

# STABILITY OF NANOBUBBLES BY QUANTUM MECHANICS

T. Prevenslik

QED Radiations, Discovery Bay, Hong Kong, China

## Abstract

Surface tension requires nanobubbles in water to dissolve instantly in stark contrast to observations that show bubbles in the bulk or on submerged surfaces do not dissolve for days. Recent claims the stability of nanobubbles comes from the slow rate of dissolution depending on the volume of the surrounding water are unlikely if in fact the volume of water being considered is supersaturated. More likely, bubble stability is caused by the electrostatic repulsion from like charges created in the bubble that oppose surface tension, but the source of charge is a puzzle. Self-ionization of the water molecule produces hydroxyl and hydronium ions, but the classical Boltzmann distribution shows the high Planck energy necessary for ionization is extremely unlikely to be available at ambient temperature. QM differs allowing direct ionization by the QED induced creation of photons from the conservation of thermal  $kT$  energy of evaporating water molecules under the TIR confinement of the bubble. QM stands for quantum mechanics, QED for quantum electrodynamics,  $k$  for Boltzmann's constant,  $T$  for absolute temperature, and TIR for total internal reflection. Simply put, QM requires the  $kT$  energy acquired from the bubble wall by evaporating water molecules to vanish under the TIR confinement of the bubble only to be conserved by the creation of QED induced photons. Under TIR, the Planck energies of the QED photons are beyond the UV allowing the ionization of water molecules to proceed without any need to invoke the Boltzmann distribution. Upon ionization, the hydronium and hydroxyl ions recombine leaving the hydronium ions with greater mobility to move into the bulk while the hydroxyl ions remain in the bubble. Nanobubbles are therefore stable as surface tension tending to dissolve the bubble is balanced by the repulsion of hydroxyl ions. However, supporting analysis is difficult and experimental verification of QED induced stability is suggested.

**Keywords:** nanobubbles, stability, dissolution, charge, quantum mechanics

## 1 Introduction

Nanobubbles are air-containing cavities in liquid water with surface molecules in a continual state of evaporation and condensation. Bubbles grow or shrink by diffusion according to whether the surrounding liquid wall is over or under-saturated with air relative to the pressure. As the solubility of gas is proportional to the Laplace pressure that increases as the diameter decreases, there is an increasing tendency for bubbles to reduce in size and dissolve in a few microseconds. However, nanobubbles are observed on submerged surfaces for days, defying the expectation of prompt dissolution as shown in Figure 1.

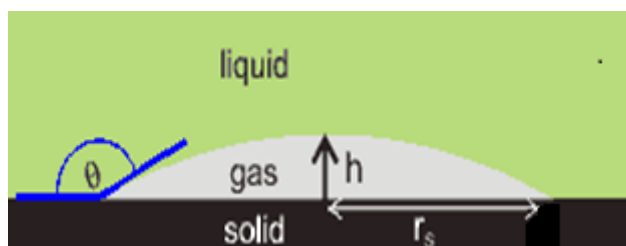


Figure 1 Nanobubble on Submerged Surface

Recently, the stability of nanobubbles is thought [1] to come from the slow rate of dissolution of gas into the surrounding saturated liquid, i.e., the bubble gas cannot enter the surrounding liquid unless it can be transferred through the entire liquid. Depending on the thickness of the liquid layer, the diffusion may take many hours rather than fractions of a second. The dissolution is

slowed down by the fact that the edge of a nanobubble –where gas, liquid and solid meet – is typically ‘pinned’ in place and does not move with time. In Fig. 1, the radius along the solid and the height of the bubble are depicted by  $r_s$  and  $h$ , respectively. As the bubble gases dissolve in the liquid wall, the bubble height  $h$  is thought to decrease thereby reducing the curvature, the driving force for dissolution.

However, the slow dissolution of gas into the liquid as the mechanism for nanobubble stability is not without controversy. Slow dissolution should show the bubbles ever so slightly shrinking over time, but this is not observed. Understandably, measurements of bubble height  $h$  over time for different liquid volume samples are recommended [2] for confirmation. But independent of experiment, it is unlikely if the liquid samples are all truly supersaturated, there should not be any difference in the bubble dissolution.

In the alternative, the most likely reason [3] for nanobubble stability is the continual charging of the bubble surface that opposes the surface tension, thereby slowing dissolution. It is clear that the presence of like charges in the bubble reduces the apparent surface tension, with charge repulsion acting to oppose the minimization of bubble area by surface tension. But,

What is the source of charging in nanobubbles?

Self-ionization [4] of the water molecule is the likely source of hydronium and hydroxyl ions to charge the nanobubble, but the Boltzmann distribution shows it is extremely unlikely that Planck energy is available at ambient temperature to sustain the robust charging observed in the stability of nanobubbles.

## 2 Theory

Nanobubble charging finds basis in the QM requirement [5] that the  $kT$  energy of the water molecule vanishes under the TIR confinement of the nanobubble. In contrast, classical physics allows the atom to always have  $kT$  energy, a comparison with QM made in Fig. 2.

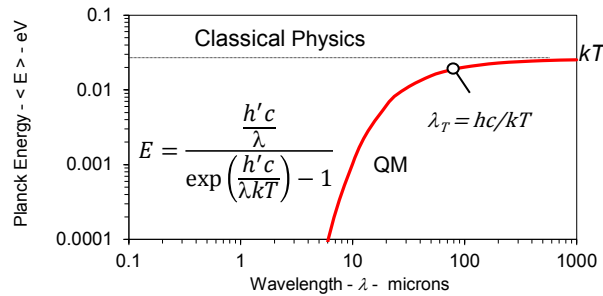


Fig. 2 Thermal  $kT$  energy of the Atom at 300 K

$E$  is Planck energy,  $h'$  Planck's constant,  $c$  speed of light, and  $\lambda$  wavelength

On the bubble surface, the molecules have thermal  $kT$  energy as they are a part of the liquid wall,  $\lambda > \lambda_T$ . But once the molecules leave the bubble surface and enter the TIR confinement of the bubble,  $\lambda < \lambda_T$ . Fig. 2 shows the  $kT$  energy of the atoms in the vapor molecules is in excess of that allowed by QM. Conservation proceeds by QED inducing the excess  $kT$  energy to create photons in the TIR mode of the bubble having Planck energy  $E$ ,

$$E = \frac{h'c}{\lambda} \text{ and } \lambda = 2nh \quad (1)$$

where  $h'$  is used for Planck's constant instead of the usual  $h$  to allow the bubble height to be called  $h$ , and  $n$  is the refractive index of water,  $n = 1.33$ . The TIR photons have high Planck energy. For bubble height  $h = 5$  to  $20$  nm,  $23 < E < 93$  eV, and therefore the QED radiation is sufficient to ionize the water molecule and produce hydronium and hydroxyl ions.

However, recombination reduces the number of hydronium and hydroxyl ions. The Planck energy of QED radiation produces high velocity ionization fragments that favor separation. Once separated, the mobility of the hydronium ion is about twice that of the hydroxyl ion, and therefore the hydronium ions are likely to move into and charge the bulk liquid positive while the hydroxyl ions remain to charge the nanobubble and solid surfaces negative. Hence, the negative charged surfaces of the bubble and solid separated by height  $h$  are repulsed from each other to balance the surface tension force. Along the solid surface over distance  $2r_s$  the bubble is pinned and does not move because the electrostatic repulsion is negligible compared to that across  $h$ , i.e.,  $2r_s \gg h$ . Hence, QM allows nanobubbles to display long time stability.

## 2 Analysis

Nanobubble stability from the repulsive charge created from QED induced hydroxyl ions is difficult to support analytically, although intuitively obvious. Consider a spherical bubble in the bulk as analogous to the more complex bubbles on submerged solid surfaces. Assume the evaporation of  $N$  water molecules having  $kT$  energy into the bubble cavity that is not allowed by QM. The excess thermal  $kT$  energy  $U_{kT}$  that somehow must be conserved is,

$$U_{kT} = N \left( \frac{1}{2} kT \right) \text{DOF} \quad (2)$$

where, DOF stands for degrees of freedom. The water molecule has  $\text{DOF} = 9$ , i.e., 3 translation, 3 rotation, and 3 vibration modes. Each DOF is taken to have  $1/2 kT$  of thermal energy.

In macroscopic bubbles, the water molecules on the interface have the same  $kT$  energy as the vapor molecules,  $\lambda > \lambda_T$ . Nanobubbles differ. Like the vapor molecules, the liquid surface molecules as a part of the TIR confinement of the nanobubble lack the heat capacity to conserve the excess  $kT$  energy of the vapor molecules,  $\lambda < \lambda_T$ . Hence, the excess  $kT$  energy may only be conserved by the QED creation of photons in the TIR mode of the bubble. The Planck energy in the TIR ionizes  $N_{ions}$  water molecules,

$$N_{ions} = \frac{U_{kT}}{U_{ionize}} \quad (3)$$

where,  $U_{ionize}$  is the ionization energy of the water molecule,  $U_{ionize} = 12.6 \text{ eV}$ . Ionization produces hydronium and hydroxyl ions, the hydroxyl ions providing the negative repulsive charge to balance surface tension. Indeed, the surface tension pressure  $P_{ST}$  is,

$$P_{ST} = \frac{2\gamma}{R} \quad (4)$$

where,  $\gamma$  is the surface tension and  $R$  is the bubble radius. The charge pressure  $P_{charge}$  is,

$$P_{charge} = \frac{\phi^2}{2\epsilon_0} \quad (5)$$

where,  $\epsilon_0$  is the permittivity. Equating [3] surface tension and repulsive charge pressures gives,

$$R\phi^2 = 4\epsilon_0\gamma = 2.55 \times 10^{-12} \text{ C/m}^2 \cong 0.1 [e^- / \text{nm}^2]^2 \text{ nm}$$

Characterization of spherical bubbles in the bulk in terms of the hydroxyl ion density  $\phi$  required for stability and total number  $N_{ions}$  of hydroxyl ions is shown for diameters  $d$  in Fig. 3. The geometric complexity of bubbles on submerged surfaces may be avoided by simply characterizing the Planck energy  $E$  in terms of height  $h$  in relation to the ionization potential shown in Fig. 4.

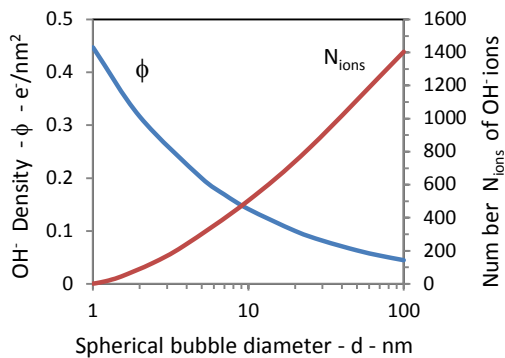


Fig. 3 Spherical Bubble in Bulk

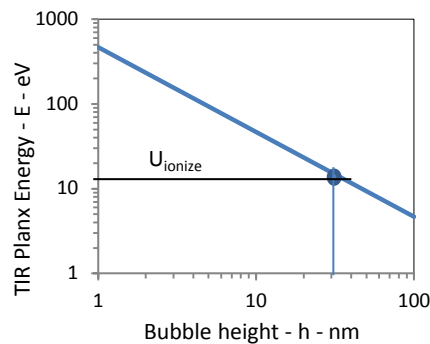


Fig. 4 Bubble on Submerged Solid

### 3 Conclusions

QED induced creation of hydroxyl ions allows the stabilization of nanobubbles in the bulk and sitting on submerged solid surfaces to proceed without the need for slow dissolution [1] of bubble gas into the liquid. However, supporting analysis is difficult. QED induced ionization does produce a high number density of hydroxyl ions, but recombination is also very high. Since the net charge density for bubble stability depends on the steady state solutions of time dependent diffusion of hydroxyl ions into the bubble wall, and since the number densities of ionization and recombination are large, analytical predictions of the differences between ionization and recombination are questionable. Experimental approaches [6] appear more feasible.

Nanobubble stability by the charge mechanism [3] is supported by the QED induced creation of hydroxyl ions from the conservation of the thermal  $kT$  energy of water molecules acquired in the liquid bubble wall that by QM is required to vanish upon evaporation into the TIR confinement of the bubble.

Autoionization is not sufficiently robust [4] to be the source of hydronium ions in determining the pH of water. Instead, the source of pH in water is more likely the ubiquitous nanobubble. More study is planned to support this conjecture/.

### References

- [1] Brenner, M. P. & Lohse, D.: Dynamic Equilibrium Mechanism for Surface Nanobubble Stabilization. *PRL*, vol. 101 (2008) 214505.
- [2] Zhang, X., Chan, D. Y. C., Wang, D. and Maeda, N.: Stability of Interfacial Nanobubbles. *Langmuir*, vol. 29 (2013) pp. 1017.
- [3] Chaplin, M.: See information and analysis of charge stabilized nanobubbles at <http://www.lsbu.ac.uk/water/nanobubble.html>
- [4] Geissler, P. L., et al., Autoionization in Liquid Water. *Science*, vol. 291 (2001) pp. 2121-2124.
- [5] Prevenslik, T.: See QED stabilized Nanobubbles, <http://www.nanoqed.org> , 2014.
- [6] Nikogosyan, D. N. & Angelov, D. A.: Formation of free radicals in water under high-power laser uv irradiation. *Chem. Phys. Lett.*, vol. 77 (1981) pp. 208-210.