = -3kP_{g,0}\frac{R_0^{3k}}{R^{3k+1}} + \frac{2\gamma}{R^2}. \tag{22}$$

Solving Equation (22) for R at the minimum yields the critical radius,

$$R_c = \left(\frac{3kP_{g,0}R_0^{3k}}{2\gamma}\right)^{\frac{1}{3k-1}}. \tag{23}$$

Using this critical radius, R_c, in Equation (21) for R gives the minimum possible value of P_∞ that can sustain a bubble in mechanical equilibrium,

$$P_{\infty,c} = P_v - 2\gamma\left(1 - \frac{1}{3k}\right)\left[\frac{\gamma}{3kR_0^{3k}P_{g,0}}\right]^{\frac{1}{3k-1}}. \tag{24}$$

The difference between the 3D Blake threshold in Equation (24) and the 2D equivalent in Equation (9) arises because of the change of the exponent from $2k$ to $3k$ in Equations (3) and (18), respectively, and the change of the surface tension pressure contribution from γ/R to $2\gamma/R$.

1.4 3D Surface Nanobubble threshold

The 3D surface nanobubble cavitation threshold can be obtained by considering the limit in which the pressures acting on a spherical cap-shaped bubble are no longer in mechanical equilibrium, in a similar way to the 2D surface nanobubble threshold derived above. The internal gas and vapour pressure can be described by Equations (1) and (2) again. The volume of a 3D spherical cap is given by:

$$V = \frac{1}{3}\pi R^3\left[2 - 3\cos\theta + \cos^3\theta\right]. \tag{25}$$

As for the 2D threshold, for gas-side contact angles $\theta < 90°$, and *pinned* lateral diameter ϕ_L, the radius of curvature R will decrease to a minimum at $\theta = 90°$, and then increase again for $\theta > 90°$, i.e. for a given R, there are two possible values for V. As in the 2D case, V can be expressed solely as a function of θ if R is related to the pinned (constant) contact diameter for CCR growth from Equation (11). Using Equation (11) in Equation (25) gives the bubble volume as a function of θ,

$$V = \frac{\pi \phi_L^3}{24 \sin^3 \theta} \left[2 - 3\cos\theta + \cos^3\theta\right]. \tag{26}$$

So Equation (2) can be expressed in terms of θ by substituting in Equation (26) to give:

$$P_g = P_{g,0} V_0^k \left[\frac{\pi \phi_L^3}{24 \sin^3 \theta} \left(2 - 3\cos\theta + \cos^3\theta\right)\right]^{-k}, \tag{27}$$

where V_0 is the original 3D bubble volume, which is obtained from Equation (26) with the initial bubble contact angle θ_0.

Substituting Equations (27) and (11) into Equation (20) gives:

$$P_\infty = P_v + P_{g,0} V_0^k \left[\frac{\pi \phi_L^3}{24 \sin^3 \theta} \left(2 - 3\cos\theta + \cos^3\theta\right)\right]^{-k} - \frac{4\gamma \sin\theta}{\phi_L}. \tag{28}$$

The critical or threshold liquid pressure $P_{\infty,c}$ is defined when $P_E > P_C$ for all bubble volumes, i.e. there is no stable equilibrium size for the bubble at liquid pressure $P_{\infty,c}$ and below. This threshold pressure can be obtained by determining from Equation (28) the critical bubble size, $V = V_c$, where P_∞ is at a minimum.

Differentiating Equation (28) with respect to θ yields:

$$\frac{\mathrm{d}P_\infty}{\mathrm{d}\theta} = -3kP_{g,0} \left(\frac{24V_0}{\pi\phi_L^3}\right)^k (1+\cos\theta_c)^{\frac{3k-1}{2}} (1-\cos\theta_c)^{\frac{-k-1}{2}} (2+\cos\theta_c)^{-k-1} - \frac{4\gamma\cos\theta}{\phi_L}, \tag{29}$$

which can be solved to find the critical contact angle θ_c when $\mathrm{d}P_\infty/\mathrm{d}\theta = 0$:

$$-\left(1+\cos\theta_c\right)^{\frac{3k-1}{2}} \sec\theta_c \left(1-\cos\theta_c\right)^{\frac{-k-1}{2}} \left(2+\cos\theta_c\right)^{-k-1} = \frac{4\gamma}{3\phi_L k P_{g,0}} \left(\frac{\pi\phi_L^3}{24V_0}\right)^k . \tag{30}$$

As before, there is no analytical solution for θ_c, and so Equation (30) needs to be solved numerically. Once found, the threshold pressure can then be determined by substituting θ_c into Equation (28) to obtain:

$$P_{\infty,c} = P_v + P_{g,0}V_0^k \left[\frac{\pi\phi_L^3}{24\sin^3\theta_c}\left(2 - 3\cos\theta_c + \cos^3\theta_c\right)\right]^{-k} - \frac{4\gamma\sin\theta_c}{\phi_L}. \tag{31}$$

References

(S1) Attard, P. Pinning Down the Reasons for the Size, Shape, and Stability of Nanobubbles. *Langmuir* **2016**, *32*, 11138–11146.

2 Variations in nanobubble temperatures

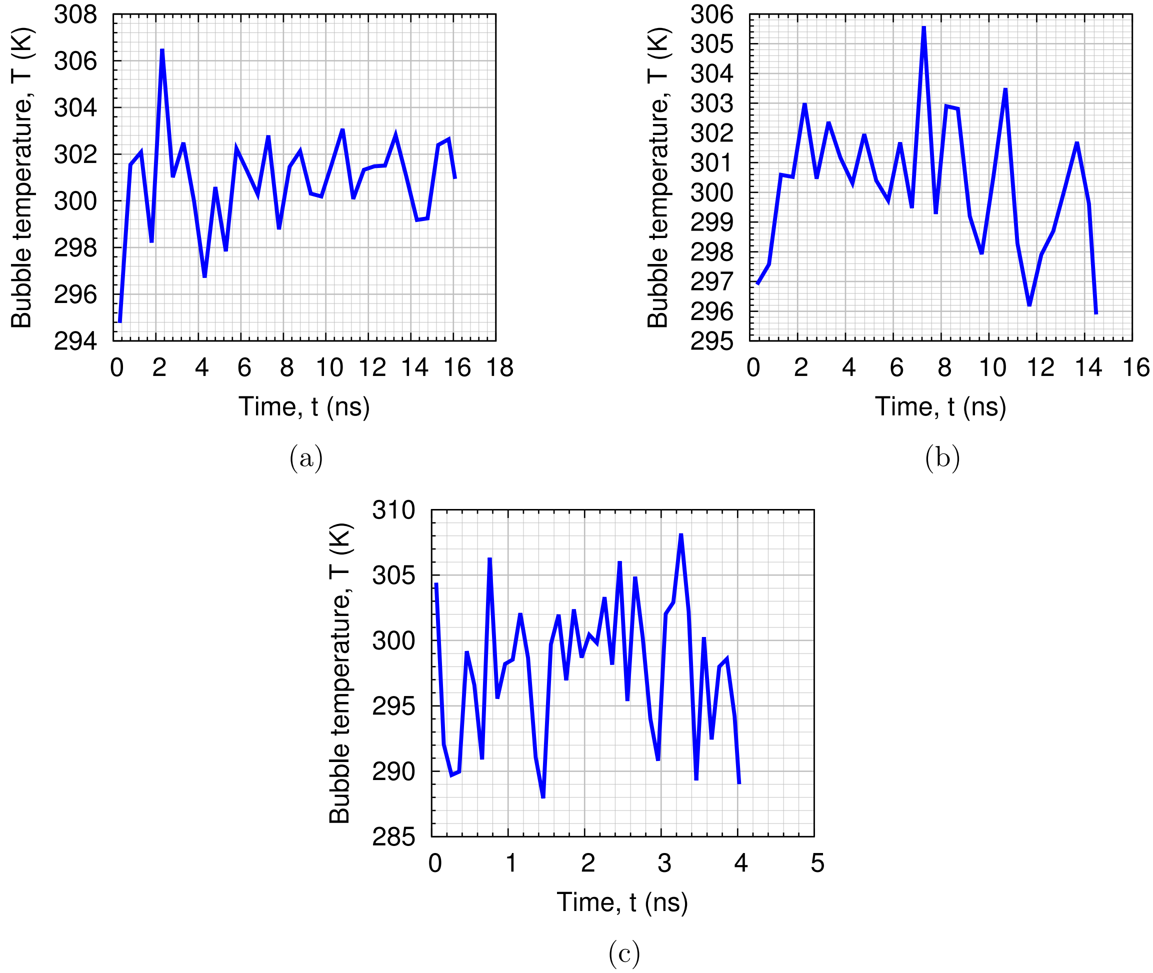

Figure S3: Typical evolution of nanobubble temperatures in 2D bubble expansion simulations of (a) stable, $P_\infty = -2.75\,\mathrm{MPa}$, (b) stable, $P_\infty = -3.75\,\mathrm{MPa}$, and (c) unstable, $P_\infty = -4\,\mathrm{MPa}$ growth cases corresponding to those in Figure 2 in the main paper.

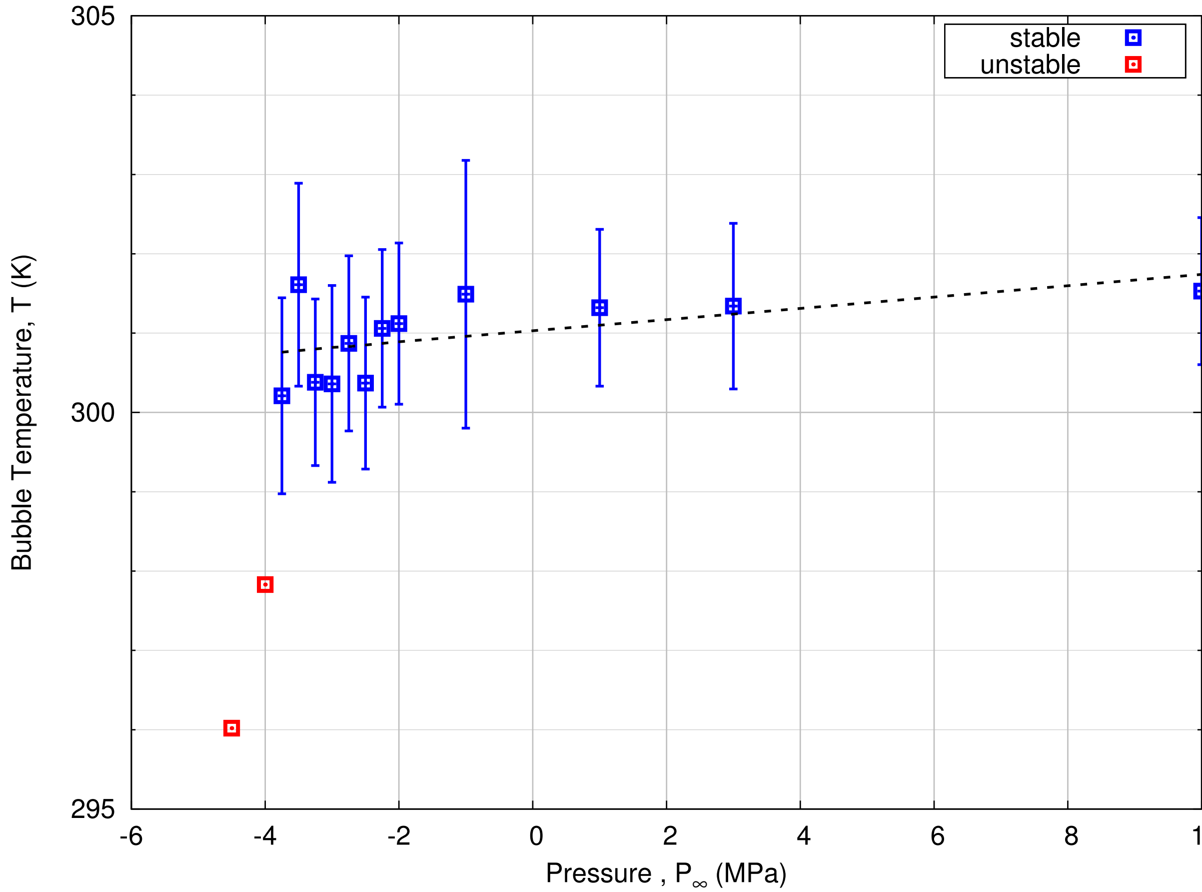

Figure S4: Variation of 2D steady-state nanobubble temperature with applied pressure. The time-averaged unstable case temperatures are also shown, although they did not reach a steady-state. The dashed line indicates the straight line of best fit through the stable, steady-state nanobubble temperatures.