

## COMMENT OPEN



## Electrostatic forces and higher order curvature terms of Young–Laplace equation on nanobubble stability in water

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Deductive arguments regarding the unexpected stability of nanobubbles in water include the excessive internal pressure of minuscule gas pockets. In this study, the derivation assumptions of the Young–Laplace equation are evaluated closely to discuss the possible modifications towards making conclusive remarks about the predictive power of the equation at the nano-scale.

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## INTRODUCTION

Nanobubbles gained tremendous attention from science and engineering community due to experimental evidence collected regarding their outstanding interfacial properties, molecular-scale size, and unexpected long-term stability<sup>1–5</sup>. Some nanobubbles were reported to be as small as 50 nm in diameter<sup>4,6–9</sup>, and their stability were measured in the order of weeks up to months<sup>10–12</sup>. These attributes not only decrease the cavity formation energy requirement of nanobubbles but also enhance gas transfer into the bulk liquid via extremely large gas–liquid interphases and long retention times in the bulk phase<sup>13,14</sup>. From a practical point of view, nanobubbles could lift the solubility limitation of gas storage in water. Nanobubble solutions behave like incompressible liquids, despite being biphasic fluids. Therefore, any gas starving system (e.g., aeration chambers, biological reactors, chemical oxidative catalysis reactors) would benefit from having a virtually unlimited supply of gas at the proximity of reactions while benefiting from the storage, pumping, and piping capabilities of an incompressible liquid. The existence of nanobubbles is irrefutable and experimentally proven. However, there has been a long-lasting debate among theoreticians regarding nanobubble stability calculations which remains still unexplained by traditional theories of gas–liquid interfaces<sup>10,12,15–21</sup>. The most fundamental theoretical tool used to study nanobubbles is the celebrated Young–Laplace equation<sup>16,22–25</sup>,

$$\Delta p = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right), \quad (1)$$

where  $\gamma$  is the surface tension,  $R_1$  and  $R_2$  are the principal radii of curvature of the liquid–gas interface and  $c_i = \frac{1}{R_i}$  is the principal curvature. The Young–Laplace equation gives a very high-pressure difference  $\Delta p$  for nanobubbles. Such high values of  $\Delta p$  would describe completely unstable domains that would induce fast dissolution. The disjuncting between the Young–Laplace theory and experimental evidence has been the essential aspect of the ‘nanobubbles’ physical existence paradigm. Can the Young–Laplace still provide an understanding of these stable nano-domains in water bodies? To answer this question, we must explore deeper and discuss possible modifications of established Eq. (1) through the review of its fundamental description and original derivation. Equation (1) can be derived by extremizing the work done<sup>26</sup> on a

surface element ( $dA$ ) by deformation of the interface as,

$$dW = -p_1 dV_1 - p_2 dV_2 + \gamma dA = 0, \quad (2)$$

where  $dV_1 = AdN$  and  $dV_2 = -AdN$  are the volume change of the two fluids that form the interface of the bubble (i.e., gas and liquid),  $dA = A(c_1 + c_2)dN$  is the area change,  $dR_1 = dR_2 = dN$ , and  $dN$  is a small shift of the dividing surface. However, more terms can be added to the right-hand side of Eq. (2), such as higher order curvature contributions, work done by gravity in case there is an excess mass on the interface, or work done by electrostatic forces in case there is a net charge build up on the interface. For our discussion on the stability of nanobubbles, the excess mass and work done by gravity on it are irrelevant, thus we will focus on the other two types of additional work that may have been oversight: higher order curvature contributions and the effect of charge on the interface<sup>22,23</sup>.

## Higher order curvature terms

A reasonable assumption one can make is nanobubbles being spherically symmetric, which leads to  $R_1 = R_2 = R$ . This can simplify Eq. (1) to  $\Delta p = 2\gamma/R$ . The higher order curvature term that can be added to the right-hand side of Eq. (2) is in the form of  $ACdc$ , where  $A$  is the area,  $C$  is the curvature coefficient to be determined, and  $c$  is once again the principal curvature. This additional term modifies the Young–Laplace equation as:

$$\Delta p = \frac{2\gamma}{R} - \frac{C}{R^2} \quad (3)$$

Even higher order than second order curvature terms can be added, and Eq. (3) can be rewritten as:

$$\Delta p = \frac{2\gamma}{R} \left( 1 - \frac{\delta}{R} + \dots \right) \quad (4)$$

where  $\delta = C/2\gamma$  is called the Tolman length<sup>27</sup>, which specifies the scale at which higher order curvature contributions become significant. Computer simulations<sup>28</sup> and semianalytic theories<sup>29</sup> have shown that Tolman length is in the order of molecular diameter<sup>30</sup>. Equation (4) can also be written as  $\Delta p = 2\gamma(R)/R$ , which allows us to define surface tension as a function of curvature instead of a constant. Since the Tolman length is always in the order of a molecular diameter, the change in the surface tension due to geometric curvature is significant only for nanoscopic bubbles and droplets<sup>22</sup>. Additional work terms can

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be added to Eq. (2) if greater curvature is assumed to require extra work.

Since curvature  $c$  is inversely proportional to the radius of curvature  $R$ , for nano-size bubbles, it is expected that higher order contributions will play an important role that has been neglected. For nanobubbles,  $R$  can be as low as 50 nm. If this value creates a high enough curvature, the minus sign in front of  $\delta$  in Eq. (4) will lead to a smaller pressure difference  $\Delta p$ , which would make the bubbles more stable. All of this ultimately depends on the value of the Tolman length, which is what has been the puzzling part of the problem. Various calculations involving both computer simulations and semi-analytical methods<sup>22,28,29,31–35</sup> lead to Tolman length in the order of a molecular diameter, which is orders of magnitude off compared to the size of nanobubbles. In other words, the curvature of nanobubbles is not high enough to explain their stability by itself.

### Influence of electrostatic forces

In addition to their surface curvature, nanobubbles have been observed to carry electric charges. It has been proven that electrostatic contribution is minimal when bubble size increases; therefore, the charge's influence is negligible for the pressure across the bubble/solution in macroscopic bubbles<sup>36</sup>. This means an electrostatic free energy term can be added to Eq. (2), which can possibly modify Eq. (1) in a way that can explain the stability of nanobubbles. Manning<sup>23</sup> investigated this possibility and calculated this term to be,

$$dU = -\frac{n^2 e^2}{64\pi^2 \epsilon_0 \epsilon R^3} dA \quad (5)$$

where  $n$  is the number of elementary charges  $e$  on the surface of the nanobubble,  $\epsilon_0$  is the permittivity constant of vacuum,  $\epsilon$  is the dielectric constant of the liquid. The inclusion of this electrostatic term will lead to Eq. (6),

$$\Delta p = \frac{2\gamma}{R} \left( 1 - \frac{\delta_e^3}{R^3} \right) \quad (6)$$

where  $\delta_e^3 = \frac{n^2 e^2}{64\pi^2 \epsilon_0 \epsilon}$  specifies a length scale at which the electrostatic contribution becomes significant. The minus sign in Eq. (6) helps the stability of the nanobubbles, similar to the minus sign in Eq. (4). The difference here is that  $\delta_e$  depends on the amount of charge  $n$ . Thus, we can conclude that if there is sufficient charge on the surface of the nanobubble, this electrostatic mechanism can be a plausible explanation for the stability of nanobubbles as well.

It should be noted that surface charge measurements by zeta-potential have shown unique behavior of nanobubbles, since those gas–liquid interfaces may present different superficial charge depending on their size and water chemistry<sup>37</sup>. The zeta potential of bulk nanobubbles in the literature range from  $-50$  to  $-20$  mV<sup>25</sup>. The negative zeta potential value has led to the predetermined idea of nanobubbles having negatively charged surfaces. The strong electrostatic repulsions between neighboring bulk nanobubbles due to negative surface charge is considered one of the possible explanations for nanobubble stability<sup>3</sup>. Zeta potential is measured by applying an external electric field across the sample solution and measuring the velocity of the movement of charged species. It is worth noting that measured zeta potential does not distinguish the charge arising essentially from the gas–liquid interface<sup>25</sup>. Charged impurities and species such as  $\text{H}_3\text{O}^+$ ,  $\text{OH}^-$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$  can change the velocities of bulk nanobubbles (even at an uncharged state) under an electric field<sup>23</sup>. Nirmalkar et al. studied the effect of pH, ionic strength, and surfactant on the zeta potential of the air nanobubbles<sup>2</sup>, and the absolute value of the zeta potential for air nanobubble solution was decreased monotonically with pH decrease. The addition of  $\text{H}^+$  ions to lower the pH neutralizes the negative charge of the slipping plane of the nanobubble in the solution<sup>38</sup>. Similarly, higher ionic strength shifted the negative zeta potential value

towards zero due to the compression of the double layer<sup>38</sup>. The magnitude of the negative zeta potential was increased with higher concentrations of anionic surfactant (e.g., sodium dodecyl sulfate) due to the adsorption of  $\text{SO}_4^{2-}$  ions on the bubble interface<sup>2</sup>. Mixing solvents (e.g., ethanol) into water has caused a decrease in the magnitude of the zeta potential. The drop has been attributed to the adsorption of ethanol molecules on the surface of the nanobubbles via hydrogen bonding<sup>39–41</sup>.

For this reason, nanobubble size and stability data obtained by similar generation principles in well-characterized background water for various gases can shed light on the mechanism of nanobubble stability in water. The curvature dependence and electrostatic forces on the stability of the nanobubbles are proposed to evaluate via computational modeling and experimental observations for gases such as  $\text{O}_2$ ,  $\text{O}_3$ ,  $\text{CO}_2$ ,  $\text{N}_2$ , and mixtures of gasses. The nanobubble packing density, gas type, supersaturation, and liquid media that are used to generate nanobubbles are essential parameters to study for nanobubble stability. The validity of the proposed terms in this study for the Young–Laplace relationship can be evaluated through surface tension reduction measurements obtained from tapping mode atomic force microscopy under supersaturated state<sup>22</sup>.

Further systematic work is required to understand the behavior of nanobubbles for different gas types and mixtures in more complex solutions.

### CONCLUSIONS

Stable nanobubbles create permanent biphasic fluid mixtures, and they resemble porous but (virtually) incompressible liquids. There is a fascinating potential for these fluid mixtures in environmental engineering applications because gases are often delivered to liquids in the form of short-lived micro-and macro-bubbles causing inefficient mass transport. The storage, piping, and pumping potential of gases in liquids attract a lot of attention from the engineering community. However, labeling the extended stability of nanobubbles as “unexpected” or “surprising” in recent publications indicates a need for a deeper understanding of their theoretical stability. In this comment, the impact of excessive surface curvature and electrostatic charges on nanobubble stability was explained based on the derivation of the Young–Laplace equation. In brief, the nanobubble stability can be attributed to their size but also the surface tension and electrostatic forces, which could yield longer stability in water.

### DATA AVAILABILITY

Data sharing does not apply to this article as no datasets were generated or analyzed during the current study.

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## AUTHOR CONTRIBUTIONS

T.Y., S.Y., J.G., S.G.-S., and O.A. contributed to the formulation and evolution of overarching research goals and aims. T.Y. and S.Y. contributed to the generation of the original draft. S.G.-S. and O.A. contributed to reviewing and editing the draft. O.A. had the oversight for the activity planning and responsibility distribution.

## COMPETING INTEREST

The authors declare no competing interests.

## ADDITIONAL INFORMATION

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