Pressure within a bubble revisited

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Abstract: We shall reconsider the pressure within a bubble, when we take into account all the cohesive forces within a liquid, which surrounds a bubble. These principles will be applied to maximum bubble pressure method, providing a new plausible explanation as to why measured bubble's pressures do not correlate with traditional Young–Laplace based theory. Finally, we shall explain why probes do not measure increased pressures within bulk liquids. © *2014 Physics Essays Publication*. [http://dx.doi.org/10.4006/0836-1398-27.4.612]

Résumé: Nous allons réexaminer la pression à l'intérieur d'une bulle, lorsque nous prenons compte de toutes les forces cohesive au sein d'un liquide, qui entoure une bulle. Ces principes seront appliqués à une méthode de pression maximale dans une bulle, fournissant une nouvelle explication plausible pourquoi les pressions de bulle mesurée ne correspondent pas à la théorie traditionnelle de Young–Laplace. Enfin, nous allons expliquer pourquoi les sondes ne mesurent pas l'augmentation des pressions au sein de liquides en vrac.

Key words: Young–Laplace Equation; MBPM; Tensiometer; Bubble Pressure.

I. INTRODUCTION

The Young–Laplace equation traditionally defines the pressure within a spherical bubble (P_b), as[1]

$$P_b = 2\sigma/r_b + P_l, \tag{1}$$

where P_b and P_l are, respectively, the pressures within the bubble, and the surrounding liquid. σ is the surface tension and r_b is the bubble's radius.

The maximum bubble pressure method (MBPM)[2–6] is used to measure a liquid's surface tension, i.e., a tensiometer. The method involves the measurement of a bubble's pressure, which grows at the tip of a capillary immersed in the liquid in question. As the bubble grows, its radius of curvature decreases until it becomes spherical, at which point the bubble's internal pressure attains its maximum. It is accepted that problems exist in that the measured bubble's pressure (P_b) is not defined by Eq. (1), which has led to the use of various equations used to the system pressure (P_s) in MBPM, i.e., Fainerman and Miller[3], wrote

$$P_s = 2\sigma/r_b + \Delta\rho g h + P_d, \tag{2}$$

where $\Delta\rho$ is the density difference between the liquid and air, g is acceleration due to gravity, and h is the capillary's depth. P_d is taken to be due to dynamic effects,[2] which is attributed to a combination of (1) "aerodynamic resistance of the capillary during passage of air" and (2) "hydrodynamic resistance to the liquid against the moving bubble."

Fainerman and Miller[3] then wrote for the measured capillary pressure (P_c)

$$P_c = P_s - \Delta\rho g h - P_d. \tag{3}$$

Equation (3) implies that the pressure within 1/2 bubble at the end of the above capillary tube is significantly less than what (1) predicts. Based on Eqs. (2) and (3), seemingly, the system pressure (P_s) is a means of navigating around the possibility that the bubble's pressure is lower than predicted by the Young–Laplace equation. Perhaps this author is missing something, but there seems to be misguided logic here. Specifically, the pressure measured in the capillary should be elevated due to both the liquid overlying the bubble, and any dynamic effects?

When the bubble is not spherical, then the nonsphericity factor (f) comes into play[3,4] and a modified Laplace equation is often utilized in MBPM methodology

$$\sigma = f r_b P_c/2. \tag{4}$$

Combining Eqs. (3) and (4), Fainerman *et al*. concluded[4]

$$\sigma = f r_b (P_s - \Delta\rho g h)/2 - \Delta\sigma_a - \Delta\sigma_v, \tag{5}$$

where $\Delta\sigma_a$ and $\Delta\sigma_v$ are, respectively, due to the aerodynamic resistance and liquid's viscosity.

It is also accepted that all MBPM tensiometers must be calibrated to liquids with known surface tensions, before being used. And even after calibration, errors of more than 10% are still often witnessed.[5]

Mayhew[7] has pointed out that there may be issues with Eq. (1) because it only considers the cohesive forces along the tensile layer. When considering the cohesive forces perpendicular to the tensile layer, Mayhew[7] concluded that the pressure within a bubble would be better defined by

$$P_b = \sigma/r_b + P_l. \tag{6}$$

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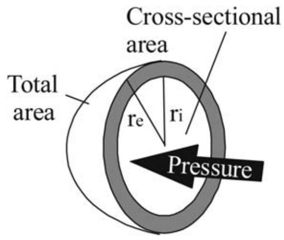

FIG. 1. The pressure in a bubble and its cross-sectional area.

In developing Eq. (1), Mayhew[7] used the following principle of hydrostatics: "The force in a particular direction from a uniform pressure on a curved surface equals the pressure times the cross-sectional area of this surface in the direction of the desired force."[7,8] This last statement is an elaboration of: Force = (Pressure) (Area). Herein, pressure really means is the difference in pressure (ΔP). Engineers use this principle of hydrostatics, when determining the pressure differentials that a tank can withstand. In this paper, we shall employ its principles to improve our understanding of pressures across a tensile layer.

The main purposes of this paper are: (a) to discuss an oversight by this author[7] and (b) to give a plausible explanation as to why MBPM experiment's measured pressures do not more readily equate to Eq. (1). Specifically, Eq. (1) may not accurately provide the pressure within a bubble.

II. YOUNG–LAPLACE EQUATION

Some of the following analysis was introduced in Adamson.[1] Herein, we shall provide more clarity by expanding its application.

Consider the cross-section of a spherical tensile layer, as is shown in Fig. 1. If r_i is the radius to the inside of the tensile layer, then the cross-sectional area is πri^2. If the pressure under consideration is along the x-axis, then the cross-sectional area is measured in the y–z plane. Applying the stated principle of hydrostatics, we can say the total force perpendicular to the cross-sectional area is the force of elongation (F_e)

$$F_e = \Delta P \pi r_i^2. \tag{7}$$

The surface tension must be equal and opposite to this force of elongation. Consider the pressure to be along the x-axis is countered by the tensile force along the x–y plane, as is shown in Fig. 2. If we consider the bubble's tensile surface, as a single layer squeezing inward over half its length ($2\pi r/2 = \pi r$), then the surface tension (τ_1) along the shown ring would be

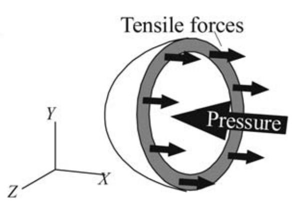

FIG. 2. The pressure in a bubble being countered by the tensile forces along the x-axis.

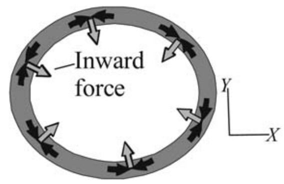

FIG. 3. The pressure along the x-axis is equated to an inward force by the tensile layer along the x-plane.

$$\tau_1 = \pi r \sigma. \tag{8}$$

Equation (8) assumes that there is only one surface to the tensile layer with a radius r (Fig. 3). In reality, we have an inner and outer surface associated with our tensile layer whose radii is, respectively, defined by r_i and r_e. Since the tensile surface is deemed thin, then: $r \approx r_i \approx r_e$. Therefore, the total surface tension (τ_1) along the shown ring consisting of two surfaces is

$$\tau_1 = \pi(r_i + r_e)\sigma \approx 2\pi r. \tag{9}$$

Applying the stated principle of hydrostatics, equating the force of elongation [Eq. (7)] to the tensile forces [Eq. (9)], we obtain

$$\Delta P \pi r^2 = 2\pi r \sigma. \tag{10}$$

Dividing both sides by: πr^2, we obtain a version of the Young–Laplace equation, i.e., Eq. (1).

III. PRESSURE WITHIN A BUBBLE

Equation (1) only considers the cohesive forces along the tensile layer. It remains this author's assertion that we also need to consider the net cohesive forces pulling on the bubble's tensile layer, which are directed into the surrounding liquid, as illustrated in Fig. 4. The summation of such forces would be taken over a ½ sphere; therefore

$$\tau_y = \sigma \pi r_b. \tag{11}$$

Equating the forces for a spherical bubble, along the y-axis, we obtain

$$\Delta P(\pi r_b^2) = 2\pi r_b \sigma - \pi r_b \sigma = \pi r_b \sigma. \tag{12}$$

Dividing through by πr_b^2 and realizing that $\Delta P = P_b - P_l$, we obtain $P_b = \sigma / r_b + P_l$ that being Eq. (6).

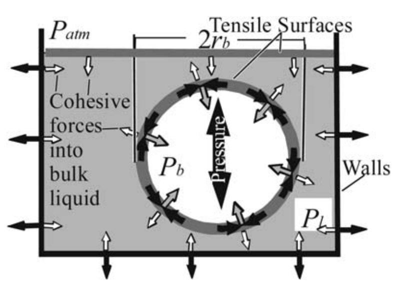

FIG. 4. All the cohesive forces exerted upon a bubble in a bulk liquid, including cohesive forces into bulk liquid and container walls.

Equation (6) compares the bubble's pressure to the surrounding liquid's pressure. If we want to compare the bubble's pressure to the atmosphere's pressure, then we would need to consider the pressure difference between the liquid, and the surrounding atmosphere. Omitting the weight of any overlying liquid, it is traditionally accepted that the two pressures are identical. Again this author asserts that this may not be the case. To calculate any pressure increase in the liquid due to net cohesive forces of the liquid along its border could be complicated, involving the consideration of all the cohesive forces of the system, i.e., calculate the net cohesive force of each molecule, and then calculate their sums in each direction.

The issue can be simplified by considering the net cohesive forces, located along the liquid's flat tensile layer and directed into the bulk liquid, as shown in Fig. 4. Next, make a simple approximation: As shown realize that the projection of the bubble's spherical surface onto the liquid's upper flat tensile surface is $2r_b$. Next surmise that since the liquid's tensile forces along the liquid's upper surface, are directed into the liquid, then this increases the pressure within the bulk liquid. Note: we further realize that the tensile forces along the liquid's bottom and the sides will not affect the pressure within the liquid because the net forces are directed into the container walls, i.e., if liquid is water then the container walls are considered to be hydrophilic, i.e., true static forces. There maybe implications if and when hydrophobic walls are used.

Furthermore, the ratio of the spherical bubble's projection ($2r_b$) to the circumference of a half spherical bubble (πr_b) is: $2r\text{b}/\pi r_b = 0.64$. When deriving Eq. (6), we considered that the cohesive forces perpendicular to the tensile layer would reduce the bubble's pressure by σ/r_b, with respect to the surrounding liquid. Adding this pressure exerted upon the bulk liquid from along the liquid's upper tensile layer, to the pressure within the bubble as defined by Eq. (6), one obtains

$$P_b = 1.64\sigma/r_b + P_{atm}, \tag{13}$$

where P_{atm} is the pressure of the surrounding atmosphere. Equation (13) states that the pressure within the bubble should be $0.64\sigma/r_b$, greater when compared to the atmosphere, than it is when compared to the surrounding liquid. Although simplistic in derivation, the reason that Eq. (13) works is that the cohesive forces into the liquid should equate to the surface tension along the bubble's tensile layer.

A more accurate equation would consider the added the weight of the overlying liquid: ρgh. In which case, Eq. (13) becomes

$$P_b = 1.64\sigma/r_b + P_{atm} + \rho gh. \tag{14}$$

The pressure within the ½ bubble must equal the pressure in the capillary: $P_b = P_c$. Equations (13) and (14) may only be an approximation. Other factors may come into play, such as the nature of the apparatus, and its components, i.e., hydrophilic versus hydrophobic, and, perhaps even the shape of the container. Even so, Eq. (14) may better explain the pressures witnessed in MBPM apparatus when the bubble is static, i.e., a syringe pump.[8] In other words, previous theory may simply have misunderstood the true pressure within a bubble by simply basing it upon the Young–Laplace equation (1).

IV. ELLIPTICAL TENSILE LAYERS

An advantage of using the principles of hydrostatics to determine a bubble's pressure is that it allows us to readily deal with elliptical tensile layers. Due to the costs of publication and the number of equations involved, this author shall leave dealing with elliptical bubbles to his book (assuming it ever gets published). For those inclined to do the calculations themselves, you simply replace the cross-sectional area of a sphere with that of an ellipse in Eq. (7), and use the circumference of a half ellipse instead of half circle in Eq. (8). This may allow one to reanalyze the nonsphericity factor (f) in Eq. (4), or Eq. (5), in the MBPM.

Two other points should be made. First: When a free forming bubble's tensile layer is elliptical, then the cross-sectional area will be greatest perpendicular to the ellipse's smallest axis. Due to the pressure being the same in all directions (Pascal's law of hydrostatics), then the force of elongation would be greatest perpendicular to the smallest axis, resulting in a net force that drives the tensile layer back into a spherical shape. Therefore, in order for bubble to remain elliptical, there must be a constraint, i.e., an external force, which causes this. Of course, in the case of MBPM, the capillary tube stops the bubble from being a free forming spherical entity.

V. MEASURING PRESSURE WITHIN A LIQUID

One may ponder why this additional pressure is not readily measured when one puts a pressure probe into a bulk liquid. The answer is simple. Consider the effects of the liquid's cohesive forces on the probes surface, wherein the pressure is actually measured. Generally, there exists an affinity between the liquid, and the probe's surface; therefore, we would expect that the liquid's cohesive forces would create a net force directed into the bulk liquid. Therefore, the net cohesive forces between the liquid and the probe would cancel out the added pressure exerted by the net cohesive forces along the liquid's tensile layer. Hence, the only pressure that is measured is that exerted by the weight of the atmosphere plus the overlying liquid.

Interestingly, if the probe's surface was hydrophobic, then the net forces along the water's interface with probe would be directed into the bulk water. Again one would not necessarily measure and pressure increases. So, how do we show that that the bulk liquid experiences a pressure increase? It really is an intuitive thing, which only becomes obvious if one examines the shapes of liquids (especially droplets) at interfaces. Again a discussion better suited for this author's book.

VI. COMMENTS ON AFFECTS TO DATA IN MAYHEW

This author[7] used data from other researchers, to clearly show that the energy required to nucleate bubbles could be envisioned in terms of: $W = d(PV)$.[7] In that analysis, Eq. (4), rather than either Eq. (1) or Eq. (12), was used to calculate the number gaseous molecules within the bubbles. It should be stated that due to the laser-induced bubble's large size, the pressure inside of the created bubbles was not affected by the surface tension along the tensile layer. In other words, the bubble's pressure approximated atmospheric pressure. Therefore, one would attain the same valid analysis, no matter which equation for the bubble pressure was used.

Also, this author[7] gave new equations for capillary rise and depression. In deriving those new equations, I employed the same principles used herein but I did not make the same mistake; hence, as far as this author is concerned, they remain valid, although unappreciated.

VII. CONCLUSIONS

Traditionally, we do not consider the cohesive forces perpendicular to a tensile, when considering the pressure in liquids, and/or bubbles. Herein, we were able to show: When we consider all the liquid's net cohesive forces, then we can clearly explain why MBPM consistently measures the pressure of a bubble at values, which are significantly lower than that predicted by the Young–Laplace equation. That is, a bubble's pressure is approximately $P_b = 1.64\sigma/r_b + P_{atm}$.

Of course, the above being the case, then we also need to understand that the liquid's affinity to pressure gauges/probes will also affect the pressure that we measure within a liquid. Therefore, when we measure a liquid's pressure, the net result is simply due to the weight of the overlying atmosphere and liquid.

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