

The Consideration of Cohesive Forces Perpendicular to the Tensile Layer in Bubbles, Droplets, Capillary Rise and Depression

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Abstract: The application of the Young-Laplace equation to bubbles, droplets, capillary rise and depression have been generally accepted for centuries, because it approximates experimental evidence. Consequentially, any cohesive forces perpendicular to the tensile has been omitted from due consideration. In this treatise, we shall investigate the mechanical implications of also considering the cohesive forces perpendicular to the tensile layer, arriving at a new perspective. [Nature and Science. 2007;5(4):43-52].

Keywords: Capillary Rise, Capillary Fall, Capillary Depression, Bubbles, Droplets, Cohesive forces

Introduction

Whether a resultant force is dynamic or static, that force when applied perpendicular to an area results in a pressure felt by that area. This concepts holds in every realm of physics except for one! Most accept the intermolecular cohesive forces along a curved tensile layer result in a pressure change across the tensile layer, without any consideration being given to the intermolecular cohesive forces perpendicular to the said tensile layer. This has rendered the science of tensile layers into that rare case where resultant forces perpendicular to an area do not contribute to pressure felt by that area. Accordingly, this paper will consider the ramifications of considering a liquid's cohesive forces perpendicular to its tensile layer, determining that such consideration may be warranted.

The science of tensile layers is too often portrayed as if there is no ambiguity. Interestingly, the question as to should tensile layers be contemplated purely in terms of some mechanical description^{1,2,3}, or based upon some thermodynamic consideration, i.e. Helmholtz free energy^{2,4,5,6}, is an ongoing debate. A verbal description for its existence Helmholtz free energy being²: “The interaction of a given molecule with its (nearest) neighbors leads to a reduction of its potential energy, i.e., intermolecular forces act to stabilize the system. However, the molecules at the surface region of this condensed matter have a smaller number of nearest neighbors, and therefore their potential energy is not decreased by as much as in the interior of condensed phase.”

The mathematical description for the Helmholtz Free energy (F) is⁷: $F \equiv E - TS$. If F is actually obtained from⁷: $TS = E + PV$. Then comparing these two equations one would be inclined to say that: $F = -PV$, therefore: $\Delta F = -\Delta(PV)$.

Although well accepted, this is problematic! Changes to Helmholtz free energy are contemplated in terms of temperature change (ΔT) at constant entropy (S) and volume change (ΔV) at constant pressure (P), plus any changes in energy associated with chemical potential, surface area etc. For the isothermal case, with no change to chemical potential, the change in Helmholtz free energy in differential form is²:

$$dF = -P_1dV_1 - P_2dV_2 + \sigma dA \quad 1)$$

Where: σ is the surface tension, dA is the change in surface area and subscripts “1” and “2” represent the two phases, which are separated by the tensile surface. 1) assumes that the energy changes associated with tensile layers, only signifies a volume change of both phases plus the energetics associated with the increased tensile layer. Seemingly forgotten is that fact that a curved tensile layer signifies a pressure change, hence any conjecture that tensile layer formation is an isobaric process is troublesome at best. Part of the justification resides in the fact that we can mathematically obtain certain results by doing so, as Pellicier² does for the Young-Laplace equation. Beyond the mathematical justification, the logic is seemingly weak. Accordingly, we must seek an improved logic based mathematical model.

Perhaps the reason for the acceptance of the Helmholtz free energy interpretation of tensile layers is that the mechanical description of tensile layers is similarly troubled. Consider the verbal description for its existence is³: “For a molecule in the bulk liquid the resultant repulsive form its nearest neighbors and the

resultant attractive force from its farthest neighbors are both zero on the average.” “In the surface there is an unbalanced force on a molecule; it is directed inwards because the decreasing density in the surface layer implies that there are fewer neighbors to give an outward repulsive force”. As plausible as such an explanation sounds, the implication is that the unbalanced forces are perpendicular to the tensile layer. So why are these unbalanced forces not considered?

The mechanical description is approximated by the Young-Laplace equation. For a spherical shaped tensile layer residing between a liquid and gas, the Young-Laplace equation is⁸:

$$P_l - P_g = 2\sigma / r \quad 2)$$

Wherein the subscripts “*l*” and “*g*” respectively signifies the liquid and gas phase, with *r* being the tensile layer’s radius of curvature. As valid as 2) may be for obtaining a result based upon the cohesive forces along a tensile layer, one must ponder: What would happen if we added to this, a consideration of the unbalanced forces resulting from cohesive forces perpendicular to the tensile layer? Hence, this paper was written.

Simple Derivation of the Young-Laplace Equation

Let us review the Young-Laplace equation derivation. There are numerous methodologies for deriving 2), such as the one given by Adamson⁹. Herein, we shall take a simpler approach in deriving 2), which was previously published by this author¹⁰ thus is given herein purely for review purposes, with the intention of adding clarity.

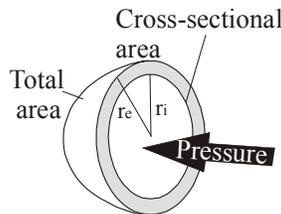


Fig. 1: Shows the pressure in a sphere and its cross-sectional area

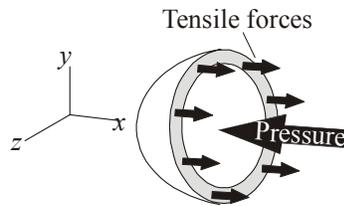


Fig 2: Shows the pressure in a sphere being countered by the tensile forces, along the x-axis

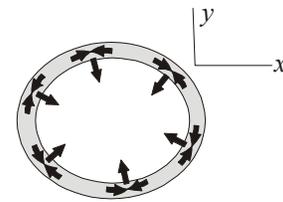


Fig.3: Shows that the pressure along the x-axis is equated to an inward squeezing by the tensile layer along the x-y plane.

When deriving the Young-Laplace equation, one may start with the following fundamental 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 force¹¹. 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: πr_i^2 . If the pressure under consideration is along the *x*-axis, as shown in Fig. 2, then the cross-sectional area is measured in the *y-z* plane. Applying the principle of hydrostatics we can say, the total force perpendicular to the cross-sectional area is the force of elongation (F_e)¹⁰:

$$F_e = \Delta P \pi r_i^2 \quad 3)$$

Where: $\Delta P = P_g - P_l$, which is the pressure difference, across the tensile layer. Equilibrium means that 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 the bubble’s surface tension is squeezing inward as a function of its length then the total surface tension (τ_1) along the ring of tensile layer, as illustrated in Fig. 3, is¹⁰:

$$\tau_1 = 2\pi R\sigma \quad 4)$$

Where: $R = (r_i + r_e) / 2$. Consider the tensile layer to be thin therefore: $R = r_i = r_e = r = r$. Equating the tensile forces to the force of elongation, i.e. 3) to 4) and dividing by: πr_i^2 , we obtain:

$$\Delta P = 2\sigma / r \tag{5}$$

Obviously, 5) is another way of writing the Young-Laplace equation, that being 2).

Bubbles, Droplets and the Young-Laplace Equation

Traditionally, the Young-Laplace equation is used to define the pressure inside of a bubble surrounded by a liquid, the pressure inside of a liquid droplet surrounded by a gas, as well as in the analysis of both capillary rise and depression. The Young-Laplace equation only considers the cohesive forces along the tensile layer conveniently omitting the liquid molecule's cohesive forces perpendicular to the tensile layer, as is shown by the white arrows in Fig. 4 and 5. If we now consider the cohesive forces perpendicular to the tensile layer, the resultant tension perpendicular (τ_{\perp}) to the tensile layer is taken over a $\frac{1}{2}$ sphere, whose magnitude is¹⁰:

$$\tau_{\perp} = \sigma \pi r_d \tag{6}$$

As illustrated in Fig 4, the cohesive forces perpendicular to a bubble's tensile layer would be directed into the surrounding liquid, from the bubble's tensile layer. Subtracting the cohesive forces perpendicular to the tensile layer, as defined by 6), from the cohesive forces along the tensile layer, as defined by 4), the pressure within a bubble (P_b) immersed in a liquid becomes¹⁰:

$$P_b = \sigma / r_b + P_l \tag{7}$$

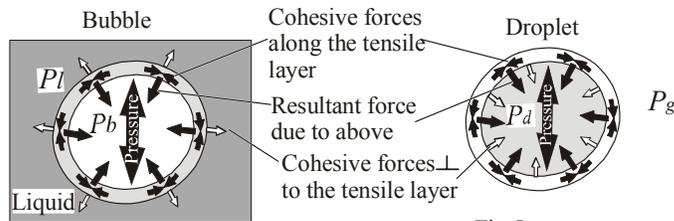


Fig 4

Fig 5

In both the above Fig 4 and Fig 5 we see two sets of forces. Black arrows are due to the intermolecular cohesive forces along the tensile layer while the white arrows are due those perpendicular to the tensile layer.

Conversely for a droplet, as illustrated in Fig 5, the cohesive forces perpendicular to the tensile layer would be directed into the droplet. Adding the cohesive forces perpendicular to the tensile layer, as defined by 6), to the cohesive forces along the tensile layer, as given by 4), results in the pressure within the droplet (P_d) becomes¹⁰:

$$P_d = 3\sigma / r_d + P_g \tag{8}$$

Until now, most researchers believe that the pressure within both a bubble and droplet are well understood, that being defined by 4). Certainly, this was this author's belief until researching the phenomena and noticing huge discrepancies in the theory. The extent of this problem can be seen by comparing Debenedetti¹² who has the pressure inside of a bubble, lower than the pressure of the

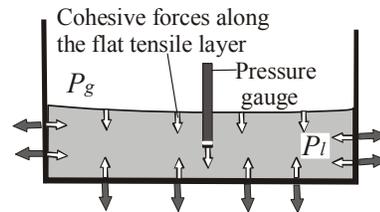


Fig. 6 Shows the cohesive forces in a container of liquid. Although the pressure in the liquid is higher due to the intermolecular cohesive forces, the affinity of those same forces to the pressure gauge would prevent the gauge from reading any pressure increase.

surrounding liquid, to Adamson⁹ has the pressure inside of a bubble greater than the pressure of the surrounding liquid. They both cannot be right.

Logic seemingly dictates that one should be able to readily probe either a bubble or a droplet with a pressure gauge. However, trying to actually measure the pressure within a spherical bubble is next to impossible. It only becomes feasible if the bubble is rigidly adhered to a surface, however the consequences of that rigid attachment should influence the pressure reading.

As for a droplet, inserting a pressure probe into it is easily accomplished. Even so, when either a bubble or droplet is rigid attached to some surface to which its tensile layer has an affinity, the shape is rarely perfectly spherical which will influence the pressure reading. Moreover, if we are considering all resultant intermolecular cohesive forces, then we must consider that the resultant cohesive forces of the liquid perpendicular to the probe's surface, which will be directed into the liquid. Hence will lower the actual pressure reading. In order to visualize this, imagine the container of liquid illustrated in Fig. 6. Considering all resultant intermolecular cohesive forces, we realize that along the container's base and walls the liquid's intermolecular forces are directed into the liquid but these are countered by the strong affinity the liquid has for the container. The only intermolecular cohesive resulting in pressure increase within the liquid would be those perpendicular to the relatively flat surface tensile layer. Obviously these are directed down into the liquid. However, the pressure gauge, due to the affinity between the pressure gauge's probe's end and the surrounding liquid, would result in a resultant cohesive force directed into the liquid therefore the gauge would not measure the pressure increase.

Interestingly, for a soap bubble, it was realized that the cohesive forces perpendicular to the tensile layer would cancel, leaving the accepted traditional result¹⁰:

$$\Delta P = 4\sigma / r_b \quad 9)$$

Capillary Rise and Depression: The Traditional Approach

Capillary rise is the elevation of a liquid by some height (h) within a capillary tube when the liquid has an affinity towards the capillary tube and the tubes radius is sufficiently small. In capillary rise, traditional theory incorporates the idea of contact angle (ϕ), and considers the tensile surface to be spherical with a radius defined by the capillary tube's radius (r_c). The traditional equation is for capillary rise being⁹:

$$h = 2\sigma \cos \phi / \rho g r_c \quad 10)$$

It seems strange that the curved tensile layer would have a radius simply defined by the tube's radius, even though it has a contact angle. Logic should dictate that the greater ϕ is, then the larger the tensile layer's radius should be. When, r_c is sufficiently small, then: $\phi \rightarrow 0$, then: $\cos \phi \rightarrow 1$, which results in:

$$h = 2\sigma / \rho g r_c \quad 11)$$

Interestingly, 11) is also traditionally used to define capillary depression, that being the fall of a liquid by some height (h) within a capillary tube when the liquid has no affinity to the capillary tube. For capillary depression, the traditional approach is treat the radius of curvature of the liquid as being equal to the capillary tube's radius, which is to say: $\phi \rightarrow 0$, hence the use of 11).

The correlation between 11) and the Young-Laplace equation [2) or 5)] can be best illustrated by contemplating capillary rise. That column of liquid has a volume (V) and a density (ρ), giving the force due to gravity exerted by the weight of the column of liquid in the capillary tube is:

$$mg = V\rho g = \pi r_c^2 h \rho g \quad 12)$$

Equating 12), to the tension as defined by 4), we obtain:

$$\pi r_c^2 h \rho g = 2\sigma\pi r_c \quad (13)$$

Dividing through by: $\pi r_c^2 \rho g$, one then obtains 11).

Capillary Rise and Cohesive Forces Perpendicular to the Tensile Layer

In order to arrive at a more general formulation that being approximately the tensile layer as elliptical, we will consider what forces are acting in the y -direction in Fig 7. The cross-sectional area of an approximate ellipse parallel to the x - z plane is:

$$A_{xz} = \pi r_x r_z \quad (14)$$

Multiplying the pressure change (ΔP_y) along the y -axis by the cross-sectional area in the x - z plane (A_{xz}) gives the force of elongation (F_{ey}) along the y -axis:

$$F_{ey} = \Delta P_y \pi r_x r_z \quad (15)$$

F_{ey} is countered by the tension squeezing along the x - y plane. Since the tensile surface approximates a $1/2$ ellipse, whose length along the x - y plane is: $\pi(r_x + r_y)/2$. Therefore, the tension along the positive y -axis due to intermolecular cohesive forces along the tensile layer [$\tau_{(y : \text{along})}$] is:

$$\tau_{(y : \text{along})} = \sigma \pi (r_x + r_y) / 2 \quad (16)$$

Since the tensile layer has an inner (r_i) and exterior/outer radius (r_e), as was discussed when deriving 4), we double 10). Therefore, for capillary rise, the tension along the positive y -axis due to the intermolecular cohesive forces along the tensile layer is:

$$\tau_{(y : \text{along})} = \sigma \pi (r_x + r_y) \quad (17)$$

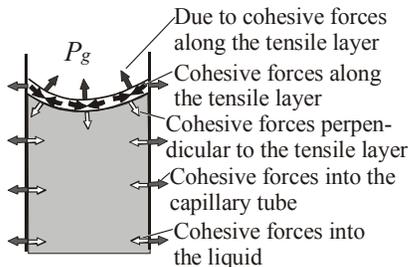


Fig. 7 Shows all the intermolecular cohesive forces within the liquid in capillary rise.

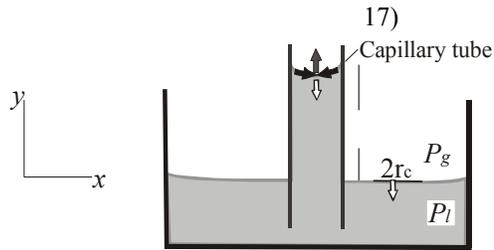


Fig. 8 Shows capillary rise of height h . Shown are the intermolecular cohesive forces that must be considered that being both those along and perpendicular to the curved tensile layer in the capillary plus those perpendicular to the flat tensile layer.

Obviously, when the capillary layer is spherical then: $r_x = r_y$, and 17) simply equates to 4), i.e. $\tau_{xy} = \tau_1$, giving the traditional result. Specifically, for the case of: $r_c = r_x = r_y$, then 17) becomes the Young-Laplace equation for capillary rise, which in this case would be:

$$\tau_{(y : \text{along})} = 2\sigma\pi r_c \quad (18)$$

Next consider the liquid's cohesive forces perpendicular to the tensile layer [$\tau_{(y : \perp)}$] in the capillary tube. Since they are of the same magnitude as those along the tensile layer, we can approximate them by writing:

$$\tau_{(y:\perp)} = -\sigma\pi(r_x + r_y)/2 \quad (19)$$

The negative sign meaning $\tau_{(y:\perp)}$ is directed along the negative y -axis hence downward into the liquid. Therefore, the net tension felt by the liquid inside of the capillary due to all cohesive forces within the capillary tube (τ_{cyl}) must be:

$$\tau_{cyl} = \tau_{(y:along)} + \tau_{(y:\perp)} \quad (20)$$

Realizing that $\tau_{(y:along)}$ and directed upward, while $\tau_{y\perp}$ is directed downward, we obtain:

$$\tau_{cyl} = \sigma\pi(r_x + r_y) - \sigma\pi(r_x + r_y)/2 \quad (21)$$

Collecting the terms, for capillary rise we obtain:

$$\tau_{cyl} = \sigma\pi(r_x + r_y)/2 \quad (22)$$

We do not concern ourselves with the intermolecular cohesive forces between the capillary tube and liquid as shown in Fig. 7 because they are perpendicular to the capillary rise with the resultant force directed into the capillary tube. This does not imply that they are not important because it is the liquid's affinity to the tube that allows for the rise in the first place. Is 22) the summation of all cohesive forces felt by the liquid inside the capillary? The answer is no!

As was discussed previously for Fig. 6, there are cohesive forces perpendicular to the relatively flat tensile layer, which will need consideration. Considering, the pressure exerted along an arbitrary line, whose length is $2r_c$ the equivalent tension felt along the arbitrary line (τ_a), would be:

$$\tau_a = 2r_c\sigma \quad (23)$$

As far as the contents of the capillary tube, is concerned, the direction of τ_a is directed upward along the y -axis. The tension as defined by 23) must be added to 22) to calculate the total tension that results in capillary rise:

$$\tau_{tot} = \tau_{cyl} + \tau_a = \sigma\pi(r_x + r_y)/2 + 2r_c\sigma \quad (24)$$

Equating τ_{tot} to the weight, as defined by 12), we obtain:

$$\pi r_c^2 h \rho g = \sigma\pi(r_x + r_y)/2 + 2\sigma r_c \quad (25)$$

Dividing by: $\pi r_c^2 \rho g$, we obtain:

$$h = [\sigma\pi(r_x + r_y)/2 + 2\sigma r_c] / \pi r_c^2 \rho g \quad (26)$$

If $r_c = r_x$, then we can rewrite 26) as:

$$h = [\sigma\pi(r_c + r_y)/2 + 2\sigma r_c] / \pi r_c^2 \rho g \quad (27)$$

27) becomes the general equation for capillary rise. For the special case of the tensile layer being spherical then: $r_c = r_y$. Collecting terms we obtain:

$$h = \sigma(1 + 2/\pi) / \rho g r_c \quad (28)$$

Which can be rewritten as¹⁰:

$$h = \sigma(1.64) / \rho g r_c \quad (29)$$

Although 29) is not identical to the traditionally accepted value [10) or 11)] for capillary rise, we can see that it is close, implying that our consideration of cohesive forces perpendicular to the tensile layer warrants consideration. What is most important is 27), which tells us that the greater the value of r_y in comparison to r_c the higher the capillary rise would be. Moreover, in capillary experiments the tube is generally wetted prior to the experiment, which should increase r_y thus increasing height (h), which helps explain why basing capillary rise on the Young-Laplace equation has remained unchallenged.

We can view the above analysis another way. Consider that capillary rise is the difference of two phenomena. 1) the upward force due to the cohesive forces along the tensile layer, as defined by the Young-Laplace equation when the tensile layer is spherical. 2) the difference between the cohesive forces perpendicular to the curved tensile of the top of the capillary and the cohesive forces perpendicular to a flat tensile layer whose length is: $2r_c$.

Capillary Depression and Cohesive Forces Perpendicular to the Tensile Layer

Capillary depression/fall seemingly correlates better with the Young-Laplace equation than does capillary rise. However, the current theory for capillary depression is poor at best and as was the case in capillary rise, current theory fails to address the fact that cohesive forces are acting in 3 directions along the tensile surface, hence the parabolic shape.

For capillary depression, once again the area of the ellipse in the x - z plane is given by 14), while the force along the y -axis is given by 15). Therefore, for capillary depression, the tension along the positive y -axis due to the intermolecular cohesive forces along the tensile layer is has a magnitude defined by 17) but is now along the negative y -axis, as illustrated in Fig 9. Therefore:

$$\tau_{(y : \text{along})} = -\sigma\pi(r_x + r_y) \quad (30)$$

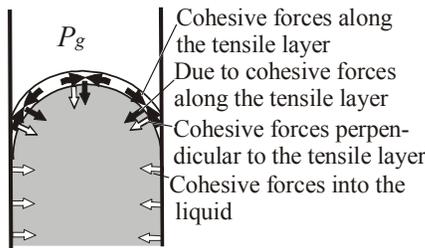


Fig. 9 Shows all the intermolecular cohesive forces within the liquid in capillary depression/fall.

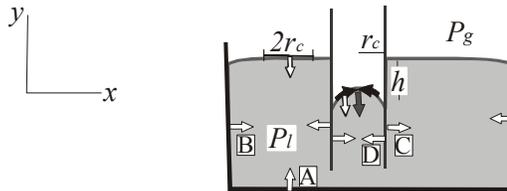


Fig. 10 Shows capillary depression of height h . Shown are the intermolecular cohesive forces that must be considered. Those being both along and perpendicular to the curved tensile layer in the capillary plus those perpendicular to the flat tensile layer plus those directed into the liquid along the container walls and capillary tube.

For the liquid's cohesive forces perpendicular to the tensile layer ($\tau_{y \perp}$) in the capillary tube, which are directed into the liquid, once again that would be defined by 19) and be directed along the negative y -axis hence downward into the liquid, as illustrated in Fig 9. Therefore, the net force felt by the liquid inside of the capillary due to all cohesive forces within the capillary tube (τ_{cyl}) must be would still be defined by 20) but the result now becomes:

$$\tau_{cyl} = -\sigma\pi(r_x + r_y) - \sigma\pi(r_x + r_y) / 2 \quad (31)$$

Collecting the terms, for all the cohesive forces along the curved tensile layer within the capillary tube in capillary depression, we obtain:

$$\tau_{cyl} = -3\sigma\pi(r_x + r_y)/2 \quad (32)$$

32) is written as if it represents all the cohesive forces within the capillary. However, looking at Fig 9 we can see that the cohesive forces of the liquid directed into the liquid along the capillary tube, were not considered. Although, due to strong affinity between the capillary tube and liquid in capillary rise, these forces were omitted from the analysis, this may not be the case for capillary depression, which we will discuss later on in this section. Considering the cohesive forces perpendicular to a tensile layer, the difference between that exerted along a curved tensile layer and an equivalent section of flat tensile layer, is still defined by 23). The net result becomes:

$$\tau_{tot} = \tau_{cyl} + \tau_a = 2r_c\sigma - 3\sigma\pi(r_x + r_y)/2 \quad (33)$$

The value of τ_{tot} will be negative, indicating that the resultant tension is along the negative y-axis. Equating τ_{tot} to the gravitational force as defined by 12), we obtain:

$$\pi r_c^2 h \rho g = 2\sigma r_c - 3\sigma\pi(r_x + r_y)/2 \quad (34)$$

Dividing both sides of 34) by: $\pi r_c^2 \rho g$, we obtain:

$$h = [2\sigma r_c - 3\sigma\pi(r_x + r_y)/2] / \pi r_c^2 \rho g \quad (35)$$

If: $r_c = r_x$, then 35) becomes:

$$h = [2\sigma r_c - 3\sigma\pi(r_c + r_y)/2] / \pi r_c^2 \rho g \quad (36)$$

For an approximation to the currently accepted equation for capillary depression we assume that the tensile surface is close to being spherical, therefore: $r_c = r_y$ and we now obtain:

$$h = (2r_c\sigma - 3\sigma\pi r_c) / \pi r_c^2 \rho g \quad (37)$$

Dividing 37) through by r_c we obtain:

$$h = \sigma(2 - 3\pi) / \pi r_c \rho g \quad (38)$$

Which becomes:

$$h = -2.36\sigma / r_c \rho g \quad (39)$$

The traditionally accepted theory for capillary depression is also based upon the Young-Laplace equation, but is directed along the negative y-axis, hence is the negative of 11). We can see that the traditional value is 85% of our calculated value. It must be emphasized that our approximation, as given by 39) is based upon the tensile surface being spherical and its radius being exactly that of the capillary. For the case of the capillary depression of mercury in a glass capillary tube, that is seemingly often the case. Since in capillary depression experiments, the tube is not wetted prior to experiment, the difference between our result, 39), and the traditional result, 40), must be explained. Firstly, in our analysis we did not consider all the tensile forces directed into the liquid. Looking at Fig 10 we can see that we omitted the following:

- A) The cohesive forces directed upwards into the liquid from along the base of the container.
- B) The cohesive forces directed into the liquid from the along the walls of the container.
- C) The cohesive forces directed into the container of the liquid from along the capillary tube.
- D) The cohesive forces directed into the capillary tube from along the capillary tube.

As for A), these cohesive forces and those from along the top of the liquid should be uniform throughout the liquid. The only real difference is the difference between the curved tensile in the capillary tube and that of an equivalent line of a flat tensile. Accordingly our analysis could have included these but we would have arrived at the same result!

However, the same cannot be said if due consideration was given to B), C) and D). Since all these cohesive forces are perpendicular to the capillary depression, then they probably do not affect the result. Having said that, this may warrant more consideration.

Secondly, another explanation for why 40) is so strongly believed may lie in the process of measurement.

Measurement in Capillary Action

Whether one is talking about capillary rise or capillary fall, this author believes that the measurement of h should be made along a line passing through the centroid of the section containing the curved tensile layer in the capillary tube, as illustrated in Fig 11. And not to either the top or bottom of the curved tensile layer in either capillary rise or fall, as is done traditionally.

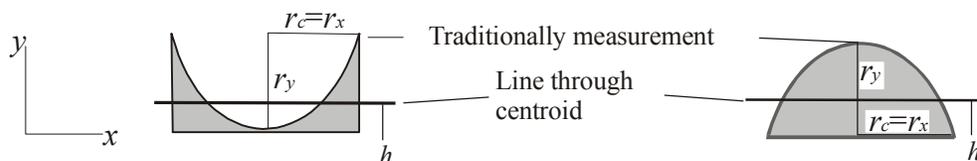


Fig. 11 Shows the top of a tensile layer in capillary rise on the left and the top of a tensile layer in capillary fall on the right. In both cases the height (h) should be measured to the plane which defines the center of mass of the capillary section.

For the case of capillary rise this would mean that the traditionally measured location gives a slightly higher value for the h than it should be. Conversely, for capillary depression the traditionally measured value would be lower than it should be, hence providing an explanation as to why 40) is so strongly believed by those using traditional theory.

Clarification

For clarification, the derivation of 7) ,8) and 9) can be found in this author's paper¹⁰, entitled: "Energetics of Nucleation". Since the paper primarily dealt with nucleation, 29) and 39) were simply stated, in order to demonstrate to the reader, that the treatment of all cohesive forces may warrant due consideration. Hence the more formal derivation and discussion of 29) and 39) were left for this paper.

Conclusions

In this treatise we did not prove that the intermolecular cohesive forces perpendicular to tensile layers must be considered when contemplating a pressure change across a tensile layer, whether it be curved or flat. By considering all the intermolecular cohesive forces, meaning both along and perpendicular to the tensile layer in capillary action, we arrive at results that are close (82.5-85%) to the traditionally accepted value when the tensile layer is approximated to being spherical! Considering, the tensile layer as being elliptical resulted in an improved approximation, although a precise calculation can only be attained, by considering the tensile layer's exact shape. Interestingly, for capillary rise the act of wetting the capillary tube should result in a higher height of rise, by increasing r_y in comparison to r_x .

In both capillary rise and depression, the measurement of height is often taken to be the highest point in the curved tensile surface, rather than a line passing through its centroid. For capillary rise this means that the measured height is too large, while in capillary depression it would be too small, thus reinforcing the traditional theory.

We also realized the some of the difficulties exist in measuring the pressure with a bubble and/or droplet. Furthermore, when measuring the pressure within most liquids, whether it is a droplet or a container of liquid, the measurement of pressure will be lowered due to any affinity between the liquid to

the end of the probe, hence nullifying from the reading any pressure increase within the liquid due to the intermolecular cohesive forces directed perpendicular to the tensile layer and into the liquid.

We are no longer befuddled by the enigma as to why we simply omit the intermolecular cohesive forces perpendicular to the tensile layer. Certainly, logic dictates that there is a resultant force associated with such cohesive forces, therefore a pressure/tension associated with them. Interestingly, the concept of contact angle was not required in our analysis leaving the astute reader to ponder whether contact angle may be a result, rather than some reason as conveyed in traditional theory⁹.

The paper is a treatise demonstrating that when one considers all the intermolecular cohesive forces, both along and perpendicular to a tensile layer that one does arrive at some interesting results. In many ways it is an elaboration of some concepts originally discussed in an earlier paper by this author, which dealt with the theory of nucleation (paper entitled: Energetics of Nucleation). Since that paper dealt with nucleation, certain equations concerning the pressure change across curved tensile layers were simply stated. It must be emphasized that the derivation of those stated equations were given to the reviewers but no comments were made.

The paper Energetics of Nucleation was deemed controversial and was not going to be published, until this author found some data from an experiment performed in 2001, in which a laser was shot into degasified water and the energy required for nucleation was calculated. The data in question could not be explained by the research group but was an exact fit to what this author was saying, hence publication. The Lauterborne group in Germany, who performed the experiment in question, has confirmed the exactness of fit.

I am an independent researcher whose interest lay in nucleation theory and thermodynamics. I have also another paper concerning work that has been accepted for publication by Physics Essays and another currently in the review process. Neither of those papers deals with cohesive forces and tensile forces that being the paper presented herein.

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References

1. Zhmud, B.V., Tiberg, F., Hallstenson, K., J. Colloid and Inter Sci. 228 pp 263-269 (200)
2. Pellicier, J., Manzanares, J.A., Mafe, S., Am. J. Phys 63 (6) pp 542-547 (1995)
3. Berry, M.V. Phys. Educ., 6 pp 79-83 (1972)
4. Navascues, G., Rep. Prog. Phys. 42 Pp1131-1186 (1979)
5. Boucher, E.A., Rep. Prog. Phys. 43 Pp497-546 (1980)
6. Reif F. "Fundamentals of Statistical and Thermal Physics", McGraw-Hill, New York 1965
7. Walton, Alan, J., Phys. Educ. 7 Pp491-498 (1972)
8. Adamson, A.W., "Physical Chemistry of Surfaces, 3rd edition" John Willey and sons 1976
9. Mayhew, K.W. Phy. Essays, 17 Pp 476-495 (2004)
10. Fogiel, M. Problem Solver in Strength of Materials, Research and Education Association, New York, 1983 (page 197)
11. Debenedetti, P. "Metastable Liquids: Concepts and Principles", Princeton University Press, Princeton 1996