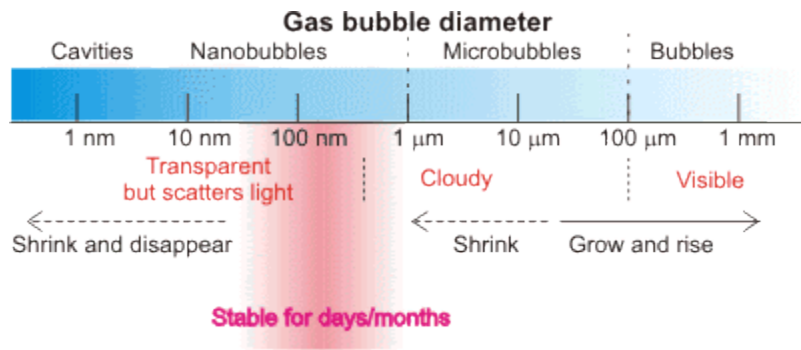


Nanobubbles

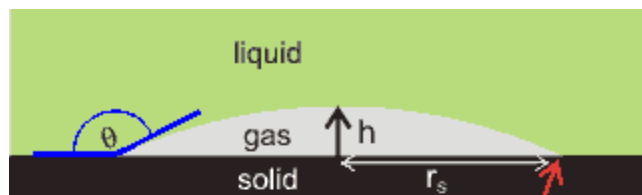
- ◀ Confined water
- ◀ Interfacial water and water-gas interfaces
- ▼ Evidence for nanobubbles
- ▼ The effect of surface charge on surface tension and nanobubble stability

Evidence for nanobubbles

Nanobubblesⁱ [1632, 1989, 2013] are gas-containing cavities in aqueous^f solution (such cavities are often called bubbles).^e They are in constant flux with gas molecules both leaving and entering continuously. They are under excess pressure as the surface tension causes a tendency to minimize their surface area, and hence volume.^a For the same volume of bubble their surface area (**A**) increases proportional to the reduction in bubble diameter (**D**; $A = 6/D$). Nanobubbles grow or shrink by diffusion according to whether the surrounding solution is over-saturated or under-saturated with the dissolved gas relative to the raised cavity pressure. As the solubility of gas is proportional to the gas pressure and this pressure is exerted by the surface tension in inverse proportion to the diameter of the bubbles, there is increasing tendency for gasses to dissolve as the bubbles reduce in size, increases greatly at small bubble diameters^a and so accelerating the process. Such dissolution is increased by the bubble's movement and contraction during this process, which aids the removal of any gas-saturated solution around the cavities. Calculations show that nanobubbles should only persist for a few microseconds [1268]. However, the ease with which water forms larger visible bubbles, under slight tensile pressure well below the tensile strength of water, and the greater difficulty that occurs in this on degassing, both indicate the occurrence of gas-containing nanobubbles (cavities). Clusters of nanobubbles (bubstons) have been proposed that are stabilized by ionic solutes and containing gas at atmospheric pressure [1826]. A model for the nucleation of stable nanobubbles in water has been developed based on water's cohesive nature [1782]. A high density of nanobubbles has recently been created in solution and the heterogeneous mixture lasts for more than two weeks [1618]. The total amount of gases in these nanobubble solutions reached 600 cm^3 (in 1.9×10^{16} 50-nm radius nanobubbles; volume converted to standard temperature and pressure) per 1 dm^3 of water, and the liquid density was about 0.988 g.cm^{-3} [1618]. The surface tension of solutions containing large numbers of nanobubbles seems to be reduced by up to about 15% [2067]. The velocity that bubbles rise through the solution has been related to the square of their radius such that 100 nm diameter bubble are proposed to take well over two weeks to rise 1 cm whereas 10 μ diameter bubbles only take 2-3 min to rise that far [1966]. Also, the electrostatic interactions between nanobubbles can be large enough for little coalescence to occur [1966] and will slow any rise even more. Thus, micron-plus sized bubbles can also last a long time but have sufficient buoyancy to rise through the solution and release contained gas at the surface before the gas dissolves.



In contrast to the theoretical view, there is now much evidence that sub-micron-sized gas-filled cavities (often called nanobubbles) can also exist for significant periods of time both in aqueous solution [974, 1172, 1269,1433, 1532, 1618] and at aqueous submerged hydrophobic surfaces [506, 1270].^d Their presence has been used to explain the behavior [1775] of water bridges [1361].^h Bulk phase nanobubbles can be detected by light scattering or resonant mass measurement [1972] (mouse over figure right) whereas surface nanobubbles can be detected by a number of techniques, prominent amongst which is tapping mode atomic force microscopy [803]. Interestingly, bulk nanobubbles are subject to Brownian motion, so behave as though they have solid shells similarly to solid nano-particles. Nanobubbles are commonly found on solid hydrophobic surfaces in solutions open to the air, where they appear to be quite stable [1272]. Bulk nanobubbles are likely to be repelled from each other, and from negatively charged hydrophilic surfaces, at distance but may attach to such surfaces through water separated films, if they closely approach [1273]. Surface and bulk-phase nanobubbles can both give rise to the otherwise difficult to explain long range attraction between hydrophobic surfaces. As the temperature of aqueous solutions rises, the solubility of non-polar gasses drops, so increasing the gas released and nanobubble volume and surface coverage [842] but generally having much lesser effect on nanobubble concentration.

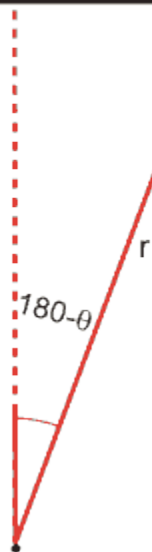


Contact angle (θ)
 $= \cos^{-1}(h/r - 1)$

Gas-liquid surface
 $= 2\pi rh$

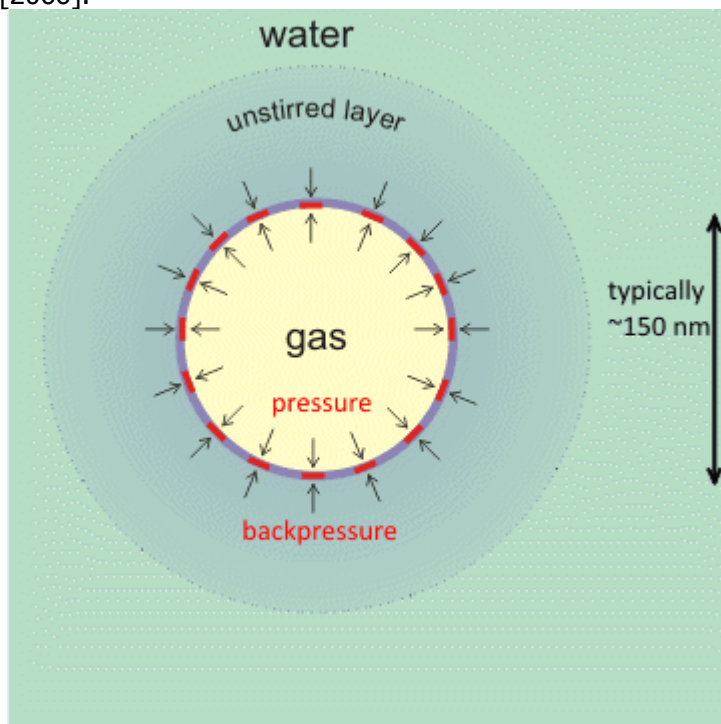
Gas-solid surface
 $= 2\pi rh - \pi h^2$

Bubble volume
 $= \pi h^2(r-h/3)$



Surface nanobubbles vary considerably in dimensions but typically they might have dimensions of $r = 50 \text{ nm} - 6 \text{ }\mu\text{m}$, $r_s = 25 - 1000 \text{ nm}$, $h = 5 - 20 \text{ nm}$, with contact angles ($\theta = 135^\circ - 175^\circ$) much greater than expected from macroscopic studies. The excess internal pressure is not great when the bubble radius is greater than about a micron.^a Surface nanobubbles explain the increased liquid slip at the interface and the resulting lower drag [1988].

The most likely reason for the long-lived presence of nanobubbles is that the nanobubble gas/liquid interface is charged, introducing an opposing force to the surface tension, so slowing or preventing their dissipation. Curved aqueous surfaces may introduce a surface charge due to water's molecular structure or its dissociation. It is clear that the presence of like charges at the interface will reduce the apparent surface tension, with charge repulsion acting in the opposite direction to the surface minimization due to surface tension. Any effect may be increased by the presence of additional charged materials that favor the gas-liquid interface, such as OH^- ions at neutral or basic pH or applying negative ions with an anti-static gun that reduces nanobubble diameter (see below) [2066].



Additional to this is the slow rate of gas diffusion to the bulk liquid surface from both surfaces and bulk-phase nanobubbles [1973, 1987]; in particular, nanobubbles in a cluster of bulk nanobubbles protect each other from diffusion by a shielding effect [2074] effectively producing a backpressure of gas from neighboring bubbles that may be separated by about the thickness of the unstirred layer. This slow dissolution will be even slower than might be expected due to the higher osmotic pressure at the gas liquid interface so both preventing the gas dissolving and driving dissolved gas near the interface back into the nanobubble [2057]. Also, it has been proposed that supersaturation around the nanobubbles may reduce the surface tension significantly, so reducing the pressure [2013] and required backpressure. This concept of a thick interfacial layer is supported by the higher forces required to penetrate greater depths of surface nanobubbles [1986, 1987]. The zeta potential of the nanobubble is shown if you mouse over the figure left. This zeta potential is reduced in the presence of higher ionic strength (positive charges interfering) and lower pH (less OH^-) and with greater diameter bubbles (thinner unstirred layer).

Nanobubbles have a tendency towards self-organization [1269] in much the same way as charged oil-water emulsions, colloids [1275] and nanoparticles. This is due to their charge, long range attraction [1322], slow diffusion and interfacial osmotic pressure gradients.

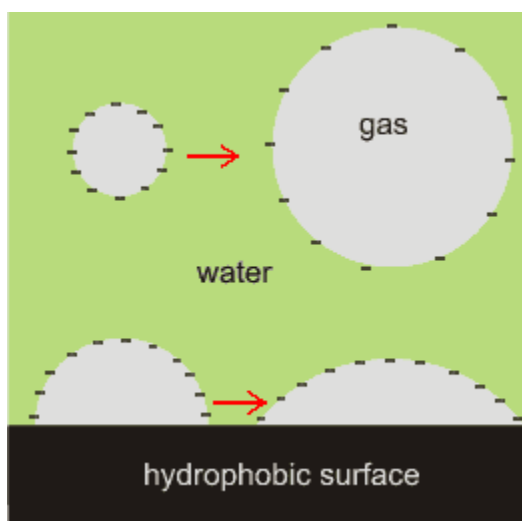
Where there are large numbers of bulk phase nanobubbles, such as in electrolyzed aqueous solutions, there is relatively large amounts of water associated with the surfaces, which can give rise to greater hydration effects due to their greater capacity for forming new hydrogen bonds. Nanobubbles have the effect of increasing the mobility of the water molecules in the bulk as shown by the increase in proton NMR relaxation time T_2 [2014].

The question arises as to why these surface charge effects are not seen to affect the determination of the surface tension when different conditions such as pH and solute are used. The answer may be partly that small nanobubbles are constantly moving such that they lose counter ions beyond their slip planes, and partly that the effect of the charged surface is stronger through the low-dielectric gas phase formed by the tightly curved surfaces.

Under 260 nm excitation wavelength, nanobubbles seem to give two wide structure-less photoluminescence bands at 345 nm and at 425 nm that may be due to the electronic charge density induced by the concentration of hydrated ionic compounds at their interface [800b]. It has been shown that nanobubbles in (still) mineral water can be magnetised and retain this magnetisation for more than a day [1780] . [[Back to Top](#) ▲]

The effect of surface charge on surface tension and nanobubble stability.

In the analysis that follows it is shown that surface charge can counter the surface tension, so preventing high pressures within the nanobubbles. Clearly the final net charge density at the surface is that required for stability. It may be expected that as the charge density increases, as the nanobubble shrinks, then some charge density will be expelled to the bulk but it is not clear to what extent this will occur; the energy required for expulsion^b must be less than the increase in energy due to the approach of the charges. In any case, surface charge density will always slow down the process of nanobubble collapse. Even at the equilibrium charge density, contained gas will dissolve if the solution interface is under-saturated (but see above), although this is unlikely if the exposed liquid water surface is also in contact with similar gas at similar pressure.



The effect of charges at the water/gas interface is shown opposite, with the surface negative charges repelling each other and so stretching out the surface. The effect of the charges is to reduce the effect of the surface tension. As the repulsive force between like charges increases inversely as the square of their distances apart the charges cause strongly increasing outwards pressure as bubble diameter lessens. As well as tending to increase the nanobubble diameters, surface charge will clearly also tend to increase the contact angles. The greater van der Waals attraction across the gas bubble also assists in flattening surface nanobubbles [1274].

The surface tension tends to reduce the surface whereas the surface charge tends to expand it. Equilibrium will be reached when these opposing forces are equal. The expected increase in surface charge density as bubbles reduce in volume has been confirmed [2068].

Assume the surface charge density on the inner surface of the bubble (radius r) is Φ ($C\ m^{-2}$). The outwards pressure (P_{out} , Pa) can be found by solving the Navier-Stokes equations to

give $P_{out} = \frac{\phi^2}{2D\epsilon_0}$, where D is the relative dielectric constant of the gas bubble (assumed unity), ϵ_0 is the permittivity of a vacuum ($= 8.854\ pF\ m^{-1}$). The inwards pressure (P_{in} , Pa) due to the

surface tension on the gas is $P_{in} = \frac{2\gamma}{r}$, where γ is the surface tension ($0.07198\ N\ m^{-1}$, $25\ ^\circ C$). Therefore if these pressures are equal, $r\Phi^2 = 2.55 \times 10^{-12}\ C^2\ m^{-3} = \sim 0.1\ (e^-nm^{-2})^2\ nm$. For nanobubble diameters of 5 nm, 10 nm, 20nm, 50 nm and 100 nm the calculated charge density for zero excess internal pressure is 0.20, 0.14, 0.10, 0.06 and 0.04 e^-nm^{-2} bubble surface area respectively.⁹ Such charge densities should be achievable; e.g. one surface anion to every about 250 surface water molecules would stabilize a 100 nm diameter nanobubble. The nanobubble radius increases as the total charge on the bubble increases to the power 2/3. Under these circumstances at equilibrium, the 'effective' surface tension of the water at the nanobubble surface is zero. The presence of charged gas in the bubble clearly increases the size of the stable nanobubble. Further reduction in the bubble size would not be indicated as it would cause the reduction of the internal pressure to below atmospheric pressure.

The theory above, would predict that greater surface charge density would allow decreased nanobubble diameter, as found in dilute salt solutions [1771]. However, nanobubble size also depends on the bulk properties and increased pH leads to increased nanobubble diameter together with the increase in OH^- concentration [506]. It has recently been shown how the stability of nanobubbles in the presence of an amphiphile varies with pH and ionic strength [1298].

It is possible that the bubble would divide to give smaller bubbles due to the surface charge. Assuming that a bubble of radius r and total charge q divides to give two bubbles of shared volume and charge (radius $r_{1/2} = r/2^{1/3}$, charge $q_{1/2} = 0.5q$), and ignoring the Coulomb interaction between the bubbles, calculation of the change in energy due to surface tension (ΔE_{ST}) and surface charge (ΔE_q) gives:

$$\Delta E_{ST} = +2 \times 4\pi\gamma r_{1/2}^2 - 4\pi\gamma r^2 = 4\pi\gamma r^2(2^{1/3} - 1)$$

$$\Delta E_q = -2 \left(\frac{1}{2} \times \frac{\left(\frac{q}{2}\right)^2}{4\pi\epsilon_0 r_{1/2}} \right) - \frac{1}{2} \times \frac{q^2}{4\pi\epsilon_0 r} = \frac{q^2}{8\pi\epsilon_0 r} (1 - 2^{-2/3})$$

The bubble is metastable if the overall energy change is negative which occurs when $\Delta E_{ST} + \Delta E_q$ is negative,

$$\frac{q^2}{8\pi\epsilon_0 r} (1 - 2^{-2/\beta}) + 4\pi\gamma r^2 (2^{1/\beta} - 1) \leq 0$$

which gives the relationship between the radius and the charge density (Φ):

$$\phi = \frac{q}{4\pi r^2} \geq \sqrt{\left(\frac{2\gamma\epsilon_0}{r} \frac{(2^{1/\beta} - 1)}{(1 - 2^{-2/\beta})} \right)}$$

For nanobubble diameters of 5 nm, 10 nm, 20nm, 50 nm and 100 nm the calculated charge density for bubble splitting is 0.12, 0.08, 0.06, 0.04 and 0.03 e⁻ nm⁻² bubble surface area respectively. For the same surface charge density the bubble diameter is always about three times larger for reducing the apparent surface tension to zero than for splitting the bubble in two. Thus, bubbles will never divide unless there is a further energy input.

The presence of salt ions adversely affects nanobubble stability causing aggregation followed by coalescence at higher salt concentrations [1435]. The aggregation behavior appears similar to that of the salting out of colloidal particles due to the screening of the particle charge by the ionic strength of the solution. Coalescence is due to changes at the gas-water interface. [[Back to Top](#) ▲]

Footnotes

^a The pressure inside gas cavities is given by the Laplace equation, $P_{in} = P_{out} + 2\gamma/r$, where P_{in} and P_{out} are the cavity internal and external pressures respectively, γ is the surface tension and r is the cavity radius. This equation is simply derived by equating the free energy change on increasing the surface area of a spherical cavity ($= \gamma\Delta A = 4\pi\gamma(r+\delta r)^2 - 4\pi\gamma r^2$) to the pressure-volume work ($= \Delta P\Delta V = \Delta P(4/3)\pi(r+\delta r)^3 - \Delta P(4/3)\pi r^3$). Although it is not certain that the Laplace equation holds at very small radii [1129, 1807] and it has been shown that surface tension may increase almost 20-fold to 1.3 N m⁻¹ for 150 nm diameter droplets [823] in the absence of other effectors such as surface charge, this equation appears correct down to about a nanometer or so, below which a small correction must be applied [1271]. However, there may well be further contributions to the work required, due to the removal of surface-bound material, as the surface area contracts, that would lower the excess pressure. In the absence of any other surface effects such as solutes or charges, the excess pressures expected in a 50 nm radius spherical nanobubbles and a 50 nm diameter surface nanobubble ($r_s=50\text{nm}$, $r=1000\text{ nm}$), due to the surface tension minimizing the cavity surface, are 5.8 MPa and 0.14 MPa respectively. It has been proposed that supersaturation around the nanobubbles may reduce the surface tension significantly, so allowing stable nanobubbles [2013]. [[Back](#)]

^b The free energy of surface absorption is expected to vary from about 4-10 kJ mol⁻¹ at higher concentrations to 25-40 kJ mol⁻¹ at low surface concentrations ($\sim 10^{-3}$ - 10^{-4} nm⁻²) [674]. [[Back](#)]

^c This equation may be simply appreciated (if not rigorously derived) by considering the charge ($4\pi r^2\Phi$) concentrated at the center of the spherical cavity exerting a force on the same charge at the surface. The force would be $(4\pi r^2\Phi)^2/4\pi D\epsilon_0 r^2$ from basic electrostatics, and therefore the pressure would be $\Phi^2/D\epsilon_0$. However the charge has been double counted, therefore the final pressure is half this value. [[Back](#)]

^d There is some dispute over whether the density depletion often found at hydrophobic surfaces is real in some cases [1487]. Some hydrophobic liquid-water interfaces behave differently, with no vapor-like layer observed [1484]. [[Back](#)]

^e Another interesting phenomenon in aqueous solutions is the antibubble where a water drop is held, surrounded by a gaseous film, within the bulk liquid [1491]. [Back]

^f Nanobubbles seem to be specific to water and aqueous solutions [1707]. [Back]

^g Similar results to these have been more recently published for dilute salt solutions [1771], where the nanobubble size is seen to increase with reduction in the salt concentration. [Back]

^h The floating water bridge is a stable nearly cylindrical tube of water of 1-2 mm diameter extending up to 25 mm between two beakers of pure water under the influence of a large (15-25 kV) applied electric potential difference [1361]. [Back]

ⁱ Nanobubbles are generally recognised as those gaseous cavities with diameters less than a micron. As such cavities (bubbles) are often greater than 100 nm in diameter but the term 'nano' applies mostly to particles of even smaller diameter, it is possible that nanobubbles will be known as ultra-fine bubbles or submicron bubbles in the future. [Back]

Source:<http://www1.lsbu.ac.uk/water/nanobubble.html>