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Energy Procedia 45 (2014) 548 – 557

Energy Procedia

68th Conference of the Italian Thermal Machines Engineering Association, ATI2013

A note on capillary rise in tubes

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Abstract

Results are presented from an experiment on capillary rise of water in inclined small-bore (Φ = 1.92 mm) cylindrical tubes. A series of thick-walled tubes with different lengths and taken from the same glass rod was used, and the angle of inclination towards the vertical, α, was varied from 0° to 88°.
Results indicate that the capillary rise progressively reduces for increasing α, contrary to Jurin's law predictions. It is observed further that the meniscus seems not to change in shape while varying the tube orientation. Possible consequences of the above observations on the statics of capillary tubes are commented. In the frame of the discussion, an alternative and more general approach for the derivation of the Jurin's law is proposed.

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Keywords: Capillarity; menisci; micro-gravity conditions; Jurin's law

1. Introduction

Capillary rise of liquids in tubes has been in evidence for centuries, since the early observations by Leonardo da Vinci. As reported in [1], eminent scientists such as Rohault, Montanari, Borelli, Hausbekee, Taylor, and Jurin investigated the capillary ascension phenomenon during the 17th, and 18th centuries. The Jurin's law, predicting the rise (or fall) in a thin vertical tube immersed in a liquid at one end, was formally established in 1728 [2]. For circular tubes it reads:

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Selection and peer-review under responsibility of ATI NAZIONALE
doi:10.1016/j.egypro.2014.01.059

Nomenclature

E	free energy [J]
F	force [N]
g	gravitational acceleration [m/s^2]
H	capillary rise [m]
l_c	capillary length scale [m]
L	capillary tube length/extension [m]
p	pressure [Pa]
R	capillary radius [m]
V	volume [m^3]
z	vertical coordinate [z]

Greek symbols

α	declination angle of capillary [°]
γ	surface tension [N/m]
θ_0	equilibrium contact angle [°]
Φ	capillary tube diameter [m]
ρ	liquid-to-air density difference [kg/m^3]

Subscripts

0-90	declination angle values
1-6	capillary tube identifier
atm	atmospheric
c	capillary
g	gravitational
G	gas
H	hydrostatic
I	inner
L	liquid
o	outer
sl	solid-to-liquid
sv	solid-to-vapour
T	total
W	wall
α	declination angle

$$H = \frac{2\gamma\cos\theta_0}{R\rho g} \tag{1}$$

Here, γ and ρ are the surface tension of the liquid, and the liquid-to-air density difference, respectively; H is the elevation of the liquid column over the free surface of the bath; R is the capillary inner radius; g is the gravitational acceleration, and θ_0 is the equilibrium contact angle specific of the liquid-solid surface coupling. Eq. (1) holds for both hydrophilic ($\theta_0 < 90°$) and hydrophobic ($\theta_0 > 90°$) couplings (in which case a negative rise of the liquid in the capillary is predicted), subject to the condition $2R << H$ (thin tubes).

The Jurin's law has been validated by hundreds of experiments. In addition, as synthesized in the following, it can be theoretically derived following different and independent approaches. The validity of the law is therefore out of question. Even so, looking at Eq. (1), it is evident that it predicts an infinite H-value under zero gravity conditions. The potential occurrence of an infinite capillary rise at zero gravity seems to have been accepted without any special concernment up to now. However, it constitutes an exception in classical physics, where the impossibility of infinite values of quantities, such as velocity or acceleration, is rather used to exclude some specific behavior of the matter or to demonstrate some property of a physical system to be modeled (as an example, the impossibility of an infinite rotational velocity is used to demonstrate the symmetry of the shear stress tensor in fluid mechanics). At the same time, the result is consistent with the idea, underlying any of the derivation procedures of Eq. (1), that the hydrostatic equilibrium of the liquid column within a capillary tube derives by the balance of two actions, one of which is provided by, or linked to, the presence of the gravitational field. As a consequence, for $g = 0$ no static equilibrium condition can exist for the system.

To verify the consistency of the above arguments, experiments in micro-gravity would be necessary, but these are obviously very complex and costly, and so far none has been reported in open literature to the authors' knowledge.

As an alternative, the capillary rise in a long capillary tube can be measured at the ground g-value and at different inclinations. Provided that the meniscus does not change in shape with tube orientation, this experimental condition is in fact equivalent to a reduction in the gravity force proportional to $g\cos\alpha$, being α the declination angle from the vertical. Curiously, even for this much simpler case no result could be retrieved from the literature.

Results of a first experiment on the effect of inclination on capillary rise are reported here for water in a series of glass tubes of equal diameter and composition.

The results indicate with clarity that the capillary rise progressively reduces for increasing α. This finding, if confirmed by further experiments and for different fluids, would open very interesting questions on the statics of capillary columns.

2. Derivation of the Jurin's law

For the purposes of the successive discussion of the experimental data, the procedures commonly used to derive Eq. (1) are summarized.

Following de Gennes et al.[1], three alternatives are available, all assuming that the fluid fraction over the meniscus vertex can be overlooked (this corresponds to the definition of thin tubes).

2.1. Hydrostatic balance

The procedure assumes that the meniscus has a spherical shape, and this allows the Laplace pressure below the meniscus to be estimated as

$$p_H = p_{atm} - \frac{2\gamma\cos\theta_0}{R} \tag{2}$$

Here, p_H designates the pressure value below the meniscus vertex, at $z = H$, and p_{atm} is the atmospheric pressure, also acting within the capillary at the level of the free surface of the bath, ($p_{atm} = p_0$). At $z = 0$ the hydrostatic pressure balance reads:

$$p_H = p_{atm} - \frac{2\gamma\cos\theta_0}{R} = p_{atm} - \rho g H \tag{3}$$

from where Eq.(1) is readily obtained.

2.2. Force balance

The liquid column inside a capillary tube is subject to two opposite forces, the capillary force resulting from the surface tension acting along the meniscus perimeter, F_c, and the column weight, F_g. Eq. (1) is directly derived from the force balance below:

$$F_c = 2\pi R\gamma \cos\theta_0 = F_g = \rho g \pi R^2 H \quad (4)$$

2.3. Free energy minimization (1)

In its static condition, the liquid column is assumed to be at a stable equilibrium state, to which a minimum of the system free energy, E, must correspond. While ascending along the cylindrical tube from $z = 0$ to $z = H$, the potential energy of the liquid column increases, while the surface energy at the liquid-solid interface decreases (for wetting conditions) proportionally to the difference between the solid-to-vapour, γ_{sv} , and the solid-to-liquid, γ_{sl}, surface tensions [3]. This latter difference is related to the liquid surface tension by the Young's equation:

$$\gamma \cos\theta_0 = \gamma_{sv} - \gamma_{sl} \quad (5)$$

The total variation of the system free energy is therefore expressed:

$$\Delta E = -2\pi RH\gamma \cos\theta_0 + \frac{1}{2}\pi R^2 H^2 \rho g \quad (6)$$

The minimization of ΔE once again provides Eq.(1).

The validity of the force balance approach (§2.2) was harshly debated in the past [4-6], and its complete equivalence to the hydrostatic approach (§2.1) has been definitely confirmed only recently [7]. All the above methods are therefore coherent even if based on totally independent principles, and this makes the Jurin's law very difficult to pose in question.

Note that for $g = 0$ one single term remains in Eq.(3), (4), and (6), thus corroborating the conclusion that $H \to \infty$ in that limit.

2.4. Free energy minimization (2)

An alternative procedure is proposed here, based on the principle of energy minimization, leaving open the possibility that some different static condition can occur as an alternative to the one assumed in the classical methods above. As in the procedure at §2.3, the thermodynamic quantity to be minimized is the system Helmholtz free energy E, since the states to be compared are at equal temperature and volume [3,8].

With reference to Fig.1, we consider the system constituted by a liquid pool in equilibrium with the atmosphere at the atmospheric pressure, and compare state A (before the immersion of the capillary in the liquid), and state B (after the final equilibrium state has been reached). The two states have the same total volume ($V_T = V_L + V_G$) and temperature.

We estimate the free energy variation of the system along a quasi-static process connecting states A and B, where the liquid rises slowly along the tube.

In an infinitesimal step of the process, the variation of the total free energy of the system, dE_T, is given by:

$$dE_T = dE_L + dE_G + dE_W \quad (7)$$

where dE_L, dE_G, and dE_W designate the contributions of the liquid, the gas, and the tube wall, respectively.

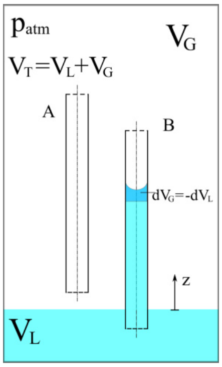

Fig. 1. A vertical capillary tube in a large confined ambient:
state A: before the immersion of the capillary; state B. at equilibrium after immersion.

From the definition of Helmholtz free energy, and for an isothermal process, we have:

$$dE_{L,G} = dU_{L,G} + TdS_{L,G} \tag{8}$$

Here, U and S respectively designate the internal energy and entropy, and T is the thermodynamic temperature. Enforcing the first TdS equation, we thus have:

$$dE_{L,G} = -p_{L,G} dV_{L,G} \tag{9}$$

The wall contribution is due to the reduction of the duct-wall surface energy when passing from the dry to the wet condition:

$$dE_W = -(\gamma_{sv} - \gamma_{sl}) 2\pi R dz \tag{10}$$

Substituting Eq.(9) and (10) in Eq.(7), and noting that $p_G = p_{atm}$, and $dV_L = -dV_G$, one has:

$$dE_T = -(p_L - p_{atm})\pi R^2 dz - 2\pi R\gamma \cos\theta_0 dz \tag{11}$$

Eq. (11) is integrated between $z = 0$ and $z = H$, to estimate the total change in free energy of the system:

$$\Delta E_T = -\int_0^H (p_L - p_{atm})\pi R^2 dz - 2\pi RH\gamma \cos\theta_0 \tag{12}$$

If p_L is given a hydrostatic distribution, Eq.(12) coincides with Eq.(6), however it has two advantages over it: i. it leaves open the possibility that the energy reduction due to the wetting of the wall can be balanced by a nonlinear pressure distribution within the tube; ii. its derivation does not need the gravitational field to be present, and is therefore more general than all the procedures mentioned above.

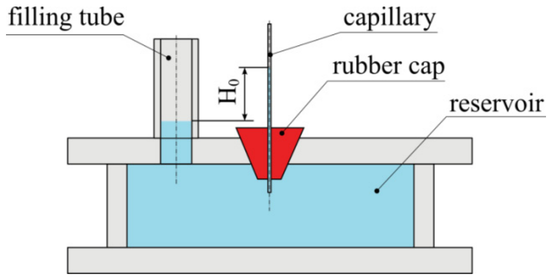

Fig. 2. Test section for the measurement of capillary rise in vertical tubes.

3. Experiments

3.1. Selection of capillaries

The selection of the capillaries to be used in the experiment was limited by the necessity of finding tubes of adequate length, so as to allow high inclination angles, and correspondingly long capillary extensions, to be observed.

Only thick-walled tubes were found to be available at reasonable costs, and a series of capillaries of different lengths was finally obtained by cutting a unique 2000 mm long borosilicate glass tube (Pirex 3.3). In this way tubes of the same composition and having the same nominal inner diameter could be obtained.

A series of six tubes was created of lengths $L_{c,1\text{-}6}$ = 100, 140, 200, 250, 300, and 500 mm. The outer and inner tube diameters were Φ_o = 5.9 mm, and Φ_i = 1.92 mm, respectively. The internal diameter was measured by SEM, with an accuracy of ±0.01 mm. The inner surface roughness was determined by a stylus tester, and resulted to be 0.07 μm. Distilled water was used as the working fluid in all the experiments.

3.2. Preliminary characterization of capillaries

A first experiment was dedicated to measure the vertical capillary rise in the tube series as accurately as possible. To this aim the test section schematized in Fig.2 was built. Transparent methacrylate was used for the cylindrical reservoir, the two covers, and the filling tube. This latter is of diameter Φ = 10 mm, a size sufficient to avoid any capillary rise effect, being Φ more than three times larger than the capillary length for water, $l_c = (\gamma/\rho g)^{0.5} \approx 2.7$ mm. A rubber cap was sealed in a hole at the center of the upper tank cover, and the capillary under test was inserted into it.

A Dataphysics OCA 20 contact angle goniometer was adapted to the purposes of the experiment. The test section was placed between the white light source and the camera of the optical bench. In each measurement the camera was in turn focalized on the free surface of the filling tube and the meniscus within the capillary. A digital surface gauge with 0.01 mm sensitivity was used to measure the heights of the free surface and the meniscus vertex, towards a common zero-reference level. For ruling the gauge more accurately, its arm was made visible on the screen, aside the enlarged images of the meniscus and the free surface. The capillary rise value was thus obtained as the difference between the two measured levels.

Due to the cylindrical geometry of the capillary, and the high thickness of the capillary walls, images were affected by refraction effects, producing dark lateral bands. This artifact did not allow the contact angle to be measured directly; the central part of the meniscus could however be observed quite neatly, as shown in Fig.3.

A series of twelve measurements was made using capillary L_1. The mean value of the capillary rise was H_0 = 10.3 mm. The method was estimated to have an overall accuracy of ±0.1 mm.

The contact angle was obtained from the extended form of Jurin's equation suggested by McCaughan [4]:

Fig. 3. Vertical capillary: magnified view of the meniscus.

$$H = \frac{2\gamma\cos\theta_0}{R\rho g} - \frac{R}{3\cos\theta_0} \tag{13}$$

The correction term to Eq.(1) appearing at the r.h.s. of Eq.(13), accounts for the liquid volume over the meniscus apex. The term is to be introduced since the capillary results to be "thick", being the inner tube diameter of the same order of the capillary rise ($H_0/2R \approx 5$). The correction term comes out to be of order 0.2 mm, i.e. 2% of the first term at the r.h.s. in Eq.(13). Surface tension and density were taken as γ = 724.946 $\times 10^{-2}$ N/m and ρ = 997.044 kg/m^3, respectively. The resulting contact angle estimate was $\theta_0 = 47° \pm 2°$.

3.3. Experimental setup and procedures for inclined capillaries

The necessity of handling long tubes impeded the above experimental procedure to be extended to the case of inclined tubes. An alternative set up was therefore created, permitting high inclination angles to be explored, even at the price of a lower accuracy level.

As schematized in Fig.4 the experimental rig was made up with a transparent plastic container of size 188x140x90 mm, bearing a tap hole on one of the shorter sides. A flexible rubber tube connected the tap to the capillary under test. A three-joint support held tightly the capillary through a calibrated teflon bush.

The measuring procedure was as follows: i. the liquid level at the free surface of the reservoir was measured first. The digital surface gauge used in the preliminary experiments was employed, but in this case the standard chisel-shaped arm was substituted by a vertical metal pin. This was slowly dropped until pricking of the liquid free surface was detected. The procedure is estimated to give an uncertainty on the reading of the free surface level of order ±0.1 mm; ii. the digital surface gauge was also used to measure the level of the meniscus within the capillary tube. In this case the gauge arm was equipped with a thin iron needle to be positioned in correspondence of the tube axis at the level of the meniscus. Ruling was made with the help of a monocular magnifying lens. The method is estimated to have an overall accuracy of ±0.1 mm; iii. for small inclinations, the angle from the vertical, α, was measured directly by a goniometric scale. For $\alpha > 30°$, the distance between two sections of the tube and their elevation on the reference level were measured; the inclination angle was thus determined by trigonometry.

All the capillaries in the series were used, and the α-values ranged between 0° and 88°.

Values of L_α, the capillary extension at the inclination α, were obtained from measured values of the capillary rise H_α:

$$L_\alpha = \frac{H_\alpha}{\cos\alpha} \tag{14}$$

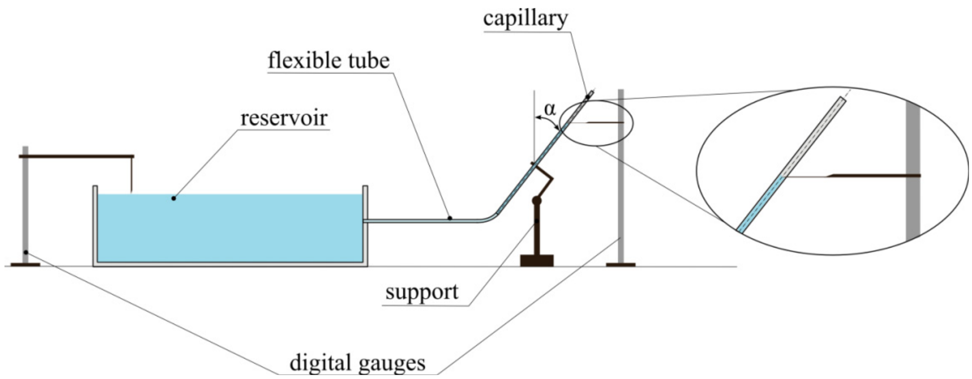

Fig. 4. Test section for the measurement of capillary rise in inclined tubes.

3.4. Test matrix

The matrix of the essays is presented in Table 1. Overall, 54 measurements were taken, each of them constituted by 5 readings, for a total of 270 readings. Obviously, only relatively small α-values could be explored with shorter tubes, and the matrix is therefore less populated for increasing α. Orientations close to the horizontal ($\alpha \geq 80°$) could only be explored with the longest capillary (tube no. 6).

Table 1. Matrix of the tests performed and corresponding mean values of H (mm) (Standard deviation of each series of readings in brackets)

α (°)→ L_c ↓ (mm)	0	10	20	30	40	45	50	60	70	75	80	83	85	other
n1. 100	10.46 (0.05)	10.43 (0.04)	10.32 (0.11)	10.20 (0.07)										37° - 10.27 (0.07)
n2. 140	10.37 (0.03)	10.35 (0.12)	10.31 (0.08)	10.18 (0.04)	10.25 (0.05)	10.26 (0.08)	10.15 (0.10)	9.55 (0.05)						
n3. 200	10.53 (0.08)	10.52 (0.11)	10.38 (0.04)	10.35 (0.07)	10.32 (0.05)	10.30 (0.05)	10.31 (0.11)	9.65 (0.06)						67°- 9.36 (0.07)
n4. 250	10.61 (0.04)	10.57 (0.06)	10.46 (0.05)	10.40 (0.08)	10.38 (0.08)	10.30 (0.04)	10.22 (0.06)	9.63 (0.11)	9.03 (0.06)					
n5. 300	10.41 (0.07)	10.36 (0.08)	10.37 (0.02)	10.28 (0.02)	10.28 (0.05)	10.30 (0.05)	10.30 (0.05)	9.67 (0.04)	9.30 (0.09)	8.69 (0.13)				77° - 8.69 (0.02)
n6. 500	10.66 (0.05)	10.71 (0.04)	10.71 (0.07)	10.66 (0.05)	10.49 (0.12)	10.49 (0.10)	10.46 (0.13)	9.70 (0.05)	9.42 (0.10)	8.81 (0.06)	8.20 (0.05)	8.00 (0.09)	7.86 (0.10)	88° - 6.75 (0.20)

The overall uncertainty of the method should account for possible variations in the tube bore size either passing from one to another, or along the capillary itself. The latter aspect becomes more and more critical for increasing the inclination angle. Since no destructive test was carried out after the experiments, to estimate the level of reliability of the experiment we only rely upon the results of repeated tests.

We first compare all the results for the vertical orientation obtained with the six tubes, with the reference value $H_0 = 10.3 \pm 0.1$ mm determined in the preliminary phase. Values of H_0 ranged between 10.3 and 10.7 mm, with a mean value $H_0 = 10.5$ mm. The same exercise was repeated for all α-values where at least three samplings had been made. For example, for $\alpha = 60°$, and $\alpha = 70°$, the maximum deviations from the averages were 0.1 mm and 0.4 mm, respectively. When considering the values of L_α, an additional source of uncertainty stems from the measurement of the declination angle, α. The overall uncertainty on L grows for increasing α, from a minimum of ±0.1 mm for $\alpha = 0°$, to a maximum of ±28 mm for $\alpha = 88°$. Obviously, such an amplification of the error is due to the very small values of $\cos\alpha$, for α approaching $\alpha = 90°$.

4. Results and discussion

Results are presented in terms of the relation $H_\alpha = f(\alpha)$ in Fig.5a. The value of the capillary rise for the vertical orientation, H_0, is also shown for reference. The results demonstrate that the capillary rise decreases monotonically for increasing α. The deviation from the reference remains very limited up to inclination values around 50°. Thereafter, however, the deviation from the reference level becomes quite well evident and definitely out of the uncertainty range of the data.

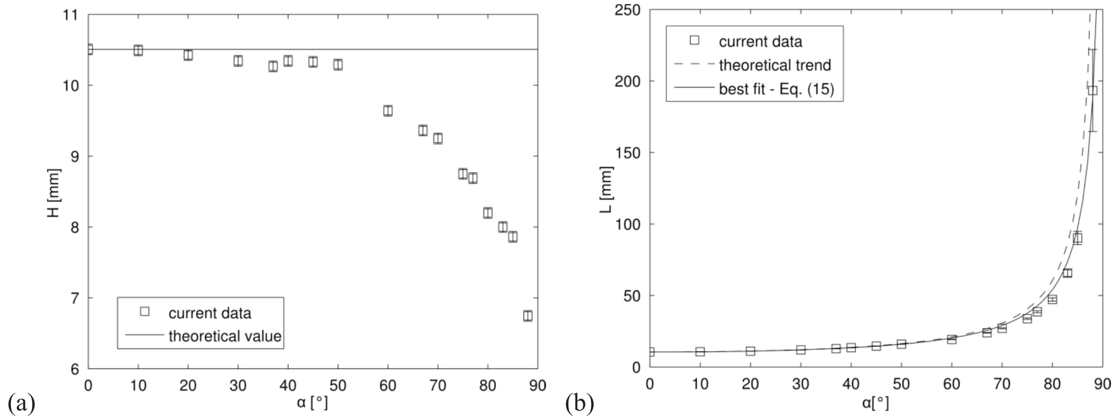

Fig. 5. Capillary rise *H* (a) and extension *L* (b) as a function of the declination angle.

The results for the capillary extension, L_α, are collated in Fig.5b. Results are compared with the theoretical prediction $L_{\alpha,th} = H_0/\cos\alpha$. Here, again, the two graphs almost coincide for α up to $\alpha \approx 60°$, but thereafter experimental results remain significantly lower than the theoretical predictions and follow a different trend.

A reasonable fit of the data in Fig.5b was obtained by enforcing a correlating equation of the following type:

$$L(\alpha) = \frac{H_0}{(\cos\alpha + k\sin\alpha)} \tag{15}$$

where the value of the constant k was assessed by means of nonlinear least squares fitting, $k = 0.021$. From Eq.(15), an estimate of the capillary extension for the horizontal orientation was obtained: $L_{90} \approx 500$ mm. The particular form of Eq.(15) may suggest that L is progressively reduced by an action proportional to $\sin\alpha$. A physical interpretation of this result is however impossible for the time being.

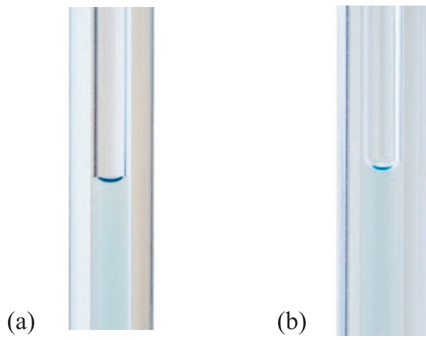

Fig. 6. Magnified views of the meniscus for (a) $\alpha = 0°$, and (b) $\alpha = 80°$.

As a first guess, we note that the behavior of inclined capillaries could be linked to a loss of symmetry of the contact angle distribution along the triple line, so as to produce a progressive reduction of the capillary force in the axial direction for increasing α. This would necessarily imply some evident deformation of the meniscus shape when α approaches 90°. To verify this possibility, photographs of the meniscus were taken, at different inclinations, using methylene blue as a colorant in order to enhance the contrast of the images. Two samples are shown in Fig.6, for the vertical orientation, and for α = 80°. The images do not allow any deflection of the meniscus shape from axial symmetry to be detected at the macroscopic scale. If one admits that the meniscus shape is insensitive to the tube inclination, an alternative interpretation of the capillary rise reduction for increasing α should consider the presence of a third axial resultant, aside the capillary force and the column weight. While the nature of such an additional force remains obscure, in the light of Eq.(12) we can now state that its presence might be linked to a non-linear pressure distribution within the liquid. Such an event cannot be excluded *a priori*, if we consider that, for instance, this would be an obvious occurrence in case the meniscus deviates from the spherical shape.

5. Concluding remarks

The experimental results presented here are to be considered just preliminary, since one single solid-liquid coupling was considered. However, they allow for the introduction of new hypotheses on the capillary rise effect, not yet considered in the literature. In fact, the capillary rise is shown to decrease progressively for increasing the declination angle from the vertical. This trend is followed with regularity for all the six capillaries in the series we tested, and cannot thus to be considered as the fruit of some experimental artifact.

The capillary extension, i.e. the tube length occupied by the liquid and comprised between the meniscus and the free surface level, increases for increasing the capillary inclination, as expected. However, the predictions based on Jurin's law do not match the experimental data, since the measured capillary extension always remains below the theoretical value, and tends to a finite value for the limiting case of the horizontal orientation.

We observe further that the meniscus seems not to lose its axial symmetry while varying the duct inclination, and that, in addition, there is no reason why the equilibrium contact angle should reduce for increasing α. All of this is consistent with the idea that within a distance of the order of the capillary length, the meniscus shape is only determined by the interaction between the solid wall and the liquid, and is insensitive to the gravitational action. The conclusion can thus be thrown that experiments performed with inclined capillaries at the ground g-value are equivalent, and therefore meaningful to investigate the capillary rise under reduced gravity conditions.

The observed reduction of the capillary rise and extension towards Jurin's law predictions, however, opens very intriguing questions on the statics of capillary tubes, and calls for additional data and observations.

Acknowledgements

The laboratory work of the undergraduate students Marcello Franchini, Matteo Mauro, and Gabriele Dazzi, is acknowleged. The authors also wish to express their gratitude to dr. Paola Fabbri, for providing the experimental facilities and assisting the experiments. The help of dr. Paolo Levoni, and mr. Enrico Salardi, was precious in the preparation of the experiments. Dr. Elena Bassoli provided roughness measurements. Photographs of the capillaries are courtesy of Filippo Barozzi. Glass capillaries were handled by FAVS – Bologna, Italy.

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