

Laplace's Law

Its Epistemological Context

By Max E. Valentinuzzi, Alberto J. Kohen, and B. Silvano Zanutto

The Macro-Cosmos—the Universe—is amazingly infinite; the Micro-Cosmos—cells, molecules, atoms, electrons...—seems to be infinite, too; but the Mind...oh, the Mind!... it projects further beyond...for sure! Isn't this brief musing epistemological in nature, searching for limits?

Science, technology, history, and philosophy are strongly related areas of knowledge. Perhaps, the best epistemologists are those who first were researchers in the sometimes called, and perhaps erroneously, hard disciplines (said with due respect and full recognition to pure epistemologists) because they, by force of education and training, had to be deeply involved in the intricacies of physico-chemical principles and laws and technological developments to carry out measurements, and need to delve back in time for those who did it or tried to do it before, often being surprised by the ingenuity shown by predecessors in much older times. After collecting experience for a long time, the scientist falls naturally into traditional philosophical doubts and questions, the how's and what's, the up to where's, and when's. Quite interesting, children from three to five years old tend to often ask questions of this kind: Daddy, Mommy, how are we here, how was I born, what is the sky, where does the sky end, and so on. Does that mean we very early in life develop such ques-

tioning attitude that soon thereafter we lose, or maybe it is repressed by parental poor response or lack of response?

In the two preceding notes about Laplace's law [1], [2], we first recalled what it is and how it is frequently mentioned or applied in physiology, finding that in this particular case, there is an apparent separation between physiology and physics supposedly backing up the subject. Moreover, mistakes are almost a rule while amazingly and fortunately, the overall practical conclusions after very heavy simplifications are correct and well demonstrated by actual experiments and postmortem studies. The second note dealt with the mathematics of the law, and we believe that we practically exhausted all the pathways leading to the final formula, both when the wall thickness is negligible and when it is finite and significant. Now, our hat displays the epistemologist's sign, upsetting perhaps some readers, but without totally leaving out the quantitative view. Hence, the objectives of the note are established as follows:

- ▼ *general objective*: To introduce, discuss, and eventually produce answers for the epistemological aspects associated with Laplace's law
- ▼ *specific objective*: To discern if a mathematical equation has the same reach when obtained from two different physical settings (in our case, a phenomenon found in capillaries

and the behavior of hollow stretchable cavities).

This is a good time to recall Thomas S. Kuhn's book [3] as an excellent and well-versed material to take into account when these aspects occupy our concerns. This highly cited and recognized physicist and philosopher of science (1922–1995) introduced and used the concept of scientific paradigm. Even though he never gave its precise definition, it may be described as *a very general conception of the nature of scientific endeavor within which a given enquiry is undertaken*. Ours herein is an enquiry, modest in relation with Kuhn's hugely

wider environment, both in space and time, but valid as such if the physical settings given above in the objectives are considered as minor subparadigms. We could synthesize more powerfully our

question by asking what is the nature of Laplace's law. The latter really comes up as the central question addressed herein.

Common knowledge does not usually go through reflexive critical filters.

What Is Epistemology?

Epistemology (from Greek, *ἐπιστήμη*, episteme, knowledge, and *λόγος*, logos, theory), as a branch of philosophy, devotes itself to scientific knowledge, clearly differentiating it from common or popular knowledge, which usually does not go through reflexive critical filters. Typical questions posed by epistemology are as follows:

- ▼ What are the necessary and sufficient conditions of knowledge?
- ▼ What sources offer possible answers?
- ▼ What is the structure of such knowledge, and what are its limits?

Broadly speaking, it may be stated that epistemology deals also with the creation and dissemination of knowledge in specific areas [4]–[10], or perhaps better, we should speak in terms of Theory of Science. Hence, the questions posed above regarding Laplace's law clearly fall within the much wider spectrum set by

these definitions; more specifically, what the nature and limits of these law are. Its historical development may supply some leads. We think this aspect calls at least for consideration and discussion when dealing with this more or less hidden (and even perhaps less significant) piece of physics.

Laplace's Law Based on Capillarity

Our previous two notes showed that the first contributions, starting with Laplace himself, originated in the capillary phenomenon. How does it manifest? Depending on the characteristics of the fluid (water, alcohol, mercury, or so on), on the material the tube is made of (glass, metal, ceramic, or so on), and on the gas (in general, air) forming the environment of the system, the liquid in the vicinity of the wall becomes concave or convex. In fact, the tube does not have to be a capillary to display such shapes. Quite interesting, and even surprising, is that the fluid goes either up or down; the smaller the diameter, the higher (or lower)

the displacement, thus defying gravity (Figure 1).

Numerical examples illustrate the following points: In a tube with a diameter of 4 m, water would barely rise 0.007 mm (negligible and essentially undetectable, but real); if the diameter is 4 cm, water goes up to 0.7 mm, but if the diameter gets down to 0.4 mm (already a capillary), the water rises up to 70 mm, giving the impression of being sucked up without an active pump! This is precisely the method clinical biochemists use to collect small amounts of blood

(with density very close to that of water) from a punctured fingertip. Thus, by definition, capillary is a tube sufficiently fine so that attraction of a liquid into the tube is significant. Those use for hematocrit determination (made of glass), for example, is in the order of 1.1–1.2 mm internal diameter and 1.5–1.6 mm external diameter. There is a widely known equation to calculate the height of the column that can be found in any physics textbook or in the Web [11], [12], i.e.,

$$h = \frac{2T\cos\alpha}{\rho g r}, \quad (1)$$

where T is the liquid–air surface tension (force/unit length), α is the angle of contact, ρ is the liquid density (mass/volume), g is the gravitational field (force/unit mass), and r stands for the tube radius (length).

To better analyze this effect and discuss it further within the context of the note, we should remember basic good old physics, the so-called surface phenomena, as described in a classic and highly recognized old textbook written by E. Perucca, in Italy, in 1932 [11]. However, we will slightly modify the derivation because, as found in other publications, the final Laplace's law appears with only one surface tension instead of two.

The contact surface between two phases is a separation surface, as between liquid and gas, solid and gas, liquid and liquid, and solid and liquid. A situation often encountered is a three-phase system formed by solid, gas, and liquid. Herein, we are interested in the latter case, where the liquid phase plays a significant role. The surface tension T of a liquid depends on its nature. By and large and as a first approximation, T does not depend much on the gas that surrounds it; however, it decreases with the temperature and is greatly modified by any contamination (ethylic alcohol in air, 22; water in air, 73; and mercury in vacuum, 435, all in dyn/cm and at 20°C). We can imagine T as the force to keep united the two edges of an ideal cut of 1 cm made over the liquid surface. The force, as said before in our previous notes, is perpendicular to the cut and tangent to the surface. Quite interesting is the fact that liquid films are contractile and cover the minimum surface compatible with the mechanical links around them and applied external forces. In other words, their potential energy is minimal (see in the following a brief description of contractile mercury droplets).

Imagine the surface separating liquid from air (or better, from vacuum). Each liquid molecule within the liquid is attracted by the surrounding molecules and such attraction quickly decreases with the distance, becoming almost zero at a distance r_m (defined as the radius of

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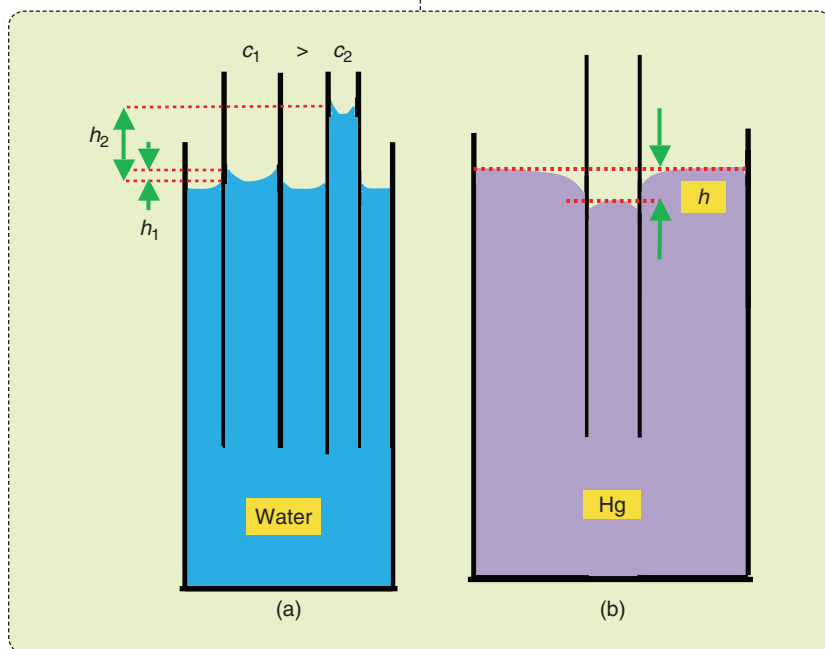


FIGURE 1 A schematic showing menisci and capillary effect. (a) Two capillary tubes C_1 and C_2 of different diameters. Menisci are concave and the larger lumen displays a lower height h_1 as compared with the smaller one h_2 . (b) A capillary immersed in mercury produces a height h negative with respect to the bigger container level. Besides, menisci are convex.

molecular action), which lies in the order of about 4 nm, if it is water. Molecules fully immersed in the liquid's bulk are symmetrically attracted by the neighboring molecules, but those belonging to the surface region are attracted by the cohesion forces resultant. Such resultant force increases as the molecule gets nearer the surface. Thus, surface tension can be looked at as an indicator of internal cohesive forces of molecular origin.

A liquid in contact with a solid wall takes one of the shapes shown in Figure 2. The shaded areas and upwards, as moving in a funnel, up to the vertex A (a) or convex border (b), encompass the fluid region (say, water or mercury). By the Virtual Work Principle (for a body in equilibrium, when a virtual deformation infinitely small is applied, the virtual work of the external forces equals the inner deformation work), point A will be in equilibrium when the resultant force \mathbf{R} is normal to the wall and verifies that

$$\mathbf{R} = \mathbf{T}_{12} + \mathbf{T}_{23} + \mathbf{T}_{13} = \mathbf{0}, \quad (2)$$

where the bold face indicates vectors. Force \mathbf{R} tends to bring A off the wall, which is impossible because of the mechanical link imposed by it; thus, equilibrium means

$$T_{13} = T_{23} + T_{12} \cos \alpha, \quad (3)$$

where α stands for the angle linking wall 3 and fluid 2 (air, usually). The T 's are the respective magnitudes of the vectors mentioned above. A virtual displacement is an infinitesimal change in the position of the coordinates of a system such that the constraints remain satisfied, and often, the principle is summarized by the following equation:

$$\delta W_i - \delta W_e = 0, \quad (4)$$

where the W 's stand for internal and external infinitesimal virtual works, respectively. The cosine of the angle α will be positive or negative for α smaller or larger than 90° .

Refer to Figure 3, where a small sphere with center O and radius dr cuts a nonplanar liquid surface Σ having a circumference Γ . The latter determines a differential area

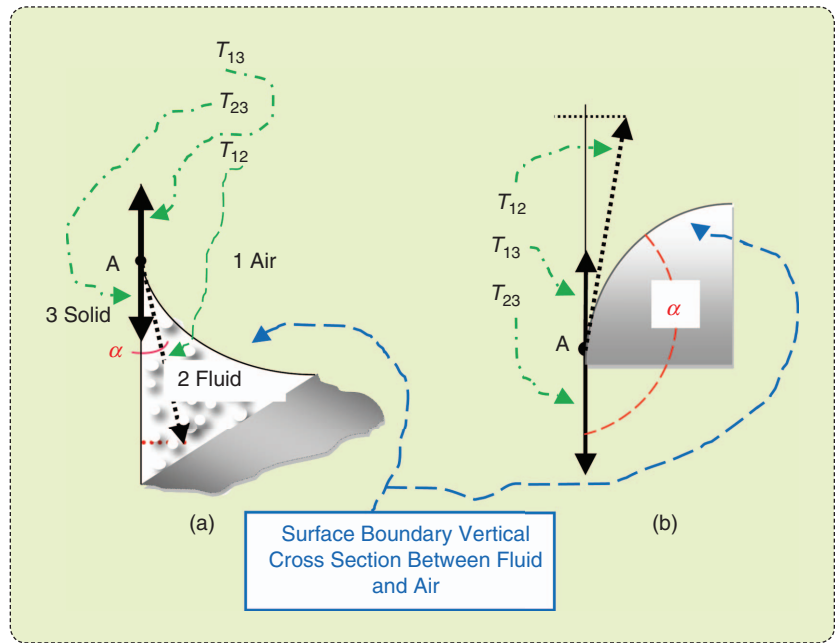


FIGURE 2 Surface tension. Two types of menisci: concave [(a) as water in glass] and convex (b), as mercury in glass. When the (a) link angle $\alpha < 90^\circ$, it is said that the fluid wets the wall and (b) when it is $> 90^\circ$, the fluid does not wet the wall. The dotted arrow represents the surface tension T_{12} between medium 1 and 2 (say, air and water). There is also a surface tension T_{23} between the solid wall (say, glass) and the fluid (downward vertical thick arrow, tangential to the inner wall surface). Finally, a third surface tension T_{13} (also tangential to the wall and pointing upward) manifests itself between air and the wall. The shaded areas on both figures mark the fluid phase (say, water or mercury).

$$dS = \pi(dr)^2. \quad (5)$$

A diameter MM' and a neighboring one form a differential angle $d\phi$, thus determining over the circumference line two equal arcs $dl_1 = dl_1' = d\phi \cdot dr$. The superficial tension applies to these two opposing arcs, respectively, forces $\tau_1 \cdot d\mathbf{l}_1 = \tau_1 \cdot d\mathbf{l}_1'$, tangent to the surface Σ and perpendicular to the arcs (boldface indicates vectors). Owing to the curvature of Σ , both forces produce an infinitesimal resultant $d\mathbf{F}_1$ that points downward toward the distant center of curvature C_1 , different than the small sphere's center cutting the liquid surface. Such force is given by

$$d\mathbf{F}_1 = 2\tau_1 dl_1 \cos \beta = -2\tau_1 dl_1 \sin \gamma, \quad (6)$$

$$\begin{aligned} d\mathbf{F}_1 &= 2\tau_1 \cdot d\phi \cdot dr \cdot (dr/r_1) \\ &= 2\tau_1 \cdot (dr)^2 \cdot d\phi \cdot (1/r_1), \end{aligned} \quad (7)$$

where r_1 is the curvature radius at point O of the section $MOM'C_1$; this radius will be positive when its direction coincide with the direction of the normal n

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and negative with the opposite direction. By the same token, a perpendicular diameter to MM' accompanied by another neighboring one would determine two opposing arcs dl_2 and dl_2' so that an equation similar to (7) is obtained, i.e.,

$$d\mathbf{F}_2 = 2\tau_2 \cdot (dr)^2 \cdot d\phi \cdot (1/r_2). \quad (8)$$

The four equal arcs dl_1 , dl_1' , dl_2 , and dl_2' , contribute to the perpendicular action along n in the amount

$$\begin{aligned} d\mathbf{F} &= d\mathbf{F}_1 + d\mathbf{F}_2 \\ &= 2\tau_1 \cdot (dr)^2 \cdot d\phi \cdot (1/r_1) \\ &\quad + 2\tau_2 \cdot (dr)^2 \cdot d\phi \cdot (1/r_2), \end{aligned} \quad (9)$$

$$\begin{aligned} d\mathbf{F} &= d\mathbf{F}_1 + d\mathbf{F}_2 \\ &= 2(dr)^2 d\phi [(\tau_1/r_1) + (\tau_2/r_2)]. \end{aligned} \quad (10)$$

Perucca [11] states that for any pair of normal sections perpendicular to each other, the addition of their respective inverses is a constant, in turn equal to the addition of the two principal curvatures, i.e.,

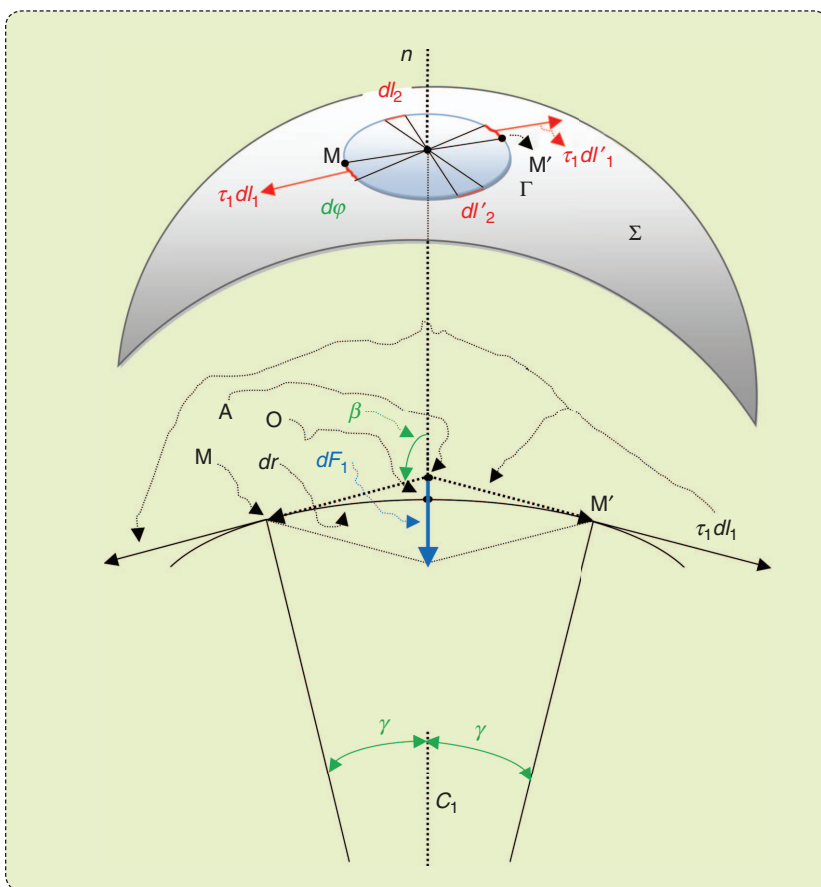


FIGURE 3 Perucca's setting. The circumference Γ above is part of a small sphere of radius dr . That circumference lies on and is part of surface Σ . Diameter MM' forms an angle $d\varphi$ with another neighboring diameter.

$$\begin{aligned} [(1/r_1) + (1/r_2)] &= \text{constant}, \\ &= [(1/R_1) + (1/R_2)]. \end{aligned} \quad (11)$$

Here, it must be reminded what Koiso and Palmer recently stated when recalling Thompson's expression for a system in equilibrium [13], [14],

$$T_1/R_1 + T_2/R_2 \equiv \text{constant}, \quad (12)$$

where $1/r_1$ and $1/r_2$ are the principal curvatures of the considered smooth surface, and T_1 and T_2 are orthogonally directed tensions, which depend on the material and normal direction of the surface at each point. Expression (12) is also equal to $[(\tau_1/r_1) + (\tau_2/r_2)]$, in which we emphasize that r_1 and r_2 stand for any pair of perpendicular radii different from the two principal axes. We remark that on the particular case of a sphere, the curvature itself is constant everywhere. Hence, consider-

ing Thompson's expression, r_1 and r_2 of (10) can be replaced by R_1 and R_2 leading to

$$d\mathbf{F} = 2(dr)^2 \cdot d\varphi \cdot [(\tau_1/R_1) + (\tau_2/R_2)]. \quad (13)$$

Integrating with respect to φ between 0 and $\pi/2$, i.e., adding up the normal actions $d\mathbf{F}$ generated by all the elements dl around the small circumference of radius dr , we get

$$dF = 2 \cdot (dr)^2 \cdot [(\tau_1/R_1) + (\tau_2/R_2)] \cdot \int_0^{\pi/2} \frac{\pi}{2} d\varphi, \quad (14)$$

$$dF = 2 \cdot (dr)^2 \cdot [(\tau_1/R_1) + (\tau_2/R_2)] (\pi/2), \quad (15)$$

$$dF = dS \cdot [\tau_1/R_1 + \tau_2/R_2] \quad (16)$$

because $\pi \cdot (dr)^2 = dS$ and the 2's in (15) cancel out. If now the surface element dS

is transferred to the left side of the equation, we end up with

$$P = dF/dS = [\tau_1/R_1 + \tau_2/R_2], \quad (17)$$

which is nothing else than our good friend Laplace's law, now showing different tensions for each radius, as it should be. Inexplicably, even though Perucca's setting of the problem is clean and well thought, the two surface tensions along the principal meridians appear as equal, losing generality and clearly violating what experience shows in pathophysiology; remember, for example, an aortic aneurism, where the dissection takes place along the longitudinal axis because only its perpendicular direction feels the pull and the former suffers no surface effect [1], [2]. To underline the concepts herein used and discussed, we must emphasize the difference between any two pairs of perpendicular radii of a small curved surface patch—such as r_1 and r_2 in (11), and how the principal radii are defined. The maximum and minimum at a given point on a surface are called the principal curvatures, and they measure the maximum and minimum bending of a regular surface at each point. To dissipate doubts, these definitions have been given by Gray in 1997 [15] and also by E.W. Weisstein [16].

Laplace's Law Based on Hollow Cavities

Our previous notes [1], [2] dealt extensively with the mathematical derivations of the law. Some were based directly on considering hollow cavities with elastic walls that, in most cases, show a finite, measurable, and nonnegligible thickness. Therefore, the concept of wall stress was introduced, often used in cardiac mechanics. Small curved patches, as small as necessary, defined by the two principal radii were the elements that any complex three-dimensional surface was decomposed into. One of the best, most direct and rigorous derivations was that produced very recently by Federico Armesto. There is no need here to repeat any of that material. It must be remarked, however, that

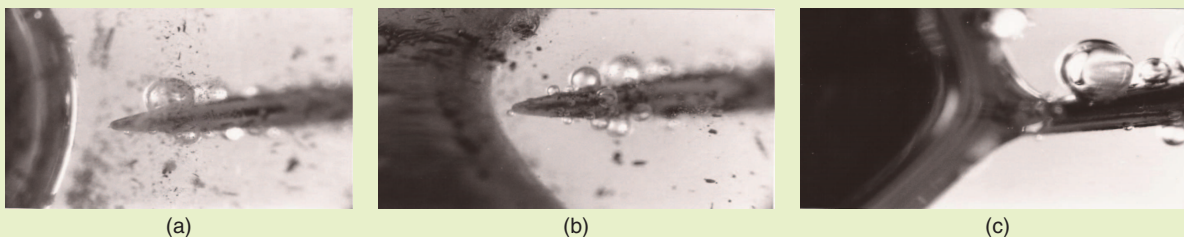


FIGURE 4 A mercury droplet immersed in a solution of dilute nitric acid and potassium dichromate. (a) A steel needle gets near the droplet surface. (b) As the needle gets closer, a local inward bending takes place. (c) When the needle touches the surface, mercury literally sticks to it.

this setting differs significantly from the capillary effect viewpoint, hence bringing up the doubt of validity of the law, even though the expression is the same.

Static and Dynamic Mercury Drops

When a drop of mercury is placed in dilute acid containing potassium dichromate and an iron wire is dipped into the liquid in close proximity to the drop, regular and rapid oscillations of the drop occur that may last for hours. At least, two related aspects can be recorded as evidences of electrochemical activity: electrical potential and impedance changes [17], [18].

When the needle is brought into contact with the droplet, oscillations stop and the impedance drops to virtually zero. The impedance increases when the droplet contracts and decreases during the expansion. Analysis of the events reveals a bistable nature that is suggestive of the electrocapillary dependence of mercury surface tension on electrode potential and polarizing current density. The needle becomes positive by approximately 0.7–0.8 V to the interior of the mercury during the second half of the expansion period, and the needle point becomes black, probably through formation of Fe_3C .

A simple explanation would suggest that the potassium dichromate decreases mercury surface tension due to repulsive forces in the double layer at the mercury–electrolyte interface. As the iron needle is advanced toward the drop, electrode current increases due to decreasing interelectrode impedance until a critical current is reached. The potassium salt then diffuses

back to the surface of the drop and increases the mercury potential resulting in a change of shape. This phenomenon exhibits transition kinetics at one interface (activation and passivation of iron), which induces a mechanical change at a proximal boundary (mercury), the events being mediated by variations in electrolyte current and electrode surface potentials. Inside the droplet, a pressure must build up following Laplace's law (Figure 4).

Discussion

The subject we are dealing with herein deserves to be discussed within the epistemological framework. Let us see why this standing finds justification. First, looking into its historical development, we found that the capillary effect was the original motivation leading to the equation and none of the authors contributing to it (Jurin, Young, Laplace, and Gauss) ever mentioned volumetric cavities under pressure. Robert Woods was the first to apply the law to hollow organs, and Karl De Snoo appears as the first to obtain an ingenious derivation followed by actual measurements in gravid uteri under dilatation, but no reference was made by the latter to the capillary action. From a physics point of view, there is no relationship whatsoever between hollow organs or balloons and capillarity; none the less, the mathematical equation is the same. Hence, is its application valid? We should say it is because the equation has been demonstrated in the two areas, starting

from the basic capillary phenomena and also from a volumetric conception (as cupolas or balloons of any shape, even including the wall thickness).

Capillaries triggered also side derivations that deserve mentioning, at least as a curiosity. Gabriel Lippmann, a physicist, showed the existence of an electric phenomenon associated with mercury when it fills capillaries. His contribution had important practical consequences in the field of cardiology, for it offered the basis for the first continuous records of cardiac

electrical activity with the development of the capillary electrometer [19]. But there was more to this application. Since the capillary meniscus is a surface tension phenomenon, mercury drops under certain conditions can show an outstanding rhythmic electric and contracting activity, where surface tension plays a decisive role [17], [18]. Figure 4 illustrates such behavior. A puzzling question deserves to be posed: Does Laplace's law hold in these drops? How could this be tested? We think it does.

After Laplace's times, and in a way to be considered as his immediate continuator in capillarity studies, Gauss in 1829 clearly stands out [2]. He manifestly recognizes Le Marquis as his antecedent in this respect and, perhaps, can even be credited with indirectly naming the law. The mathematical formulation does not appear as clear enough and is rather cryptic using a notation not current nowadays. However, it is deemed as

Potassium dichromate decreases mercury surface tension due to repulsive forces in the double layer at the mercury–electrolyte interface.

a big step in the treatment of the subject. The principle he adopted is that of virtual velocities, gradually transformed later on into the principle of the conservation of energy. Gauss pointed out the importance of the angle of contact between the two interacting surfaces; thus, he supplied the principal defect in Laplace's work. Besides, Gauss mentioned the advantages of the method of measuring the dimensions of large drops of mercury and large bubbles of air in liquids under certain conditions by Segner and Gay Lussac, afterward carried out by Quincke [2].

Conclusion

Laplace's law explains all the capillarity phenomena as it leads to the pressure within a soap bubble or how a small bubble dumps its air into a bigger one if both are interconnected, a fact well known in certain respiratory diseases, such as atelectasis [1], [2], [11]. The demonstration given by Perucca and some of the demonstrations given in [2] clearly show that, no matter what the initial setting is (either capillary effect or hollow elastic container), the law is valid and beyond any doubt. Surface tension puts into evidence forces and generates an internal pressure within well-defined boundaries. In one sentence, it was mentioned that two fully different physical phenomena (capillarity, where three phases are components, and elastic hollow bodies sustaining pressures) converge to the same mathematical equation. As a corollary, we might add that calling Laplace's law of physiology would not be appropriate but rather DeSnoo-Barrau's because the latter was directly obtained from a hollow organ (the uterus).

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