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The Wilhelmy method: a critical and practical review

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A brief history of the Wilhelmy technique for surface tension and contact angle measurements introduces the equation and the methods necessary to apply this modern and automatic procedure correctly. Many simple practices may avoid systematic errors and allow reliable results to be obtained for both quantities. The paper analyzes not only simple runs – that is, applications to standard shapes such as cylinders and parallelepipeds, rigid, non-porous samples immersed in probe liquids of low viscosity – but also non-simple runs – that is, applications to non-standard samples such as disk-shaped samples, porous and flexible samples, planar samples with different contact angles on their two opposite faces, and to the case of more viscous fluids. Many experimental details such as the size ratio of specimens to the liquid container may be extremely important; their role and the history of discussion about these topics are reviewed and discussed herein. Also, the possible determination of contact angles other than the usual advancing and receding ones is addressed.

Notation

$2p$	perimeter of the maximum cross-section of a cylindrical/discoidal sample along the immersion plane
A	cross-sectional area of the sample in a standard Wilhelmy measurement
A_{LV}	area of the liquid-vapor interface
A_{SL}	area of the solid-liquid interface
C_a	capillary number
$c = \rho g / \gamma$	squared reciprocal of capillary length
$F(h)$	total force on the sample immersed at a depth h
$F_1(h)$	force on the sample immersed at a depth h without considering the weight mg (tare)
$F_{\text{drag}}(v)$	viscous forces applied to the sample as a function of the immersion rate
g	acceleration due to gravity
H	height of the meniscus in the Washburn equation
h	depth of immersion of the sample in Wilhelmy measurement
h'	depth of immersion of the sample corrected for the ratio of cross-sectional areas of container and sample
L, s	width and thickness of a parallelepipedic sample, respectively
l	height (thickness) of a cylindrical sample
m	mass of the sample in the Wilhelmy measurement
P	wet perimeter of the sample in Wilhelmy measurement
P_1, P_2	wet lengths of the two faces of a differently sided sample
R	radius of a cylindrical sample
r	radius of the capillary in the Washburn equation
S	cross-sectional area of the container in the Wilhelmy measurement
t	time (in Washburn equation)
V	volume of the sample immersed in the test liquid

v	immersion rate (speed) of the sample in the Wilhelmy measurement
v^*	defined by Equation 7
W_M	gravitational potential energy of the meniscus
w	in the original paper by Wilhelmy, this symbol was used for the contact angle
α	inclination of the sample with respect to the vertical in the Wilhelmy measurement; note that in the paper by Wilhelmy, this symbol was used to indicate the quantity $\gamma \cos \theta$
γ	surface tension of the test liquid in Wilhelmy measurement
θ	contact angle measured by the Wilhelmy microbalance method
θ_1, θ_2	contact angles of the two faces of a differently sided sample
μ	dynamic viscosity of the test liquid
ρ	density of the test liquid

1. Introduction

The Wilhelmy technique is one of the most ancient methods used for measuring surface tension or contact angle. It was proposed in 1863 by F. L. Wilhelmy, an original physical chemist. He was born in 1812, on Christmas day, in Stargard (now Poland) and went on to study pharmacy in Berlin. After that, he returned to work with his father until, in 1843, he went to Heidelberg, where he received a doctorate in 1846, defending a thesis on ‘heat as a measure of matter cohesion’.

He remained an amateur scientist, and the majority of his achievements were obtained not at the university, where he worked as a professor only for a few years, but in his house. He was also a member of the Physics Society (Deutsche Physikalische Gesellschaft), which he founded with H. G. Magnus in Berlin.

His most well-known paper¹ was published in 1850, ‘The law by which the action of acids on cane sugar occurs’, a classic experiment on the saccharose ‘inversion’ reaction. He carried it out using a polarimeter, and in the interpretation of the results, he introduced for the first time the concept of the chemical reaction rate. Unluckily, his role was misunderstood for many years until Wilhelm Ostwald recognized the importance of his work in 1909, in his Nobel Lecture.²

In 1863 (Wilhelmy died in 1864), he published a paper founding the topic of the Wilhelmy method in wettability:³ ‘On the dependence of the capillarity constants of the alcohol on substance and shape of the wetted solid body’ (see Figure 1).

It is worthy of note that this paper is commonly cited as volume 119, but Wiley has currently modified the volume numbers of the

1863. ANNÄLEN No. 6.
DER PHYSIK UND CHEMIE.
BAND CXIX.

I. Ueber die Abhängigkeit der Capillaritäts-Constanten des Alkohols von Substanz und Gestalt des benetzten festen Körpers;
von Ludwig Wilhelmy.

(Vorgetragen in der Sitzung der physik. Gesellschaft vom 24. April 1863).

Die aus dem Nachlass von Wertheim veröffentlichte Untersuchung desselben über Capillarität¹) führte zu dem für die Theorie ungemein wichtigen Resultat (welches übrigens durch eine kurze Mittheilung²) bereits bei Lebzeiten des Verfassers bekannt geworden war), daß das Volum der an einem festen Körper capillar gehobenen Flüssigkeit nicht der Länge der Contact-Linie zwischen Flüssigkeit und fester Substanz einfach proportional, vielmehr auch von der Gestalt der letzteren, durch welche die Krümmung jener Linie bedingt wird, abhängig sey. —

Wertheim hatte die, pro Längen-Einheit der Contact-Linie gehobene Flüssigkeits-Menge überdies abhängig gefunden von der Oberflächen-Beschaffenheit der Wand, nämlich von dem Grade ihrer Politur, dagegen konnte er einen Einfluß der Substanz der Wand für die Fälle, auf welche sich seine Untersuchung erstreckte (Platin, Kupfer, Messing und Glas), nicht wahrnehmen.

Die Art und Weise, wie Wertheim die Verschiedenheit der pro Längen-Einheit gehobenen Flüssigkeits-Volume

1) *Annales de Ch. et Phys.* T. 63, p. 129.

2) *Comptes rend.* T. 44, p. 1022.

Poggendorff's Annal. Bd. CXIX.

journal, as indicated in the paper.³ Other minor differences in volume number may be found in literature for this same paper,⁴ while the initial page number 177 is correctly reported.

Wilhelmy introduced the use of the plate method in evaluating the ‘capillary constant’, which is not the same quantity that is meant today by this word. The quantity denoted with α in his paper corresponds to what is now indicated as $\gamma \cos \theta$ and, thus, for a perfectly wetting liquid, to the surface tension of the liquid. In his paper, the contact angle, denoted with the symbol w , is not considered as a quantity to be determined, simply because he used plates made of clean glass or metal whose contact angle is supposed to be zero.

For many years, this method has been applied for this aim and/or for monitoring the surface tension variation in the trough used for monolayer film operations. Noticeably, a similar method was proposed and used by Agnes Pockels,^{5–8} one of the most famous scientists working in the field of film liquid monolayers, and was then rediscovered by Langmuir.⁹ Pockels did not cite the Wilhelmy paper, but she understood German and through her brother Fritz was able to know the German-written scientific literature. Pockels was born in Venice, what is today Italy. But at that time, the town belonged to the Austro-Hungarian Empire, which her father served as an army officer. ‘In a rectangular tray filled to the brim with water, she used a simple balance to determine the force required to detach a small wooden disk from the surface of the water, a value that Ludwig Wilhelmy had shown was in direct proportion to the surface tension’ (Chemistry World, 2017).¹⁰

It is worthy of note that in the common presentation of the topic, the role of Agnes Pockels is not clearly established, since she was not only an amateur scientist like Wilhelmy, but also a woman, performing experiments in her kitchen. Pockels used a rigid (wooden) disk or a ring wire cleaned on a flame; the usage of a ring wire is in fact the introduction of the method later proposed by Harkins and du Noüy.

The Wilhelmy method for surface tension evaluation remained one of the most important techniques, and it was only in 1919 that a new technique entered surface laboratories. In fact, the first du Noüy ring method (consisting of the immersion of a perfectly cleaned metal wire and the following determination of force at rupture) was proposed only in 1919,^{11,12} but it had the defect of requiring the surface break to analyze the liquid properties. (It is worthy of note that in the last paper,¹² du Noüy criticizes the results obtained by Harkins.¹³ In a note, Harkins indicates that the results were obtained using a drop weight method starting from 1912, but that those results needed the long development of a correction procedure and were published only in 1917.) In contrast, it was possible to apply the Wilhelmy method to not only check the surface tension variation, the differential behavior of a surface monolayer with respect to a reference surface, but also investigate a single surface without any surface break, at least after 1925.¹⁴ Moreover, the du Noüy technique used a torsion wire balance with some modification to manage the verticality of the ring. The 1925 paper by Frumkin¹⁴ describes a

Figure 1. No certain portrait or photograph of Wilhelmy is present in the literature or on the Internet, so the authors decided to substitute it with this copy of the first page of his paper³ on the subject. Reproduced with kind permission of Wiley

relative method that applies the Wilhelmy equation to a system in which only the starting condition is evaluated in an absolute way (breaking the interface) and the subsequent process is followed without any further breaking. This idea was then followed by others, such as Dervichian¹⁵ and Harkins and Henderson.¹⁶

In 1934, F. E. Bartell and G. B. Hatch¹⁷ used the immersion of a galena sample to evaluate the contact angle, but by estimating the shape of the newly formed meniscus and not the produced force, so that their work cannot be regarded as an application of Wilhelmy's original idea; this was not tensiometry, but goniometry, even if performed in a different context.

However, the second most important application of the Wilhelmy method – that is, contact angle determination – was proposed and practically used only after many years, in 1947, by Collins¹⁸ to determine the perimeter of a fiber and its contact angle. It is worthy of note that in the paper by Collins,¹⁸ there is already a suggestion of the idea of adding a weight to the sample in order to improve the experimental results, a trick that the authors have independently rediscovered and applied and which is discussed in the following sections. Collins¹⁸ defended his proposal with a discussion at the end of his paper with Cassie. He wrote

Exploratory experiments have been carried out which suggest that by measuring the surface tension thrust or pull on a fibre immersed in a liquid it may be possible to estimate fibre perimeter, increase of perimeter with swelling, or the contact angle of a liquid against a fibre. (Collins, 1947: p. T77)

An improved method very similar to the modern one, based on linear force extrapolation, was proposed by Guastalla in 1948 (together with his wife)¹⁹ and later better developed in 1956.²⁰ Guastalla used a torsion balance instead of a common microbalance, but the final result was the same. Moreover, it is worthy of note that in the historic first plot of force against immersion, the inclination of the force is positive, not negative, because the torsion balance evaluates the force directed upward and the immersed body was a waxed hydrophobic surface (see Figure 2).

When using this approach, the interface breaking is not the core of the measurement as it was in the methods applied originally; nor is it a relative measurement as in Frumkin's equipment. For the very first time, with Collins¹⁸ and Guastalla,^{19,20} the Wilhelmy non-breaking approach for surface tension and contact angle measurement was presented in detail in the scientific literature.

As with the paper by Collins,¹⁸ Guastalla's work²⁰ was published in a specialist journal. The later paper by Ihrig and Lai²¹ published in the *Journal of Chemical Education*, a journal dedicated to the didactics of chemistry, may mark the definite acceptance of the modern Wilhelmy method for contact angle determination. However, it may be noted that in the book by Bikerman,²² published in 1958, the Wilhelmy method for contact angle is not considered at all, although Bikerman, then at the Massachusetts Institute of Technology, should

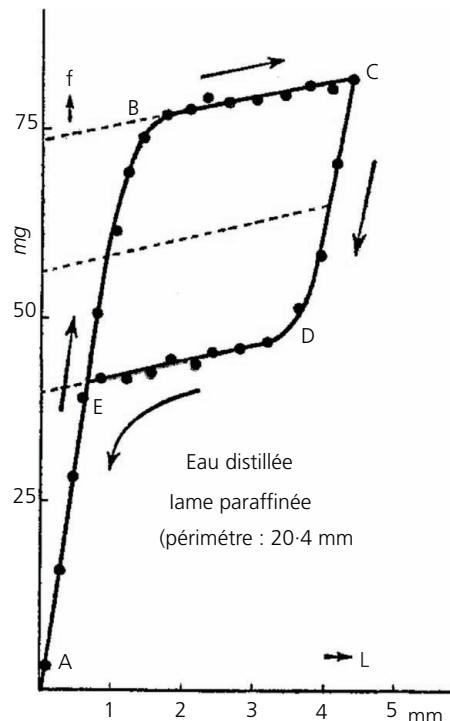


Figure 2. The force-against-immersion plot obtained by Guastalla and Guastalla¹⁹ in 1948. Reproduced with kind permission of Académie des Sciences, Institut de France

certainly be regarded as an outsider, a very original researcher. Undoubtedly, the introduction of the Wilhelmy technique in handbooks and university textbooks was certainly slower. Nowadays, however, 40 years later, in a modern classic handbook such as that by Lyklema,²³ the method is fully acknowledged (in section 1.8a, p. 139), for both interfacial tension and contact angle and for breaking and non-breaking implementations.

The modern form of the experimental device was developed only after 1963 when the modern electronic microbalance was patented and mass-produced by Lee Cahn,²⁴ who founded Cahn Instrument at Palo Alto, California.

A very important theoretical contribution to the analysis of the Wilhelmy experiment was also given by Jordan and Lane²⁵ in 1964. They explained the reason why there was no significant problem in the simple traditional equation used for the calculation of the surface tension and that it was substantially unnecessary to know or calculate the exact shape of the meniscus, at least on a symmetrical object. A complete analysis may be also found in the monumental book by the Russian researcher A. I. Rusanov and by Prokhorov.²⁶ This book is also one of the few cases in which the differences among the breaking/non-breaking methods of using the Wilhelmy idea are clearly exposed.

Thus, the method worked out by Wilhelmy himself and the method described here are essentially different and they should not be mixed with

each other. In the same time in literature it is the second method that the name of Wilhelmy is often related with. This is not correct, but with regard to the fact that nowadays the first method is rarely used in serious investigations, while the method described in this Section, on the contrary, is a very wide-spread one, we decided, without being afraid of confusion, to keep for the latter the name of ‘Wilhelmy plate method’ which became traditional. (Rusanov and Prokhorov, 1996: p. 180)

It should be noted that the importance of the problem of the exact shape of the meniscus in the case of a parallelepipedic sample, solved in fact by Jordan and Lane,²⁵ depended on the role of the breaking method. Rusanov and Prokhorov²⁶ attribute the merit of the answer to this question to Orr *et al.*,²⁷ in 1973, but the authors believe that Jordan and Lane²⁵ had already published the actual solution in 1964.

Another scientist who gave a very important experimental contribution to this topic was certainly J. D. Andrade,²⁸ with his study on polymer surface dynamics in the 1980s.

Many other aspects and contributions will be acknowledged in the next sections of this paper.

2. The Wilhelmy experiment: some very general conditions

A dedicated microbalance or a balance for density measurement (thus with a hook support below the standard plate) may be used; the liquid container should be moved vertically up and down by a very low-vibration motor at a controlled speed.

The speed of the liquid should be inversely correlated to its viscosity.

An axisymmetric or plane-symmetric sample should be used so that the horizontal forces are always balanced and the net final force is only vertical. This condition can be satisfied using cylindrical or parallelepipedic samples; other symmetric shapes will be considered in the following sections.

If the sample is significantly hydrophobic,²⁹ lyophobic or hydrophobic, it should also be sufficiently rigid to avoid bending. The combination of low density, low thickness or low rigidity may make it impossible to perform the experiment. Such a remark holds true also for experiments on single fibers.

In this case, however, the simple trick proposed by Collins¹⁸ may be sometimes applied, consisting of the addition of a (chemically inert) weight to the lowest portion of the sample; this topic will be discussed in the following sections.

As a rule, the sample should have a distance from the borders of the container larger than 5 mm, to prevent the formation of a capillary bridge which may significantly affect the force balance.

The container should also have a very large diameter with respect to the immersion section of the sample, to avoid significant variation in the liquid level during immersion. It is worth noting that due to

the finite size of the container, the liquid level variation cannot be prevented completely, but it can be reduced to a few microns. Alternatively, such variation should be modeled and the collected data adjusted accordingly, a topic partly covered by Lyklema.²³

A similar consideration holds for the meniscus itself, with the only difference that while for the liquid reference level the variation is always positive, in the case of the meniscus, it may be positive or negative; it may sum up or compensate for the immersion mechanism. A preliminary evaluation of these quantities should be done for all runs.

In case of a significant variation in the reference liquid height, the material of the container should be perfectly wettable (very clean glass) to avoid the effect of advancing/receding meniscus on the container border. The advancing/receding of the border meniscus may change its volume and consequently the liquid level. But if the container is perfectly wettable with respect to the used liquid, its contact angle, and thus its meniscus volume, will not change during the experiment. In other words, the hysteresis of the material of the container should be zero, and a zero contact angle is a good practical alternative. In practice, an opportunely sized glass beaker preventively treated in a radio-frequency plasma chamber may realize this condition for most of the common liquids.

3. The standard equation

If the conditions considered in the previous section are fully satisfied, the experiment will be considered ‘simple’, and a very straightforward equation may be used to analyze the data (see Figure 3)

$$1. \quad F(h) = mg + P\gamma \cos \theta - \rho g V$$

where $F(h)$ is the total force measured on the sample immersed at depth h , m is the sample mass, P is its perimeter, V denotes the volume of sample immersed in the liquid of density ρ and surface tension γ , θ is the contact angle at the ternary interface of the

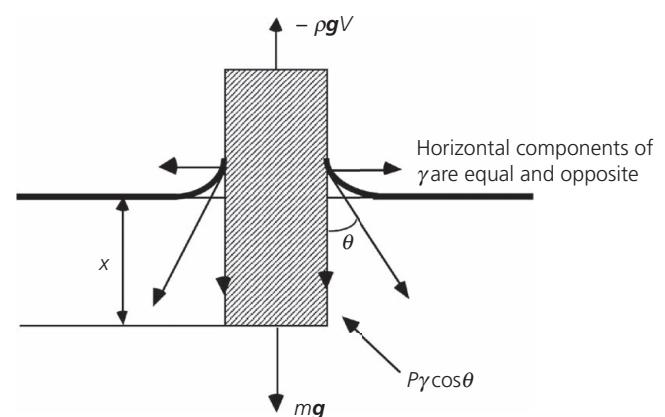


Figure 3. A simple schematic diagram illustrating the balance of forces acting on the solid sample in a typical Wilhelmy experiment

considered system (test liquid, film or plate sample and air) and g stands for the local acceleration due to gravity. Since mg is a constant, it can be set that $F(h) - mg = F_1(h)$. Extrapolating the equation to the condition of zero depth of immersion (ZDOI), $h = 0$, the following is obtained

2. $F_1(0) = P\gamma \cos \theta$

where the constant weight mg is now included in the left-hand term $F_1(0)$. From this relationship, P , γ or $\cos \theta$ can be calculated when the other two parameters are independently known.

In the specific case of the surface tension, the best results are obtained when both advancing and receding portions overlap, due to the fact that advancing and receding angles are zero. However, it is possible to conceive that only the receding angle is zero.

In the case where the perimeter is being searched for, it is worthy of note that the number of points is very high and so the standard deviation is low, but no information is present on the effective shape of the cross-section (square, rectangle, circle or more complex shapes); this may be an important limitation. Note that this task was Collins²⁰ original aim in his 1947 paper.

This calculation may be carried out by using the advancing and receding zones of the run (see Figure 4) and choosing an appropriate portion of the collected data.

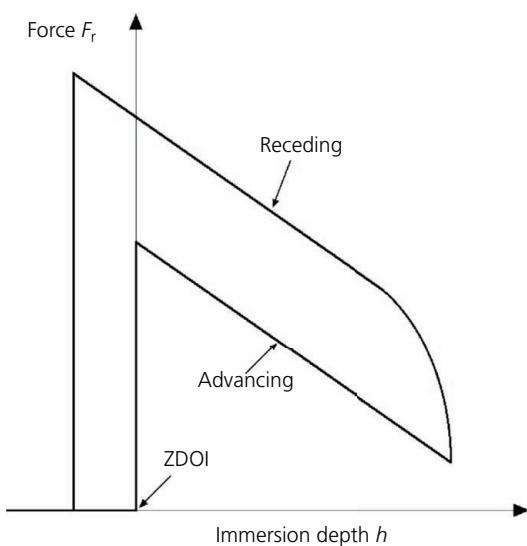


Figure 4. The ideal appearance of a typical run in the Wilhelmy experiment. ZDOI denotes the zero depth of immersion, the height at which the sample touches the liquid surface for the first time, at the beginning of the advancing stage of the measurement. According to the usual convention, F_r is the force measured by the microbalance on the sample, directed downward and without considering the weight of the sample itself. The figure is from Della Volpe and Siboni³¹ (© European Physical Society). Reproduced by permission of IOP Publishing. All rights reserved

In recent literature, some analysis is available about the error related to the measurement of the contact angle,³⁰ which is found to be higher for very low and very high values, but no simple indication is given concerning practical methods for checking the quality of each run.

What is the appropriate zone of advancing and receding useful for the calculation of the contact angle? Is there any method to check this choice in an absolute way?

The condition is simply that the advancing and receding zone must have an inclination related to the immersing section of the sample, expressed by the obvious formula $-\rho g A$, where A denotes the immersion section (for instance, Ls , where L is the width and s is the thickness of the parallelepipedic sample, or the cross-sectional area of the cylinder) and ρ is the liquid density. Since in a simple run the section is a constant and may be promptly calculated from the lateral size of the sample, one may easily check if such a condition is satisfied.

For instance, if a cylindrical or parallelepipedic sample is not perfectly vertical, then its immersion cross-sectional area will be higher and consequently so will be the inclination of the advancing or receding (or both) zone. This may also help to check if the sizes of the sample are actually constant (irregular sample shape).

In short, a good run will show the slope of the advancing and receding portions of the plot, which is constant in the mean and equal for both stages of the measurement: the two lines must be parallel, a very simple trick which may also work as an internal quality check of the run. Eventually, a predefined maximum percent error may be set as an acceptable value, depending on the incertitude in the determination of the sample sizes.

Noticeably, although the preceding check is very simple to perform, it is not included in the common commercial software, to which, however, it may be easily uploaded; the authors of this paper have used it for many years with appropriate, self-developed software.

4. Important conditions for designing and performing a simple run

4.1 The sample and container size

In the case when the sample is too big with respect to the container size, the liquid level will significantly change during the experiment. This remark is not so frequently made in literature;^{23,26,27} however, the possible variation in the liquid level can be easily estimated in the following way to establish in advance a practical limit and eventually correct the recorded data.

Using a container and sample with cross-sectional areas of S and A , respectively, if the sample is immersed to a length h , then a volume of liquid equal to Ah is moved above the old reference

level with a final height variation of $Ah/(S - A)$; the new immersion will thus be $h' = h + Ah/(S - A) = h[1 + A/(S - A)]$.

To remain in the boundary of a simple run, the height level variation should be always lower than a couple of recording steps. A recording step is the immersion interval between two weight recordings during the run; generally, this parameter is decided before the run by imposing a certain immersion rate. A typical microbalance is able to record one datum per second, so the uncertainty will be on the order of ± 1 step.

For a rectangular section sample of 1 mm by 1 cm immersed by 2 cm at a rate of 20 $\mu\text{m}/\text{s}$, the container would have to have a minimum surface area of 100 cm^2 . A similar calculation can be made for the length of the meniscus; using centimeter–gram–second units, $P\gamma/\rho g \text{ cm}^3$ is a rough evaluation for the order of magnitude of the meniscus volume. Considering the previous example and a zero contact angle, the first effect corresponds to 0.2 cm^3 and the second one to 0.16 cm^3 .

It is worthy of note that in the original paper by Wilhelmy,³ this problem is addressed, but given the method details, it is taken into account by a simple correction constant in the original equation, k^3 , because the immersion length was constant during the experiment.

4.2 The liquid viscosity and the immersion rate

To solve the problems posed by the possible variations in the liquid level, one could think to increase the immersion rate v . Unfortunately, for this parameter, an upper bound exists related to the acceptable shape of the meniscus. The literature^{32,33} estimates that to maintain a meniscus shape reasonably close to the static condition, and thus to obtain data comparable with the usual drop measurements not significantly affected by the viscous forces, the capillary number ($C_a = v\mu/\gamma$, μ being the dynamic viscosity of the test liquid) should be as low as possible. A practical choice of 10^{-4} – 10^{-5} is good, because it gives a shape to the meniscus which is fully comparable with the static one. In water-like liquids, this corresponds to an upper bound on the immersion rate of about 100 $\mu\text{m}/\text{s}$.

4.3 The temperature control and the liquid evaporation

Another practical problem which may be encountered during Wilhelmy runs is temperature control. The duration of the experiment and the surface area of the liquid are both larger than in those other methods, and this makes it more difficult to control the temperature parameters. To prevent evaporation, which may contribute to the variation in the reference level of the liquid, one should completely close the experiment chamber, which is practically impossible, or flow through the chamber the vapor of the used liquid, a procedure that may also contribute to condensation ‘within’ the microbalance. The latter may be avoided by dual-vapor-flow control, clean and dry air in the microbalance and liquid-vapor-saturated atmosphere in the

measurement chamber. This kind of control was available in some Cahn microbalance models, but it is more difficult to implement and more expensive. Continuous control of the temperature in the liquid and check of the liquid level at the end of the experiment may provide a cheaper alternative.

4.4 The sample inclination

The sample inclination is one of the most common sources of error. As discussed in the previous section, the cross-sectional area estimate obtained by the slope of the force-against-immersion graph allows determining if the sample has a significant inclination, but one would also like to assess to what extent such an inclination actually affects the final contact angle estimate. In the usual case of a thin parallelepipedic sample, this goal can be easily achieved by considering that if the sample is not perfectly vertical, the surface tension forces on the two opposite faces have different vertical components. Denoting with L the width of the sample and neglecting its thickness, the total vertical surface tension force is not simply $2L \cos \theta$, but can be better approximated as $L \cos(\theta + \alpha) + L \cos(\theta - \alpha)$ for small values of the sample inclination angle α relative to the vertical direction.

This sum is reduced by means of the prosthaphaeresis formulas of trigonometry to the simpler relationship $2L \cos \theta \cos \alpha$.

Using this formula, one may immediately arrive at three conclusions: (a) the effect of the inclination is always that of measuring an angle closer to 90° (i.e. with a lower value of the cosine), thus lower than the true contact angle θ if this is higher than 90° and higher if it is lower than 90°; (b) this difference, being proportional to $\cos \alpha$, may be acceptable only if α is lower than 10–15°, corresponding to a 5% difference; and (c) the importance of this error may be stronger when the angle θ is very high or very low.

5. A more complete equation

The Wilhelmy technique has many advantages in comparison with the other methods for wettability measurements: it is fully automatic, thus having a lower role of the experimenter, and it has a precise definition of the kinetic stages of advancing and receding (rate and time, absorption). There are also, however, some limitations: the sample must be homogeneous and have a symmetric shape, and the volume of the liquid is higher. But it is possible to address some of the limitations of the method, and this is the topic of the following sections.

5.1 Higher dipping speeds

The simpler modification of the original Wilhelmy approach is related to the presence of a drag, a viscous resistance due to the immersion or emersion rate of the sample in the used liquid. Literature analysis³³ introduces a simple modification as a further term on the right-hand side of Equation 1 depending on the rate of sample immersion, something like $+F_{\text{drag}}(v)$, where v denotes the immersion rate. Such a force contribution is always opposite to the direction of the movement: it is negative during the

insertion and positive during the withdrawal. As a consequence, the shape of the plot of Figure 4 is modified as in Figure 5; the advancing and receding portions are no longer parallel, but they diverge as shown in the figures of Morra *et al.*³³ The effect of this change on the obtained contact angle is not easy to determine, but is always present.

5.2 Flexible and lyophobic samples

A common case is the analysis of polymeric films. These materials show generally low density, often lower than that of water. Moreover, they are soft and flexible and their wettability is low. At the very least, their advancing angle may be higher than 90°. The combination of these properties makes it possible that during the advancing stage, the film cannot penetrate the liquid surface and floats on the liquid.

A very simple way to solve this problem is to use a metal clip of a planar shape and made of a pure metal – for example, gold. In this way, it is possible to know in advance the density and, thus, from the weight, the volume of the clip.

The clip may be fastened on the end of the film, so that it will immerse during the first steps of the run. The final effect on the force plot will be to increase the buoyancy effect of an amount that one can calculate from the volume of the clip and from the density of the liquid. In this way, the film will penetrate the liquid and the run will be performed correctly; all the checks previously listed may be carried out and the problem is solved.

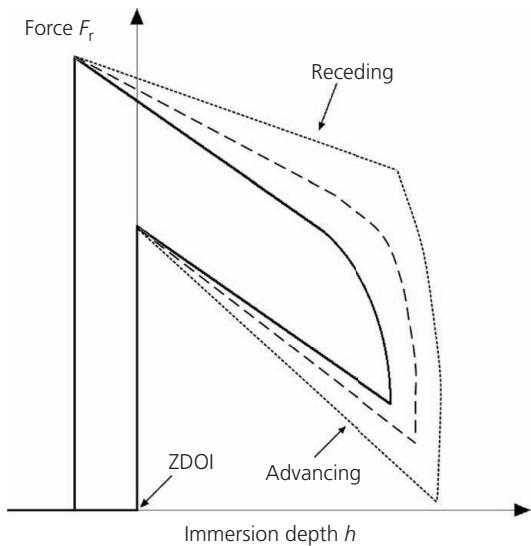


Figure 5. Schematic diagram illustrating the effect of viscous forces on the Wilhelmy plot. At low immersion rate, viscous forces are negligible and advancing and receding portions of the graph turn out to be parallel (solid line). When the immersion rate is significantly large, viscous forces become important and the advancing and receding portions tend to diverge (dashed line). The larger the immersion rate, the stronger the viscous forces and the greater the divergence (dotted line)

5.3 Differently sided samples

In the current literature, the common opinion is that ‘if to the front and back faces of a sample have been given different treatments, then the average value may have little significance’ (Good, 1992: p. 1277).³⁴ This is quite obvious, but there are some alternative strategies to follow to obtain single face wettability. In fact, if a sample has two unlike faces, there are, at least, two possibilities

- (a) the sample has intrinsically two different faces
- (b) the different faces are the by-product of some process applied on an originally uniform sample.

A flat and rigid sample may be often cut obtaining two identical samples whose corresponding parts may be faced to yield a single sample, thus exposing alike portions to the liquid. For samples which are also lyophobic, this strategy allows a very good run, because the capillarity effect of the liquid is not able to penetrate the eventual thin empty space between the two faces. A difficulty occurs when the non-exposed face is lyophilic, because the liquid may penetrate and change the tare weight.

In this case, an adhesive tape may be used to mask one of the faces or both if the liquid is not able to interact with the adhesive; in this way, one may obtain the adhesive tape wettability, and introducing its value in the following equation, the contact angle of the residual face may be found

$$3. \quad F(h) = mg + P_1 \gamma \cos \theta_1 + P_2 \gamma \cos \theta_2 - \rho g V$$

where the subscripts 1 and 2 refer to the dissimilar faces of the sample. This equation is formally analogous to the well-known Cassie–Baxter equation (CBE),³⁵ which describes how the overall contact angle depends on a non-homogeneous surface composition. However, the CBE was developed to analyze surfaces in which inhomogeneities are distributed along the sample perimeter in randomly arranged microscopic domains, so that no net horizontal component of surface tension results. In the case that is being analyzed, on the contrary, there is a macroscopic separation of different surface contributions on two dissimilar faces, and a net horizontal component of surface tension is present.

The only basic requirement to apply this strategy is that the horizontal component of surface tension, which holds zero for symmetric samples, is not able to incline or rotate the sample; such an occurrence should be checked experimentally through the methods described in the previous sections (parallel inclination of advancing and receding zones).

An example of practical application was shown by Della Volpe.³⁶

5.4 Non-standard shapes

The sample shapes most commonly used are parallelepipeds or cylinders, but such shapes are not always those of the objects to test nor can these shapes be easily obtained from them. For this

reason, some (few) papers are devoted to different geometric shapes and to the appropriate methods to apply.

Dryden *et al.*³⁷ were the only ones who dedicated a paper to shapes such as cones. Being a chapter of a book, it is likely that it was less popularized. The paper was aimed to verify that experimental wetting curves match calculated data when all parameters are known. The inverse problem, that of determining contact angle from experimental data, was not investigated in that study.

Della Volpe and Siboni³⁸ dedicated a comment to the case of discoidal shapes for which the Andrade treatment was limited, showing also how to calculate the contact angle. Nevertheless, it is relatively common to find commercial programs developed for this aim, but no check of such numerical tools has been done (in the authors' knowledge) in the scientific literature. The sample is modeled as a right circular cylinder of small height l compared to its radius R , which is immersed in the liquid with its circular ends (faces) placed vertically.

The direct estimate of the vertical force acting on the sample as a function of the contact angle, the liquid surface tension and the immersion depth is a very difficult task, due to the non-trivial shape of the sample that implies (*a*) changing length and shape of the three-phase line and (*b*) changing inclination of the sample surface at the three-phase line relative to the vertical (see Section 4.4), at the different stages of immersion.

That is why the general method used for this kind of analysis is based on the estimate of the potential energy of the system. It is the sum of various contributions: the gravitational potential energy of the sample, the gravitational potential energy of the liquid displaced by the sample, the gravitational potential energy W_M of the meniscus and the interfacial energy referred to as the liquid–vapor, solid–liquid and solid–vapor interfaces. This ‘energetic’ point of view is well documented in the literature.^{39,40} After some simplifications, one finds that at a given immersion depth h , the equilibrium condition is satisfied when the force of the balance (positive if downward) is³⁸

$$4. \quad F_1(h) = -\gamma \frac{dA_{LV}}{dh} - \frac{dW_M}{dh} + \gamma \cos \theta \frac{dA_{SL}}{dh} - \rho g V(h)$$

where A denotes the interfacial area of the phases indicated in the subscripts, h is the immersion, $V(h)$ is the immersed volume of the sample and the other terms have the meanings already described in the text.

A microscopic and detailed calculation of each derivative allows estimating the explicit equation for the force for each shape with a very good agreement between the theory and the experiment.

However, the agreement may be optimized by introducing a correction due to the thickness of the sample (see Figure 6); this

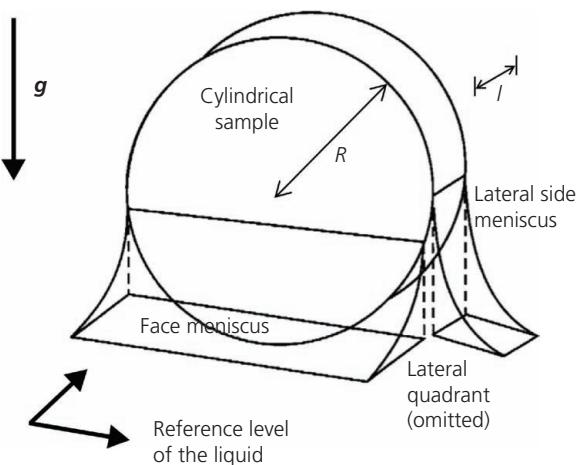


Figure 6. Face and lateral side menisci for a cylindrical or discoidal sample. This figure shows schematically the model on which the correction to the Dryden–Andrade model is based for thick disks, according to Della Volpe and Siboni.³⁸ The vertical dimensions of the menisci are exaggerated for clarity.

was done by Della Volpe and Siboni³⁸ by considering the shape of the lateral menisci but neglecting the four lateral quadrant menisci whose limited importance has also been proven for the standard parallelepiped samples (less than 1% of the final menisci volume).

Moreover, differently from the conclusions of Dryden *et al.*³⁷ the equation may be solved in terms of θ , and the contact angle obtained is in good agreement with the value for standard samples of analogous composition.

The solution of the equation, due to the presence of complex trigonometric terms, cannot be expressed analytically and must be obtained by numerical methods.

Using a Monte Carlo approach, it is also possible to estimate the error for the contact angle; since the confidence intervals of the model parameters (e.g. sample thickness and radius, liquid density and surface tension) are known, one may generate random values of such parameters within their confidence intervals and compute the corresponding contact angle estimate. By repeating this procedure a suitable number of times, a distribution of contact angle estimates is obtained, from which the error in the contact angle can be deduced.

In the case of cylindrical and discoidal samples, two other methods also turn out to be useful. One is an iterative procedure based only on the force values pertaining to the central zone of the sample. Such an approach is valid not only for disks but also for planar-convex, biconvex or concave-convex samples with a small curvature. In particular, this includes intraocular and contact lenses, besides real disks.

A similar technique was illustrated by Smith *et al.*⁴¹ but in that case, the meniscus height was not considered and the authors described the

wetting of the disk diameter at an immersion depth equal to the disk radius; such an assumption is generally incorrect, since it is verified only for $\theta = 90^\circ$, when the meniscus height vanishes.

The basic idea is to focus attention only on the central portion of the experimental curve, which corresponds to the immersion of the diameter zone (or even only the diametrical point). The authors postulate that when the meniscus wets the diameter of a disk or thin lens, it is substantially equivalent to the meniscus wetting a plane wall with a length equal to the sample perimeter. Obviously, this is an approximation, but it works sufficiently well. The method assumes that the contact angle θ is the solution of the equations

$$5a. \quad F_1(h) = 2p\gamma \cos \theta - \rho g V(h)$$

$$5b. \quad h = R - \frac{2}{c^{1/2}} \sin\left(\frac{\pi}{4} - \frac{\theta}{2}\right)$$

where $c = \rho g / \gamma$, $F_1(h)$ denotes the force acting on the sample as a function of the immersion depth h , $V(h)$ stands for the immersed volume as a function of h and $2p$ is the perimeter of the maximum cross-section of the sample along the immersion plane (i.e. the cross-section with the largest perimeter, thickness l included; for a disk this maximum is $2p = 2l + 4R$, reached at the diameter). $F_1(h)$ is obtained from the experimental data or, if necessary, from their linear interpolation. The value of the immersion depth h at which the meniscus exactly covers the diameter of the sample is given by Equation 5b. The set of Equations 5a and 5b can be solved by an iterative procedure, which is proved to converge; see the paper of Della Volpe and Siboni³⁸ for the mathematical details.

It is noteworthy that another method for the wettability of the side portion of the disk (which should be equal to the main face one) may be applied particularly for thick disks – that is, cylindrical samples of appreciable height; in this case, the method is based on the observation that laterally the curvature of the meniscus disappears for a certain specific height depending on the contact angle. Therefore, by measuring the height of occurrence of a plane meniscus on the lateral side, a rough but fast estimate of the contact angle may be obtained directly, without any microbalance, but using a ruler and visual inspection to determine the angle between the meniscus and the tangent of the sample surface.³⁸

5.5 Wicking samples

Wicking phenomena are generally regarded as a handicap for the use of the Wilhelmy method; a porous material or a powder cannot be analyzed, at least with the standard procedure. This depends on the fact that liquid absorption changes the weight (and reasonably also the properties) of the original sample.

There are, however, some alternatives.

The common strategy is the use of the Washburn equation to recalculate the contact angle. This strategy is strongly doubtful.

This equation provides a kinetic model for the rise of a liquid in a cylindrical capillary and is written in the form

$$6. \quad H^2 = \frac{1}{2} r v^* t$$

with r as the radius of the capillary and H as the height of the meniscus at time t . The coefficient

$$7. \quad v^* = \frac{\gamma}{\mu} \cos \theta$$

expresses the ability of the liquid to penetrate into the porous solid in terms of the liquid variables: the surface tension γ , the dynamic viscosity μ and the contact angle θ of the liquid on the solid. In the original paper by Washburn,⁴² an equation for a system of porous capillaries was obtained, simply considering the case in which the porous body ‘may be taken as equivalent to the penetration of n cylindrical capillary tubes of radii r_1, \dots, r_n ’ (Washburn, 1921: pp. 280–281).⁴² However, it was clearly stated that such an approach was valid unless one of the following cases occurred: (a) the pores of the body could not be taken as equivalent to a cylinder; (b) the cross-section of the pore changed with its length; (c) the pores contained an enlargement or were blind; or (d) the pores were of molecular size. It is apparent from this list that the conditions for the applicability of the Washburn equation are seldom satisfied, particularly due to the requirement of constant cross-section of the pores along their length.

In 1955, Studebaker and Snow⁴³ proposed a procedure based on the assumption that by using a perfectly wetting or a non-perfectly wetting liquid, the ‘mean’ pore radius of the porous material did not change. As a consequence, one should be able to evaluate the contact angle of non-perfectly wetting liquids in a porous material from absorption measurements. This approach was developed in a more complete form in other papers.^{44–47}

The basic idea is to consider that a mean value of the pore radius may be used and evaluated by means of a perfectly wetting liquid. After that, any other measurement may be carried out using the same mean quantity and introducing the new liquid parameters to determine the corresponding contact angle value.

This strategy is widely used in literature, but there are many cases where the value obtained by this measurement will deviate significantly from the true pore radius.

There are many reasons for the possible disagreement between the true pore radius and the mean value obtained in this way.

In actuality, the motion in a porous medium is not completely stationary, since the invading liquid always comes in contact with a new surface of the solid matrix; this is in contrast with the common approach of the Navier–Stokes equations for fluid movement. The effects of viscosity and compressibility of the removed fluid (typically, air) during imbibition are ignored.

Moreover, at a given pressure, the invading liquid that accumulates on the walls of the pore may become unstable and fill the pore. This mechanism, known as pinch-off,⁴⁸ depends on the contact angle, and it may lead to non-wetting liquid entrapment in adjacent pores. Chains of trapped drops of the wetting liquid, separated by bubbles of the removed fluid in the same capillary, may support large pressure differences due to hysteresis of the contact angle (the Jamin effect⁴⁹).

Dullien *et al.*⁵⁰ and Dullien⁵¹ concluded that the frequent disagreement between the mean radius of pores obtained by applying the Washburn equation and by mercury porosimetry was caused by a fundamental limitation in the Washburn model. Generally, the value of pore radius is one to two orders of magnitude lower than that obtained from mercury porosimetry. Dullien proposed a new model by studying the liquid flow through capillaries with an alternating value of radius. The Dullien model provides an estimate to the effective pore radius appearing in the Washburn equation in terms of a minimum and a maximum pore size that can be measured experimentally from pore structure data. Two experimental pore size distributions are used: that obtained by mercury porosimetry, for the minimum pore size, and the quantitative photomicrographic pore size distribution, for the maximum one.⁵⁰ The equivalent radius reckoned by his model is, at least qualitatively, in agreement with the radius values obtained by applying the Washburn equation. Finally, from an experimental point of view, it is clear that the exact size of the sample may significantly affect the result.⁵²

For all these reasons, the common method for estimating the contact angle from wicking measurement is strongly doubtful or even flawed.

On the other hand, it is possible to correct a Wilhelmy run in an absorbing sample without hypothesizing any previous contact angle or mean radius, simply supposing that the absorption, in a sample where the liquid cannot attain the top of the sample during the experiment, depends on the square root of the time. This simple correction may ‘normalize’ the behavior of the advancing and receding Wilhelmy run, producing a result in which both are parallel and their common inclination (that usually varies its size by the absorption, as it is in the case of wood or non-woven fabrics) turns out to be in agreement with the known cross-sectional area of the sample. To do this, some preliminary Wilhelmy runs are carried out on the sample in a perfectly wetting liquid, simply to extract the effective maximum wetting perimeter. This datum is then used along with the subtraction of the absorbed liquid weight, estimated as proportional to the square root of time. The combination of these two corrections allows one to obtain a typical shape run. The

results obtained may be considered as having at least a ‘comparative’ role – that is, they may be used to compare samples of the same size and porosity but different composition and wettability. Some results obtained in this way on many different materials have been published, and the details of the results help to compare the used stones, wood or non-woven fabrics samples⁵³ (see Figures 7(a) and 7(b)). To obtain better results, the length of the sample should be large enough to avoid the liquid reaching the top of the sample during the run.

6. Equilibrium or ‘most stable’ contact angle

The theory of contact angles has been developed using the concept of the Young contact angle, an equilibrium quantity related to perfectly smooth and homogeneous surfaces. On real surfaces, it is commonly accepted that one can obtain ‘metastable’ equilibrium states, in which the shape of the meniscus along the triple line is not fully equivalent to the ‘equilibrium’ meniscus (see Figure 8).

For its similarity to the contact angle situation, it is useful to remember the water undercooling. Having an extremely pure sample of filtered and degassed Milli-Q water in an opportune vessel, with extremely clean and flat walls under nitrogen, one can reduce its temperature very slowly, accurately avoiding any shock and vibration. It is possible to attain a temperature as low as -40°C , without the solidification of liquid water occurring. If during the cooling under 0°C even a single shock is given to the container, all the water freezes instantaneously.

Note that if using great experimental care, the reproducibility of the water undercooling is exceptional, but no researcher would conclude from these facts that water freezes or melts at -40°C , an extreme and metastable state, which cannot be confused with ‘true’ equilibrium.

Nevertheless, in a certain sense, this is exactly what happens in the case of the contact angle.

Great experimental care has been used to reproduce metastable states of the meniscus which are commonly used as the advancing contact angle or, in other rarer cases, the receding contact angle, whose stability is so low that no shock or vibration is allowed during a common experiment, and it is a common care to mount the goniometer or the Wilhelmy microbalance on an antivibration table. The results are very good from the point of view of the precision – that is, of the reproducibility of the contact angle values – but not from the point of view of the accuracy – that is, of the actual existence of a ‘stable’ (or, however, not metastable) equilibrium state.

Already in 1945, Pease (1945: p. 107)⁵⁴ wrote

There are, however, three different contact angles which can be measured. Bartell and his group in recent years have developed particularly refined techniques for determining ‘advancing’ and ‘receding’ contact angles (for the literature, see reference 1).

Fundamentally these are the same angles that are measured when the

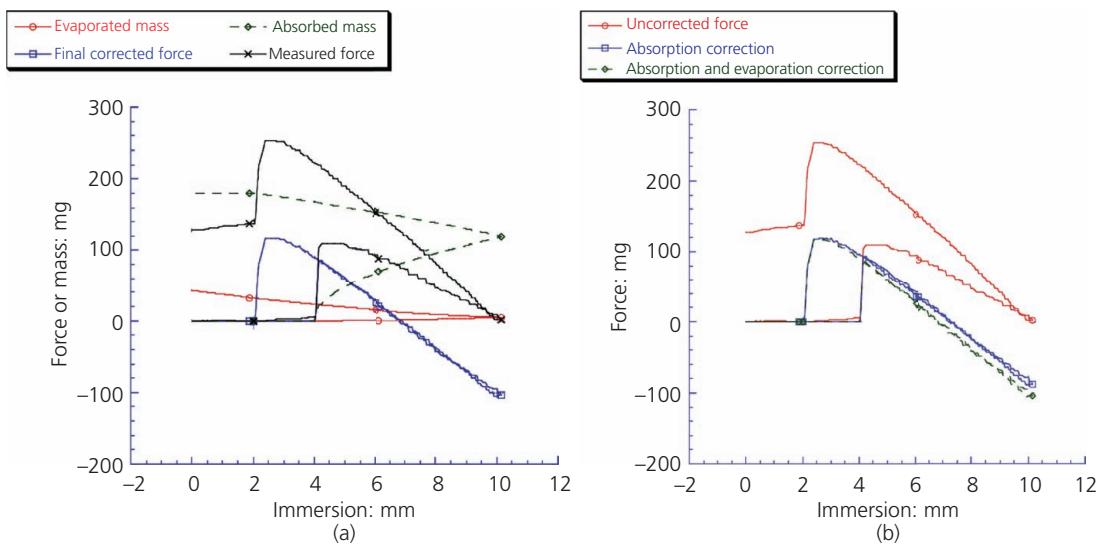


Figure 7. (a) The results of a Wilhelmy experiment performed on a porous stone sample, corrected to take into account test liquid absorption and evaporation. The graph shows separately the detected force, the absorbed liquid mass, the evaporated liquid mass and the final force, calculated by eliminating the absorption and evaporation effects. The symbols are defined in the figure key. The unit mg corresponds to the force **mg**, which is precisely equivalent to 0.986 dyn. Figure from data of Brugnara *et al.*⁵³ (b) The same as (a), showing the measured force, the force calculated by removing the effect of the liquid absorption only and the force estimated by considering both absorption and evaporation. As in (a), the symbols are defined in the figure key and the unit mg stands for the force **mg**, corresponding to 0.986 dyn. Figure from data of Brugnara *et al.*⁵³

solid surface is very carefully advanced or removed from the fluid. Their reality has been established, and each of them is entirely specific

for any system under investigation. In addition, there is the ‘equilibrium’ contact angle, ordinarily having an intermediate value. Techniques for the measurement of the latter are less refined but, in the author’s experience, measurements are reproducible within $\pm 2^\circ$, using essentially the method of Nietz (3).

(The paper by Nietz⁵⁵ cited in the text of Pease⁵⁴ was probably the first to introduce the idea of equilibrium angle.)

The Wilhelmy method, as described until now, is particularly efficient in the measurement of the advancing and receding states, because as important a parameter as the immersion rate may be precisely set. In contrast, the so-called static angle, which is, unfortunately, the most commonly measured contact angle, is fully undetermined from the point of view of the kinetic parameters of its formation.

But the superiority of the Wilhelmy method in the determination of the contact angle is confirmed by the ability to also obtain a stable equilibrium state, that is better known as the ‘most stable contact angle’.²⁹ This is hopefully very close to the equilibrium contact angle, as repeatable as the advancing or receding angle, but not significantly influenced by the roughness and partially by the heterogeneity of the surface.

This angle may be obtained by providing mechanical energy to the system as vibrations of the liquid.

The idea of this method comes from a long list of experimenters.

Figure 8. Schematic plot illustrating the qualitative trend of surface free energy against the experimental contact angle in a triphase system. The local minima correspond to the metastable equilibria of the system. The shape of the local minima, and particularly the height of free energy barriers between adjacent local minima, is important in determining the actual mobility of the meniscus. CA, contact angle. From Marmur *et al.*,²⁹ reproduced with kind permission of ICE Publishing

In the oldest papers, the researchers have simply applied what Fowkes and Harkins⁵⁶ called the slight shaking technique^{56–58} to obtain faster the equilibrium meniscus shape corresponding to the most stable angle. In very few recent papers, direct vibrations obtained by mechanical or acoustical methods have been applied to the solid surfaces,^{59–61} studying the results along with the variation in the defects present on the surface or with the characteristics of single ‘spike-like’ movements.

A practical method was proposed in 2001⁶² and 2002⁶³ and in slightly different ways reproposed by Sedev *et al.*⁶⁴

It is worthy of note that even a book reported this idea⁶⁵ even if from a different point of view: the reduction and/or elimination of the hysteresis through vibration, but concluded that the approach is not completely reproducible, a conclusion that does not agree with the authors’ experience.

What is different in Wilhelmy vibrated methods with respect to the drop is that the vibration is applied to the liquid and not to the solid. This corresponds to a lower frequency (the natural resonance frequency inversely depends on the mass) and also to an easier reproducibility, given the different size ratio between the drop and the vibration source, commonly consisting of a loudspeaker.

However, it is worthy of note that the use of a vibration should be done ‘cum grano salis’: the vibration is introduced in the system, slowly increasing its amplitude to avoid sprinkling of drops from the liquid, and then the vibration is maintained for a short time (few seconds) and finally the signal is faded, reducing its amplitude and allowing the system to remain as close as possible to the lowest possible energy minimum. The details of the method are very important to ensure its reproducibility.

7. Conclusions

The ‘Wilhelmy method’ is a term referring to a procedure invented more than 150 years ago by an original physical chemist, Ludwig F. Wilhelmy. In so long a time, the name has been used for conceptually different techniques, all based on the detection of a force during the immersion of a sample of various shapes in a liquid. This method has been automated in the past 40 years, but commercial programs also do not allow one to appreciate completely the many important aspects of the measurement. Obviously, the authors do not claim to have completed this task. The present paper tries to summarize only some elements, according to a very personal opinion, which are often neglected, from both a practical and a theoretical point of view. The difficulty in performing such a task is a further proof that ‘surfaces were invented by the Devil’, as the famous physicist Wolfgang Pauli wrote many years ago.

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