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SURFACTANT INFLUENCE ON RIVULET DROPLET FLOW IN MINITUBES AND CAPILLARIES AND ITS DOWNSTREAM EVOLUTION*

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Abstract

During our investigations of two-phase flow in long hydrophobic minitubes and capillaries, we have observed transformation of the main rivulet into different new hydrodynamic modes with the use of different kinds of surfactants. The destabilization of rivulet flow at air velocities <80 m/sec occurs primarily due to the strong branching off of sub-rivulets from the main rivulet during the downstream flow in the tube. The addition of some surfactants of not-so-high surface activity was found to increase the frequency of sub-rivulet formation and to suppress the Rayleigh and sinuous instabilities of the formed sub-rivulets. Such instabilities result in subsequent fragmentation of the sub-rivulets and in the formation of linear or sinuous arrays of sub-rivulet fragments (SRFs), which later transform into random arrays of SRFs. In the downstream flow, SRFs further transform into large sliding cornered droplets and linear droplet arrays (LDAs), a phenomenon which agrees with recent theories. At higher surface activity, suppression of the Rayleigh instability of sub-rivulets with surfactants becomes significant, which prevents sub-rivulet fragmentation, and only the rivulet and sub-rivulets can be visualized in the tube. At the highest surface activity, the bottom rivulet transforms rapidly into an annular liquid film. The surfactant influence on the behavior of the rivulets in minitubes is incomparably stronger than the classic example of the known surfactant stabilizing influence on a free jet. The evolution of a rivulet in the downstream flow inside a long minitube includes the following sequence of hydrodynamic modes/patterns: i) single rivulet; ii) rivulet and sub-rivulets; and iii) rivulet, sub-rivulets, sub-rivulet fragments, cornered droplets, linear droplet arrays, linear arrays of sub-rivulet fragments and annular film. The formation of these many different hydrodynamic patterns downstream is in drastic contrast with the known characteristics of two-phase flow, which demonstrates one mode for the entire tube length. Recent achievements in fluid mechanics regarding the stability of sliding thin films and in wetting dynamics have allowed us to interpret many of our findings. However, the most important phenomenon of the surfactant influence on sub-rivulet formation remains poorly understood. To achieve further progress in this new area, an interdisciplinary approach based on the use of methods of two-phase flow, wetting dynamics and interfacial rheology will be necessary.

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Keywords

Surfactant; Marangoni stress; wetting dynamics; interfacial rheology; two-phase flow; rivulet; sub-rivulet; sub-rivulet fragment; sliding droplet; cornered droplet; linear droplet array; Rayleigh instability; sinuous instability; minitube cleaning; meandering; two-phase flow maps

1. Introduction

New aspects of capillary and wetting phenomena regarding liquid or two-phase flow in micro-channels with characteristic dimensions of about 10 microns have recently been discovered because of new interest in micro-fluidics [1,2]. Traditionally, this subject has been considered as a hydrodynamic component in colloid science [3]. Indeed, capillary hydrodynamics of droplets and bubbles, as well as of film flow, have attracted considerable attention from colloid scientists during the past decade [4–9].

The subject of this paper is relevant to micro-fluidics in spite of the fact that two-phase flow was investigated in minitubes and capillaries with an internal diameter of approximately 100 times larger than that of micro-channels used in micro-fluidics. This statement is valid because the water-to-air volumetric ratio (WAVR) in our case was very low, about 10^{-3} , and at this small volume fraction, the resulting two-phase flow features (droplets or film) are characterized by dimensions in the range of 10 to 100 micron.

The conditions for droplet flow and film flow, driven by high-velocity turbulent air streams at high shear stress, in minitubes are very different from the slow laminar flow conditions employed in micro-fluids. In particular, the capillary number $Ca = \eta V / \sigma$ in our experiments may be orders of magnitude larger than in micro-fluidics. As a result, we have observed new capillary hydrodynamic modes which, to our knowledge, have not been encountered in micro-fluidics or in traditional investigations of two-phase flow.

Although the study of these new capillary hydrodynamic phenomena was not the topic of our applied research, we realized that they offer new opportunities for solving important practical tasks. One of these tasks relates to the advanced cleaning of narrow (0.5–2.5 mm) and long (2 to 3 m) Teflon® internal channels/tubes of flexible endoscopes used in the diagnoses and treatment of many diseases.

In our previous work [10–12], we focused on the cleaning of long and wide tubes/pipes (50 – 100 mm diameter and 50 m in length), such as those used in dairy processing. We discovered that the application of two-phase flow in cleaning channels and lumens offers significant advantages compared to cleaning with liquid flow [10–12]. In this respect, the main process that effects detachment of contaminant particles from a tube wall is due to droplet-wall collisions, where mist droplets are permanently produced by the two-phase flow. The above process is manifested in a special regime of two-phase flow dynamics known as “annular-mist” flow [13, 14].

Under some flow conditions, annular film may exist along the entire tube surface independent of tube length. At a sufficiently high velocity of turbulent air stream, so-called nonlinear “roll” waves appear on the film surfaces. These roll waves are unstable and generate mist droplets in the air stream which collide with the liquid film downstream due to turbulent diffusion, and this in turn results in restoring the film volumetric velocity. The above process can be described by the joint occurrence of two opposite processes, namely: 1) annular film transformation into mist droplets, and 2) mist transformation into annular film. The simultaneous occurrence of these opposing processes is a prerequisite for the onset of

their dynamic equilibrium which leads to the existence of annular film and mist at any position along the tube. This form of the annular-mist regime of two-phase flow has attracted much attention and is described in numerous publications [13,14]. For the long tubes, the annular-mist mode offers a unique opportunity to effectively clean tube walls by droplet erosion, contingent upon providing droplet-wall collision uniformly at any tube length.

While the modeling of annular-mist flow has been accomplished in the theory of multiphase flow, the elementary act of droplet-wall collision is a topic of capillary hydrodynamics [15–17] and of colloid science [18–24]. Investigations in this field are motivated by the numerous industrial applications of droplet impact, including ink-jet-printing, spray generation, spray coating, spray cleaning, spray cooling, fire suppression and agricultural spray deposition. The modeling of these processes has already established the important regularities of spray deposition, in particular the conditions for the onset of droplet bounce [24–27].

In comparison with the typical task of spray cleaning a flat surface, cleaning of a tube with the application of two-phase flow is characterized by many peculiarities. In spray cleaning, the spray characteristics are usually known and this provides information about the initial condition of droplet impact. In the case of tube cleaning, this information has to be extracted from knowledge about the mist formed during annular-mist flow based on modeling, or on measurements and modeling as covered in the theory of multiphase flow [28–29]. The transport of detached contaminant particles from the tube wall and their transport to the tube exit are complicated by the possibility of particle reattachment to the wall, and by other processes occurring along the tube length.

A very large shear stress arises during the initial moments of the inertial deposition of a droplet on the tube wall due to the droplet velocity at the moment of collision, which does not decrease very much compared to its high initial velocity. In this case, the droplet velocity is approximately equal to the mist velocity, and using this high droplet velocity is valid at a small distance from the wall. The generated large shear stress causes detachment of a contaminant particle when the droplet collides with a particle attached to the tube wall. Droplet impact may occur in the regimes of splashing or bounce [15–19]. If either splashing or droplet deposition occurs, the detached particle moves downstream to the tube exit together with the film flow. If bounce occurs, particle attachment to droplets is possible, and particle transport to the tube exit may take place together with mist; otherwise, the particle may deposit onto the wall and then move with the film flow to the tube exit.

While visualization of the inertial interaction with the attached particle during droplet impact is very difficult, some information may be obtained from the measurement of tube cleaning by annular-mist flow. To interpret the results, comparison with cleaning the same tube using liquid flow (no air) at the same applied pressure, e.g., 207 kPa (30 psi), was used. When contaminant adhesion to the wall is weak, both types of flow (two-phase flow and liquid flow) can provide high-level cleaning. However, when dealing with strongly-attached contaminant particles, the degree of cleaning by liquid flow is low. On the other hand, we discovered that the application of two-phase flow under certain conditions can provide a high degree of cleaning for such strongly adsorbed/adhered contaminants. These findings confirm that droplet erosion [30,31] is an effective mechanism of contaminant detachment. Naturally, appropriate conditions for providing rather uniform droplet collision with the entire tube surface for a sufficient time must be provided to achieve this high-level cleaning. The above scenario works well in situations where the annular-mist flow can be arranged, such as in the case of wide diameter tubing, and when the system of interest can tolerate the requisite high pressures.

In a specific application, a high degree of cleaning of narrow endoscope internal channels/tubes with respect to removing highly-adhering microorganisms [32,33] is necessary to prevent cross infection between patients being treated using the same endoscope. We tested the hypothesis regarding whether two-phase flow can achieve such high-level cleaning of endoscope internal channels/tubes [35]. This problem is recognized as a difficult task not easily achievable by liquid flow. The medical industry attempts to solve this by routinely manually brushing some channels; however, this requires manual intervention and cannot be used to clean the very narrow air/water channels of the endoscope (about 0.6 – 4 mm inside diameter). Another reason for the inability to achieve the necessary high-level cleaning is due to the constraints on the level of applied pressure that can be used for cleaning such delicate medical devices like endoscopes. At low operating pressures, achieving the acceptable high air velocity necessary to effect high-level cleaning with the annular-mist flow is impossible due to the high hydrodynamic resistance of the narrow channels. Accordingly, the air velocity of about 80 m/sec necessary for the onset of the annular-mist flow [34] cannot be achieved in these narrow-long tubes, and as a result, the possibility of utilizing the droplet-erosion mechanism in cleaning cannot be realized.

In attempts to overcome the above technical limitations, we explored the possibility of enhancing droplet generation, at small film thickness, by adding surfactants to the liquid used to make the two-phase flow. The results of the initial experiments indicated that the use of surfactants in this system deserves attention. Further investigations revealed that the role of surfactants is not limited to their influence on droplet generation, but also on the nature of two-phase flow as a whole. We found that adding surfactants resulted in a cardinal change in two-phase flow modes in narrow tubes. Since the hydrodynamic modes we discovered were found to be the most important in promoting hydrodynamic detachment, we have systematically investigated the effect of surfactants by direct visualization of such modes in narrow tubes.

Tube diameter and length, surface hydrophobicity, liquid-to-air ratio, surfactant nature and surfactant concentration were all found to affect the hydrodynamic modes of the two-phase flow in narrow tubes. Specifically, combinations of the above variables were found to significantly affect the flow modes on the tube wall and on droplet generation. In general, droplet generation is much stronger when a surfactant is added. However, the majority of the tested surfactants did not affect mist generation, while their influence on the hydrodynamic mode was essential. Surprisingly, no direct correlation was found between the level of mist generation and the cleaning of the narrow tubes. These findings point to the existence of an alternative mechanism to explain the strong contaminant detachment achieved in narrow tubes in the absence of the annular-mist regime. This mechanism appears to be linked to the formation of another hydrodynamic mode and to other means which create high shear forces during the cleaning of long narrow tubes at the flow conditions where the annular-mist regime cannot be obtained.

Taking this into account, we paid special attention to the literature of two-phase flow in minitubes, independent of whether mist droplets are produced. Study of the literature indicated that available information about the hydrodynamic modes of two-phase flow in minitubes is very scarce. Almost nothing is known about two-phase flow under the conditions which we found to be favorable for cleaning, namely, high-velocity turbulent air stream at about tens of meters per second and low water-to-air volumetric ratio (WAVR) about 10^{-3} . Moreover, some hydrodynamic modes revealed in our direct visualization of two-phase flow in narrow tubes, to our knowledge, have not been described in the literature.

Our direct visualization of two-phase flow was focused on using long, narrow Teflon® tubes under a rather broad range of conditions, namely tubes with an internal diameter ID=1.2–6.0

mm at pressures in the range of 34.5 to 276 kPa (5 to 40 psi) at different WAVR. The liquid phase of the two-phase flow mixture was either pure water or aqueous solutions of surfactants. We examined about fifty (50) different surfactants because the hydrodynamic modes observed by direct visualization have shown strong dependencies on both the nature and concentration of the surfactant used.

While relevant literature about two-phase flow in minitubes is scarce, recent achievements in capillarity and wetting [36,37], in particular those regarding sliding droplets and film flow, were found useful in the characterization of the hydrodynamic modes we observed in our experiments. The characterization of these modes and their physical bases define the structure of this paper. In the next sections, we briefly summarize some relevant capillary hydrodynamics processes with the goal of applying them in the interpretation of our visualization results.

It should be noted that we have encountered great difficulties in establishing some of the regularities of our observations because there are many kinds of sliding liquid “entities” in the experimental images we obtained. Among the important sliding entities, we will focus on the following: main rivulet, sub-rivulets, sub-rivulet fragments, sliding cornered droplets, sliding droplets, linear droplet array and linear array of sub-rivulet fragments.

In order to arrive at a generalized picture of the two-phase flow modes in minitubes, about 70,000 high-speed images (4 milliseconds per frame) were obtained in our study. This allowed us to characterize the hydrodynamic modes inherent to two-phase flow in hydrophobic minitubes. The characterization of such hydrodynamic modes is the primary objective of this research. The second objective of our research is to understand the influence of surfactants on two-phase flow modes in minitubes.

2. Background and Review

2.1. Two-phase flow in narrow channels

During two-phase flow, gas-liquid interfacial distribution can take a large number of possible forms depending on the conditions selected. However, these forms can be classified into types of interfacial distribution called flow regimes or flow patterns, mostly based on general visual observations [38]. Although flow patterns have been reasonably well-defined for medium and large diameter tubes, the situation is different for small diameter tubes where surface tension forces become important.

In large diameter tubes, gravity affects liquid distribution. Correspondingly, the flow patterns for the vertical and horizontal orientations are significantly different. Flow patterns are normally characterized qualitatively with idealized drawings, as shown in Fig.1. The dependence of such patterns on operational parameters has always been represented by so-called two-phase flow maps (Fig. 2).

Surprisingly, equivalent flow maps were not developed for very small diameter tubes where surface tension forces play a significant part. Kim et al [39] performed some of the first studies of two-phase flow in capillaries. They concluded that since capillary slug flow exists in both horizontal and vertical tubes, surface tension forces dominate over gravity forces. Damianides and Westwater [40] also studied two-phase flow in tubes with diameters ranging from 1 to 5 mm. These authors concluded that the surface tension between the gas and the liquid is an important variable for two-phase flow in air-water systems with Pyrex glass tubes at diameters < 5mm. Graska [41], using liquids with different surface tensions, concluded that the liquid/gas surface tension is a significant variable in two-phase flow through Pyrex glass tubes with an ID of <5 mm. Overall, it has been recognized by

researchers [42–46] that surface tension forces become important for channels of hydraulic diameter <10 mm, or in rectangular channels with small gap widths <5 mm.

Since the role of surface tension is significant in the behavior of two-phase flow in narrow tubes, interdisciplinary investigations are necessary taking into account the experience of colloid science in wetting dynamics, thin-film stability and surfactants. The inherent limitations of previous papers prevented establishing a close link between colloid and interface science and traditional two-phase flow investigations.

Although prior pressure maps were constructed in rather short tubes [13–14], the information provided focused on the bulk behavior of two-phase flow. On the other hand, the most interesting colloid hydrodynamic phenomena have been observed in long narrow tubes (length about 2–3 m) as reported in the present contribution. The typical tube length used in previous studies was between 0.2 and 0.3 m in the published literature [47–49], and even shorter, 0.15 m in [42] and 0.06 m in [40]. Notably, the liquid flow rates used in such studies were rather high, i.e., the mass quality (X) of the mixture was much less than 1, while the most interesting colloid hydrodynamic phenomena were observed by us at very low liquid flow rate, with X approaching 1:

$$X = G_G / (G_G + G_L) \quad (2.1)$$

where, G_G and G_L are the mass fluxes of gas (air) and liquid (water), respectively.

2.2. Discovery of rivulet flow in minitubes

Earlier investigations in minitubes were mostly devoted to comparing the pressure drop of two-phase flow to that of single-phase flow due to the importance of this parameter in fluid dynamics calculations. The systematic investigations of flow patterns in minitubes and the effect of surface wettability on such patterns were accomplished by Barajas and Panton [50] by changing the tube materials. These authors used several partially wettable and partially non-wettable materials in their investigations. They found little difference among the partially wettable materials, but they found a significant shift in flow regime transition for the partially non-wettable material. Pyrex, polyethylene and polyurethane, which were used in the above study, had equilibrium contact angles of 34° , 61° and 74° , respectively. The contact angle of a fluoropolymer FEP is about 106° .

Tubes made from the above materials with internal diameters in the range of 1 to 2 mm were employed in the experiments in [50]. The following eight (8) hydrodynamic patterns were found [50, Fig. 10] within the broad range of mass quality as defined in Eq. 2.1:

- a. **Wavy.** A stratified flow with waves at the interface that travel in the direction of the flow.
- b. **Plug.** This flow pattern contains intermittent plugs of gas (elongated bubbles longer than tube diameter) surrounded by a continuous liquid phase.
- c. **Slug.** This flow pattern contains intermittent slugs of liquid formed by waves of liquid growing until they touch the top of the tube.
- d. **Annular.** In this flow pattern, the liquid flows as a film along the tube wall and the gas flows through the center. Roll waves generally propagate down the tube length at the liquid-gas interface.
- e. **Bubble.** This flow pattern contains dispersed vapor distributed as discrete small bubbles in the continuous liquid phase.

- f. **Dispersed.** This flow pattern is very similar to the annular flow pattern except that the majority of the liquid is entrained as droplets in the gas flow. The liquid film on the tube surface still exists.
- g. **Rivulet.** A stream of liquid flows on the tube surface. The stream generally does not flow straight down the tube length, but twists its way down the tube length much like a river. The stream of liquid may be found flowing on the bottom or sides of the tube, as well as on the top of the tube.
- h. **Multiple rivulets.** This flow pattern is very similar to the rivulet flow pattern, except that multiple streams of liquid propagate down the tube length of the tube surface.

The most interesting finding [50] was found at low water fluxes, namely the appearance of rivulet flow. For $\theta=34^\circ$, rivulet flow was not observed. However, rivulet flow was found for the case of polyethylene tubes with $\theta=61^\circ$. These authors stated, “This is because the increased contact angle inhibits the liquid from spreading on the tube wall, thus preventing the annular flow from developing” [50]. This short statement characterizes the main regularity of previous studies regarding the onset of either annular flow or rivulet flow in minitubes. Wetting appears to promote annular film formation and non-wetting promotes rivulet formation. The second important regularity was observed at a larger contact angle of 74° for polyurethane [50]. At high gas velocities, there was a small region of the multiple rivulet flow pattern and there was a considerable increase in the size of the multiple rivulet flow region at the expense of a reduced annular flow region [50]. These regularities and their dependence on gas and liquid velocities are illustrated by the flow maps (Fig. 2). The authors [50] state “at high gas velocities, the shear rate forces cause the single rivulet to break into several streams.” These previous findings are important and will be compared with the results of our visualization of two-phase flow in minitubes.

2.3. Surfactant influence on two-phase flow in minitubes

In spite of the consensus regarding the strong impact of surface tension forces on two-phase flow modes in minitubes (Section 2.1), the possibility of influencing such modes with surfactants has not been specifically addressed in the literature. Although surfactants were used to investigate whether they affect two-phase pressure drop in tubes [50], interest in characterizing their effect on the two-phase flow modes has been low. According to [51], the addition of a surfactant caused the pressure drop to increase compared to water alone. On the other hand, in [52], no quantitative change in pressure drop was reported when using surfactant solutions. While the annular film flow was observed in the latter work, the above authors did not mention rivulet formation. It is possible that the reported absence of a clear influence of surfactants on pressure drop in two-phase flow has resulted in decreased interest in this topic.

2.4. Rivulet meandering and sub-rivulets

Prior publications regarding rivulet formation during two-phase flow in minitubes have been surprisingly few [50]. In contrast, much attention has been paid to the mechanics of the rivulets formed during liquid flowing on an inclined flat surface, or when the liquid is driven by an air stream in the same geometry. It is obvious that the conditions for rivulet formation on an inclined plane are simpler to consider, and accordingly, modeling of such flow is easier. In spite of this simplification, we have found that the knowledge obtained from rivulet flow on a flat surface is relevant to the problem of rivulet formation and evolution in minitubes. To our knowledge, there has been no attempt to establish a link between rivulet flow on an inclined plane and in minitubes. Fig. 3a shows a schematic diagram of the typical experimental set-up used to study rivulet behavior on an inclined surface. Water is injected

at the top of an inclined plate through a rather small opening. The substrate used is in the form of a polymer sheet placed on the surface of a rigid metal plate. The tilt angle, α , of the plate can be adjusted from 0° to 87° . During previous studies, pictures and movies were taken by digital cameras placed above the plate and perpendicular to it.

When the liquid contact angle with the plate material is very low, film flow arises. This type of flow is characterized by the complete wetting of the surface by the liquid. This continuous film can be laminar or turbulent, or it may also include waves. If the plate material is partially non-wettable or partially wettable, several different regimes are observed as the flow rate of the liquid is increased [53–54]. At very low flow rates, a series of droplets slide successively down the surface. When the flow rate increases, the distance between two sliding droplets decreases until a point is reached where successive droplets touch each other and a single straight laminar rivulet is formed. This linear laminar rivulet flow pattern received the most attention in earlier investigations.

Towell and Rothfeld [55] described the shape and the velocity field of the linear laminar rivulet by simultaneously solving the Navier-Stokes and the meniscus equations. From this solution, they derived the dependence of the characteristic rivulet dimension on the liquid flow rate. They gave a general solution to the problem and showed that for systems with a “bad wettability,” the rivulet cross-section can be assumed to be a segment of a circle. For systems with a good surface wettability, they showed that the general solution can be simplified by assuming a “flat wide rivulet” of rectangular cross-section.

A further increase in the liquid flow rate is accompanied by an increase in the width and height of the rivulet until a first critical flow rate is reached where the straight laminar rivulet changes to a meandering stream (Fig.3b). Nakagawa and Scott [53] assumed that contact-angle hysteresis is the most probable reason for meandering. If the flow rate exceeds a second critical value, the meandering rivulet is no longer stable and a pendulum or oscillating rivulet is formed. At some liquid flow rates, the original rivulet decays and sheds several smaller rivulets at a constant frequency. The rivulet decay frequency (number of sub-rivulets that are created per unit time) increases with increasing liquid flow rate. Surprisingly, at even higher flow rates, the rivulet restabilizes and becomes straight again, but its thickness varies like braids. [56].

The influence of surface tension on the patterns of rivulet flow down a plate was characterized in [57], using plates made from stainless steel and polypropylene, and using a water-ethanol mixture (Fig. 4). Interestingly, qualitatively similar dependencies are found in our experiments (Section 4), where the surface tension decrease was accomplished due to the addition of a surfactant. The points in Fig. 4 corresponding to the transition from one flow pattern to another are called the “transition points” [57]. In comparison with the situation for pure water, sub-rivulet formation occurs at a lower flow rate when the surface tension is about 45 dynes/cm. At a surface tension below 29 dynes/cm, no meandering or oscillating rivulet flow exists and the linear rivulet domain grows. At even lower surface tension, the linear broad rivulet formed is indistinguishable from that of film flow due to high surface wettability.

Figure 4 in [57] also shows some experimental values of the rivulet decay frequencies (measured at $\alpha=70^\circ$) for a variety of liquid/solid systems as a function of the liquid mass flow rate. For the same flow rate and physical properties, bad wettability led to higher oscillation frequencies. The decay frequency increased approximately linearly with increasing liquid flow rate. However, no straightforward dependence on viscosity or surface tension could be deduced according to [57].

According to [55,57], two limiting rivulet shapes exist leading to two different functional dependencies between rivulet width and rivulet flow rate, where the coefficient depends on the contact angle. For 96% ethanol on stainless steel ($\theta = 8^\circ$) and for water ($\theta = 68^\circ$), the dependence of rivulet width on the liquid flow rate for the limiting cases of flat rivulet and rivulet of circular cross-section were confirmed by experiments [57]. The equation for the total energy of the steady rivulet was derived which allowed one to obtain the equation for the frequency of rivulet delay [57]. Both equations were confirmed by comparison with experimental curves using different solid-liquid systems. This agreement was achieved only for the conditions corresponding to a rivulet with a circular cross-section because this was assumed in the developed theory [57].

Investigation of the rivulet shape at any θ becomes possible for a steady thin draining rivulet with prescribed volume flux and of constant but unknown width. If the cross section is thin, the lubrication approximation can be applied and the shape of the rivulet is deduced [58]. This is relevant not only to flow down a flat plate but also to flows around cylinders and along slowly varying topographies [59]. This approach perhaps creates a perspective to extend this achievement to modeling the rivulet flow in tubes. It is also useful to mention that subsequent studies [60, 61] considered the case where surface shear due to an air stream was used to drive the rivulet flow.

The above same problem was considered in [62], but without the application of the lubrication approximation, i.e., for not so small aspect ratio $\varepsilon = H/L_R$, where H is the height, and L_R is the rivulet width. Moreover, accounting for two driving forces is accomplished in [62], i.e., for gravity and for aerodynamic drag. Accordingly, the derived equation for flow rate (Q) is a binomial where the first and second terms represent the influence of gravity and wind, respectively. The first term is proportional to $L_R^4 \tan^3 \theta$ and the second term to $L_R^3 \tan^2 \theta$. These products are constant when Q is fixed. One concludes that at a certain Q , the decrease in contact angle is accompanied by an increase in the rivulet width, which agrees well with numerous experimental data. The unrestricted increase in L_R , when θ tends to zero, characterizes the transition from the rivulet mode to film flow. The rivulet is almost flat with the exception of the vicinity of its boundary, when θ is rather small, which corresponds to the initial model [55].

The developed theory [62] allows for the investigation of the onset of rivulet splitting. If a rivulet is to split, the conditions must be energetically favorable for it to do so. Hence, for splitting to occur, there must exist another rivulet of flux $q \leq Q/2$ such that

$$E(Q) > E(Q - q) + E(q) \quad (2.2)$$

i.e., the energy contained in the two smaller rivulets is less than the energy of the single initial rivulet. However, since the flux and energy are defined in terms of the width L [62], the stability is determined by:

$$f = E(L_Q) - [E(L_{Q-q}) + E(L_q)] \quad (2.3)$$

where L_Q denotes the width of the rivulet with flux Q . When $f > 0$, it is energetically favorable for the rivulet to split, and if $f < 0$, the rivulet is unlikely to split. The energy/length ratio of the rivulet involves kinetic, potential and surface energies, as well as viscous dissipation. The sum of these energies must remain constant although the individual terms may vary. Since the theory [62] is developed for the straight steady rivulet as the rivulet

moves down the slope of an inclined surface, its kinetic and surface energies remain constant. Potential energy will be lost and this must be balanced by viscous dissipation.

The theory [62] allows for the calculation of the components of energy and for the determination of the sign of f at different Q . However, this theory does not predict splitting for the wind driven rivulet, while it does predict the onset of splitting for the gravity driven rivulet. Because in this theory the aspect ratio $\varepsilon = H/L_R$ is assumed to be a small parameter [62], the error increases with increasing contact angle. The theory predicts (Table 1 in [62]) that with decreasing the contact angle, sub-rivulet formation occurs at smaller Q . This contradicts the experimental data [57] represented in Fig. 4 for smaller σ , which demonstrates the necessity of larger Q for sub-rivulet formation with decreasing σ , and a concomitant decrease in θ .

Although there are many common features in rivulet and sub-rivulet formation in the experiments with the inclined plane discussed in this section and in [50], the conditions are essentially different. This difference in conditions is the reason for the large difference in the onset of rivulet and sub-rivulet flow. The theory [62] does not predict the onset of the sub-rivulet mode in the presence of wind flow along the flat plane. The experiment with two-phase flow in narrow tubes revealed the sub-rivulet mode [50].

In the published literature, there is significant contradiction regarding the influence of wettability on sub-rivulet formation. Sub-rivulets along a flat plane are possible at a rather small contact angle of about 10° [62]. In contrast, sub-rivulets in narrow tubes were not observed at $\theta < 61^\circ$ [50], but did appear at $\theta = 74^\circ$ [50]. This drastic difference in the wettability influence may be interpreted by the difference in the mechanisms of sub-rivulet formation on a flat plate and inside a tube. Another possibility is that the work [62] is erroneous because it contradicts the experiments reported in [57] whose results are in qualitative agreement with our experimental results.

The theory of stationary meanders was proposed only recently [63] on the basis of simple force balance, including inertia, capillary forces, and hysteresis of wetting. The theory agrees well with the experimental data provided in the paper regarding the dependence of the first critical flow rate on the inclination angle, obtained for advancing θ_A and receding θ_R contact angles of 70° and 35° , respectively, for the case of polyethylene tetrathalate using the set-up shown in Fig. 3a. In addition, the theory predicts the final radius of curvature of the meanders. Unfortunately, the authors tested their theory using only their own experimental data.

2.5. Wind-driven rivulet break-off

There has been no systematic experimental investigation of wind-driven rivulets in spite of the fact that [64] finds that wind-driven rivulets exhibit completely different behavior from the behavior observed for gravity-driven rivulets on inclined surfaces. The experiment [64] was performed with the horizontal orientation of the surface, while the aerodynamic drag, caused by the air stream, was the driving force. The new hydrodynamic mode is characterized in Fig. 5. Although the authors claim that they found a new mode, unique to shear-driven rivulets only, this mode was actually reported in [65] for gravity-driven rivulet flow in vertical parallel-wall channels.

The authors explain that the rivulet tip stops due to the difference between advancing and receding contact angles [66,67]. This effect has been utilized by several investigators to examine the critical conditions for a droplet to stick to an inclined surface in spite of the gravitational force, and to find the terminal velocity of droplet sliding on an inclined surface [68–71]. The above critical conditions occur when the aerodynamic force, which grows with

increasing droplet dimension, starts to exceed the mentioned capillary force. The onset of dripping flow at a sufficiently low flow rate may be possible in narrow tubes, which is described in Section 5 as “sparse/dry zone.” However, the conclusion made by the authors in [64] that their mode is universal contradicts the visualization results in [50] and in our work.

2.6. Sliding, rolling and cornered droplets

Recent experiments on an inclined plate found stationary droplets of different angle-dependent shapes that slide down the plane without changing shape [73]. Gravity-induced droplet sliding has attracted more attention than shear-induced sliding of droplets, similar to the situation where gravity-driven rivulets moving down an inclined surface (Section 2.4) have attracted more attention than shear-driven rivulet motion (Section 2.5). Given that in our experiment sliding droplets are driven by the aerodynamic drag force, one concludes that there is a rather broad gap between the existing literature data and our experiments in which sliding droplets arise during the last stage of the evolution of rivulet flow.

Works that focus on the evolution of falling sheets or ridges [74,75], i.e., the advancing edge of a fluid film or long one-dimensional drops on an inclined “dry” substrate, contribute to understanding droplet sliding. In particular, the notion of flat drops is identified in [76] as the solution with universal behavior, i.e., drops whose amplitude, velocity and dynamic contact angles do not depend on mean film thickness.

The model of a cylindrical droplet [77] allowed one to consider a large range of sliding droplets. The velocity of small droplets with a large contact angle is dominated by friction at the substrate, and the velocity of the center of mass scales with the square root of the size of a droplet. For large droplets or small contact angles, however, the viscous dissipation of the flow inside the volume of a droplet dictates that the center of mass velocity scales linearly with the size.

As for the situation of a spreading droplet, a precursor film [78–81] or slip at the substrate helps to avoid a divergence problem at the contact line, but introduces new ad-hoc parameters into the model. This stress singularity at the contact line is alleviated if the droplet rolls. Perhaps the first model of droplet rolling was proposed by J. J. Frenkel [68] and is discussed in [82], while references [83,84] are usually cited as earlier. Recently, large interest in rolling droplets has arisen due to publications [85,86]. In these publications, the rolling mode is addressed for the case of sufficiently high contact angles.

Modeling processes near the receding surface of a flat droplet revealed a decrease in the receding contact angle with velocity. Modeling of the processes near the receding surface of a sliding flat droplet contributes to understanding sliding droplets in a way similar to how modeling for the advancing front allowed the solution of the problem of stress singularity.

A simple result of modeling has been that the dynamic receding contact angle decreases. It is obvious that higher velocity causes a larger perturbation of the receding meniscus and a larger concomitant decrease of the receding contact angle. Hence, there is a critical velocity at which the meniscus disappears. The simple derivation of the equation for the critical velocity is given in Section 6.2 of monograph [5]. Sliding with velocities smaller than the critical one is referred to as sliding in the meniscus regime.

The problem of the receding meniscus is relevant to the phenomenon of forced wetting (Section 3.3 in monograph [5]). An equilibrium meniscus exists near a vertical plate submerged into a bath. If the plate is slowly drawn out of the bath, this perturbs the meniscus in a way similar to that which occurs during the sliding of a flat drop. Meniscus deformation is the result of competition between two forces: the capillary force and the

viscous force. The capillary force stabilizes the meniscus, while the viscous force destabilizes the meniscus. The liquid near the wall tends to move together with the wall due to shear stress. When the velocity exceeds the critical velocity, a large sheet adjacent to the wall moves together with the wall and separates from the meniscus. The plane becomes coated by a liquid film of a certain thickness. It is obvious that the film thickness increases with increasing velocity. This dependence is described by the Landau-Levich-Derjaguin law [5].

$$e \sim K^{-1} Ca^{2/3} \quad (2.4)$$

where

$$Ca = \eta U / \sigma \quad (2.5)$$

is the capillary number

$$K^{-1} = (\sigma / \rho g)^{0.5} \quad (2.6)$$

is the capillary length which scales with the height of the equilibrium meniscus. Ca characterizes the competition between the capillary force and the hydrodynamic viscous force, which particularly manifests itself in the forced wetting.

The Landau-Levich-Derjaguin theory was developed with the assumption that the contact line remains straight in spite of the plate movement. As illustrated in Fig. 6a however, a different scenario is possible, if, for example, the contact line is pinned at the edge of the plate [89]. The contact line can incline relative to its direction of motion at a well-defined angle; contact lines inclined in opposite directions meet at a sharp corner with an opening half-angle ϕ . This inclination permits the contact line to remain stable at higher speeds since the speed U_n normal to the contact line is decreased according to $U_n = \sin\phi U$. Yet another critical speed U_{riv} at the corner ejects a rivulet. An analogous sequence of transitions is observed for a drop running down an inclined plane (Fig. 6b).

The numerical solution of the evolution equation [76] showed the transition from an oval stationary drop with a cusp at its back, and further to a drop that periodically pinches off small satellite drops at the cusp (Fig. 7a). When there is a rather high coverage by the cornered droplets, the same approach [76] allows one to predict the long-term behavior of the collective processes. The coalescence of sliding droplets leads to the formation of rivulets (Fig. 7b). Hence, both the transformation of rivulet flow into the array of sliding droplets and their transformation during rivulet flow are possible.

2.7. Free jet and Rayleigh instability

When a liquid jet emerges from a nozzle as a continuous body of cylindrical form, the competition that arises on the surface of the jet between the cohesive and disruptive forces gives rise to oscillations and perturbations. The properties of most interest are the continuous length of the jet which provides a measure of the growth rate of the disturbance, and the drop size which is a measure of the wave number of the most unstable disturbance. Also of interest is the manner in which the jet is disrupted.

Rayleigh [90] employed the method of small disturbances to the conditions necessary to cause the collapse of a liquid jet issuing at low velocity, for example, a low speed water jet in air. Rayleigh compared the surface energy (directly proportional to the product of surface area and surface tension) of the disturbed configuration with that of the undisturbed column. The conclusion to be drawn from Rayleigh's analysis of the breakup of non-viscous liquid jets under laminar flow conditions is that all disturbances on a jet with wavelengths greater than its circumference will grow. The incorporation of the liquid viscosity and the aerodynamic interaction in the Rayleigh theory was accomplished by Weber [91]. Sterling and Sleicher [92] proposed a semi-empirical modification to the Weber theory by introducing the empirical hydrodynamic reduction factor, and achieved better agreement with experiment.

At low air velocity, when aerodynamic interaction is negligible, the Rayleigh waves predominate and the surface tension destabilizes the jet. At high air velocity, when the aerodynamic interaction predominates, the surface tension opposes aerodynamic disturbance of the jet and manifests itself as the stabilizing factor [72].

At first glance, the opposite influence of σ on jet stability at weak and strong aerodynamic interactions may cause a similar opposite influence when a surfactant is added, which causes a decrease in σ . However, in addition to the decrease in σ , the presence of a surfactant will set up the Marangoni effect, namely, the surface liquid flows towards the area of smaller surface concentration of surfactant (larger surface tension). In the meantime, droplet formation due to the Rayleigh instability occurs because of the formation of narrow necks on the jet surface with concomitant surface extension. This in turn leads to the stretching of the neck surface with the associated decrease in the surface concentration Γ , which initiates the Marangoni flow into necks. Hence, the Marangoni flow into necks hampers the growth of the axisymmetrical Rayleigh waves. This is the most plausible mechanism for jet stabilization by a surfactant.

The surfactant influence on surface waves and jet stability was analyzed by Levich [88], who concluded that surfactants can suppress surface waves and correspondingly retard the jet collapse at any wave length. The Levich theory predicts that the larger the surface elasticity [93]

$$\varepsilon = \Gamma(d\sigma/d\Gamma)$$

the stronger the surfactant will be and its influence on surface waves.

Laboratory observations have shown that the presence of a surfactant may have an important influence on the instability of a jet or a thread (very thin liquid jet) and consequently, on the distribution of the droplet size resulting from the breakup [94]. The surfactants are also known to affect chemical reactions in such systems as well [95–97].

While the axisymmetrical waves whose growth is Rayleigh instability occur at lower velocity, the onset of sinuous waves and sinuous instability occurs at higher velocity; the latter is confirmed by experiment (Fig.8).

2.8. Rayleigh instability of annular film and the surfactant influence

The cylindrical shape of annular film predetermines its Rayleigh instability, which was investigated perhaps for the first time in [98], and more systematically in [99]. When the thickness of annular film is sufficiently small, the instability causes the development of a series of annular collars attached to the cylinder.

Studies of the influence of surfactants on the stability of an annular liquid layer lining the interior of a tube have been motivated, to a large extent, by their application in pulmonary fluid dynamics. In the lung, a liquid lining protects the cells of the alveolar surface against mechanical damage [99]. The surface tension of the liquid-air interface tends to minimize the interfacial area, and thus favors airway collapse during exhalation. To stabilize the lining, biological surfactants are naturally secreted by the alveolar cell types to decrease the surface tension. It is generally accepted that the physical mechanism responsible for the formation of liquid bridges occluding the airways is due to the Rayleigh capillary instability of a cylindrical interface.

Carroll and Lucassen [100] found that under extreme conditions, the presence of a surfactant may reduce the growth rate of the most unstable perturbation by a factor of four. The presence of a surfactant becomes important when the thickness of the annular film is not small in comparison with the internal radius of the tube. If the film thickness is small, the role of surfactants is negligible according to the theory in [101]. While the annular film in narrow tubes is subject to Rayleigh instability, the influence of surfactants on it is negligible because the film thickness is normally small in comparison with tube radius.

2.9. Stability of annular film flow

At high velocity, the development of waves leads to destabilization of film and to the mist formation regime known as annular mist flow [34]. With respect to our experiment, we consider not so high air velocities where annular film flow predominates.

For down-flowing liquid film, its breakup was observed by some groups, for example [102]. The breakup occurs below a critical thickness, an observation which supports that the down-flowing liquid film may exist only above a minimal thickness.

The breakup of a flowing liquid film typically occurs when the liquid flow rate decreases below the value that is required to maintain a continuous film on the underlying surface. The liquid flow rate and the film thickness at breakup are known as the minimum wetting rate (MWR) and the minimum liquid film thickness (MLFT), respectively [102,103]. MLFT increases with increasing contact angle. Correspondingly, the smaller the contact angle, the smaller the thickness of the down-flowing film will be without the possibility of rivulet formation. Reported analytical approaches for predicting MWR and MLFT are based mainly on the minimization of the total energy of a stable liquid rivulet formed following the film breakup.

Co-current or counter-current shear rate, caused by aerodynamic flow, affects MLFT. MLFT decreases for down-flowing liquid film and co-current interfacial shear. Conversely, increasing the counter-current interfacial shear increases both MLFT and MWR. These investigations show that both the axial air stream and the orbital components of annular film movement (affected by gravity) influence the stability of annular film as well as the contact angle value. However, the only obvious conclusion that can be made is that decreasing the contact angle contributes to annular film stability due to more complicated conditions of the problem. In annular film flow in a horizontal tube, the direction of aerodynamic shear stress is perpendicular to the gravity force.

3. Experimental

Surfactants—The surfactants used in this study and their equilibrium surface tension (at 0.1% concentration by weight) are given in Tables 1–5. To prepare surfactant solutions, water purified by reverse osmosis (RO) was used.

Apparatus—The apparatus illustrated schematically in Fig. 9 allowed us to perform optical examination of the two-phase flow inside transparent Teflon® endoscope channels, to control the flow conditions used in the test, and to measure all operating parameters under both static and dynamic conditions. The apparatus consisted of a source of compressed air, various connectors and valves, two pressure regulators, a flow meter, pressure gauges, a metering pump (Fluid Metering Inc., Syosset, NY, Model QV-0, 0–144 ml/min), a metering pump controller (Fluid Metering Inc., Stroke Rate Controller, Model V200), various stands and clamps (not shown), various tube adapters, and an imaging system which included a microscope, digital camera, flash, and various lights to illuminate the imaging stage.

The compressed air source was a 4.5 kW (6-HP) [114 liter (30-gallon) tank] Craftsman air compressor. The compressor has two pressure gauges, one for tank pressure and one for regulated line pressure. The maximum tank pressure is 1034 kPa (150 psi). The compressor actuates when the tank pressure reaches 758 kPa (110 psi). The line pressure was regulated to [414 kPa (60 psi)] for the majority of the tests, with the only exceptions being the high pressure test [552 kPa (80 psi)] used to define the hydrodynamic mode for the 0.6 mm (ID) “elevator-wire channel.” The regulated compressed air was supplied to a second regulator via 4.6 m (15') of 9.5 mm (3/8') reinforced PVC tubing. The second regulator was used to regulate the pressure for each test. The air then fed into a 0–283 liter/min (0–10 SCFM) Hedland flow meter with an attached pressure gauge. This gauge was used to set the test pressure via the second regulator that preceded it, as well as to read the dynamic pressure during the experiment. The flow meter fed into a “mixing” tee, where liquid was metered into the air stream via an FMI “Q” metering pump. The metering pump was controlled by an FMI pump controller. The outlet of the mixing tee is where adapters for varying model endoscope tube diameters were connected.

For each experiment, we measured the air pressure, the liquid flow rates according to the calibration of the metering pumps and the air flow rates by the air flow meter. The volumetric flow rate of air as well as the linear velocity of air in the minitubes was calculated after converting the flow rate at 1 atmosphere. The liquid-to-air ratios were calculated under standard conditions (1 atmos. at 25°C). The air flow rates used in the experiments were measured to $\pm 2\%$ of the reported values.

Visualization—To acquire an image of the flow mode inside the channel, we used a Bausch and Lomb Stereozoom-7 microscope (1x–7x), a camera to microscope T-mount adapter, a Canon 40D digital SLR camera, and a Canon 580EX speedlite. The camera to microscope adapter's T-mount end was bayoneted to the camera and the opposite end was inserted in place of one of the eyepieces on the binocular microscope. The flash was attached to the camera via a hot shoe off camera flash cable and directed into a mirror/light diffuser mounted below the microscope stage. The mirror/diffuser was a two-sided disc with a mirror on one side and a soft white diffuser on the opposing side. This could be rotated to change the angle of the light that was directed towards the stage as well as to switch between the two sides. The microscope was equipped with illumination from both top and bottom with respect to the tube. A Bausch and Lomb light (Catalog # 31-35-30) was inserted into this porthole and used in conjunction with the Canon 40D's live view feature for live viewing as well as for focusing. The live view feature shows a real time image on the 75 mm (3') LCD screen on the back of the camera. The channel to be photographed was placed on the microscope stage and taped into place. Photographs were taken with an exposure time of $1/250^{\text{th}}$ of a second with the flash on full power using an optional remote cable to reduce vibration. Certain tests required single shots while other tests required photographs to be taken in “burst mode.” In burst mode, the camera shoots 5 frames per second at equal intervals. The images were stored on a 2GB compact flash card and transferred to a PC via a multi-slot card reader. The images were loaded into Adobe CS3 to be resized, to adjust the

levels (contrast, brightness, color), and to be sharpened, generally using the “unsharp mask” filter. This was done so that the features in the tubes could be better seen and identified. The images were analyzed one by one with the naked eye either on a 0.6 m (22”) LCD monitor or via color prints from a color laser printer.

Model Test—Teflon® tubing (McMaster-Carr Company) with different internal diameters and lengths was used to create the flow regime maps. The gas pressure for these experiments was set at desired values from 0 to 552 kPa (0 to 80 psi) at the second regulator. The liquid flow rate was varied from a low flow rate of about 3 mL/min to a high flow of about 120 mL/min, or higher if necessary. Images were taken at generally 5 positions measured from the inlet along the length of each tube (generally about two meters in length): 1) 0.350–0.45 m; 2) 0.65–0.75 m; 3) 1.10–1.20 m; 4) 1.43–1.65 m; and 5) 1.90–2.10 m near the end of the tube. At each position, microphotographs were taken at a range of flow rates, from low to high, with a total of 5 and 9 flow rate steps in each test. 20–30 photographs were taken for each position for analysis.

Image Analysis and Map Construction—The image analysis consisted of examination of all microphotographs obtained from each combination of flow rates and channel positions to determine the prevailing surface flow entities and hydrodynamic modes. The surface flow entities of interest included rivulets (straight and meandering), droplets (random), linear droplet arrays (LDA), sub-rivulets, sub-rivulets “fingering” off of the main rivulet, sub-rivulet fragments, turbulent/foamy rivulets, liquid films, foam, and all transition points between these features. These liquid features were used to describe various modes of flow (flow regimes) and these modes were then put into “maps” which show the prevailing modes of flow as a function of distance from tube inlet at different liquid flow rates at the selected air pressure. Qualitative features were used to define the flow regimes observed and quantitative analyses of images were used to compute the Treatment Number.

Method to Make Two-phase Flow in Minitubes—Two-phase flow has traditionally been generated by introducing a liquid mist into a turbulent gas/air stream. The air velocity necessary for providing quasi-steady coupling of mist deposition and mist generation in large tubes is above 80 m/s. To achieve such velocities in narrow long tubes, the necessary air pressure would have to exceed the pressure limitation specified for flexible endoscopes, normally 110 to 193 kPa (16 to 28 psi). Taking this constraint into consideration, when the cleaning solution was introduced into the air stream in the minitubes at about 207 kPa (30 psi), no atomization was used in our experiments. The liquid was introduced into the tube along with air at the specified flow rates and the liquid-to-air ratio needed for the test.

4. Visualization of Rivulet Droplet Flow in Long Narrow Minitubes

Among the many thousands of images acquired by high-speed video-microscopy, we demonstrate only a few. On different images, the liquid splits into different shapes and geometries referred to in this paper as “surface flow entities,” and different kinds of surface flow entities have been identified in our study. Due to the large number of combinations, comprehensive analysis of all surface flow entities would be difficult. For this reason, we focus only on key sliding entities to illustrate the hydrodynamic modes and on the associated physical interpretations. Some general conclusions could only be made after the relationships between the different kinds of sliding species were understood. In this paper, we discriminate such sliding entities in Fig 10, which include: main rivulet, sub-rivulets, sub-rivulet fragments, sliding droplets and sliding droplet arrays.

4.1. Rivulet meandering in minitubes

While a single rivulet is only present in the vicinity of the tube entrance, additional surface flow entities were observed downstream. All these sliding entities originate from the main rivulet. Understanding rivulet behavior is therefore important in identifying the mechanisms of rivulet transformation into the other surface flowing entities.

One of the central features that we have observed in many images was that the bottom rivulet rises along the tube wall towards its ceiling (Fig.11) and afterwards sinks to its bottom, as illustrated by the drawing in Fig.12a. This meandering movement takes place simultaneously with the predominating axial movement of the rivulet which is driven by the air stream. Rivulet meandering in the minitube extends over both the left-side and the right-side walls of the horizontally-positioned tube. Sometimes the rivulet meanders until it reaches the tube exit and sometimes its amplitude decreases downstream depending on the flow conditions used. This behavior may also be caused by bubbles whose concentration increases downstream when surfactants are used.

The rivulet trajectory is not steady. The steady sinuous-like trajectory can be described by the introduction of only the local axial velocity whose direction changes along the tube but does not depend on time. For the characterization of a non-steady meandering rivulet, two components of velocity have to be introduced for any of its cross-sections: local axial velocity and local transverse velocity. Both local axial velocity $U_{ax}(t)$ and local transverse velocity $U_{tr}(t)$ are periodical functions of time (Fig. 12b).

4.2. Sub-rivulet separation from main rivulet

At about 193 kPa (28 psi) air pressure, rivulets with diameters many times smaller than the main rivulet are observed in the majority of the images. We call them sub-rivulets because their origination from the main rivulet can be readily identified in the images. The image shown in Fig.10 demonstrates the main rivulet on the tube bottom and two sub-rivulets on the tube ceiling. Fig.13 shows a sub-rivulet separating from the main rivulet like a branch from a tree. This and other similar images show that this separation occurs mostly at the top position of a meandering rivulet when it suddenly changes its flow direction from the top to the bottom of the tube. We call this the “sinking” portion of the rivulet.

In existing models, the rivulet cross-section can be divided into several segments. Because the velocity of a liquid film decreases rapidly with decreasing film thickness, the velocity near the rivulet edge is very small in comparison with the velocity of its central core (Fig. 14a). This observation does not violate rivulet flow integrity when the rivulet flow is straight. When the rivulet at the top position in the tube changes the direction of its movement, separation of its slow edge from its rapid core is possible (Fig. 14b). This process is significantly facilitated by the air stream.

In its top position, the meandering rivulet moves almost in a horizontal position. In the sinking portion of the meandering rivulet, gravity creates the transversor vertical component of velocity.

During sinking, when the rivulet moves from its top position, the edge of the rivulet moves more slowly in comparison with the rivulet core. This delay results in stretching the edge zone of the rivulet in the vertical direction and decreases its connection with the main rivulet stream (Fig. 15). The main rivulet normally moves axially due to shear stress caused by the air stream and moves vertically due to gravity. The stretched edge moves axially because the gravitational force acting on it is negligible due to its small thickness. The stretched edge separates from the main rivulet (as a sub-rivulet) due to this difference in the direction of their movements, as illustrated by Fig 16.

The frequency of sub-rivulet formation from the main rivulet in the case of pure water is rather low. However, the addition of some surfactants drastically increases the frequency of sub-rivulet formation. The sub-rivulet cross-section is very sensitive to the action of surfactants as well. This cross-section is rather small when the liquid phase is pure water. We observed that the addition of some surfactant leads to a significant increase in the sub-rivulet diameter by about 3 times. Since sub-rivulet formation is accompanied by an increase in surface area which is accompanied by an increase in surface energy, the process for sub-rivulet formation is hampered. One may conclude that decreasing the water surface energy should promote sub-rivulet formation.

The real mechanism of surfactant influence may be more complicated due to the shrinkage of water surface preceding sub-rivulet formation followed by its stretching. Quantification of the concomitant Marangoni stresses is extremely difficult in this case because of the unknown two-dimensional distribution of surface velocity during rivulet meandering.

4.3. Sub-rivulet fragmentation due to Rayleigh instabilities

Rayleigh instability predisposes a rivulet to break up, just as it predisposes a free jet to break into droplets. This is confirmed by our observations and is documented in the majority of the high-speed images obtained during our investigation. The images shown in Fig.17 show the typical periodic structure of the sub-rivulet in the form of periodic distribution of “necks.” However, there is an essential difference from the observation of the classical Rayleigh destabilization of “free jet.”

In the situation of a free jet, as soon as a cylindrical fragment of a free jet forms, it momentarily shrinks into a droplet. Droplets are usually seen in images of free jet, while pre-existing cylinder-like fragments are not visible. In contrast, during two-phase flow in minitubes, sub-rivulet fragments are seen during sub-rivulet destabilization without any rapid visible transformation into a droplet. This is because the onset of strong viscous resistance on the boundary with the tube wall retards the process of transformation into droplets. The reason why gaps between adjacent potential fragments do not form is because the potential fragments move with the same axial velocity, while their transverse displacement is hampered by the hydrophobicity of Teflon®.

In spite of these complexities, there are some mechanisms which promote the expansion of gaps between sequent potential sub-rivulet fragments (SRF) which then leads to the formation of a linear array of SRF (LASRF). Our visualization revealed LASRFs on large portions of the images (Figs. 18, 19 and 20).

In addition to LASRFs, random distribution of SRFs with respect to their axial and radial positions in the tube occurs often. The example provided in Fig. 21 corresponds to the simultaneous fragmentation of at least two (2) sub-rivulets because a rather large number of SRFs within one cross-section of the tube cannot be explained by the fragmentation of a single sub-rivulet.

The separation of SRF from LASRF in the transversal direction may occur under the influence of wall inhomogeneity. Among the many types of fragments arising from surface inhomogeneity, we consider the presence of attached droplets. When the LASRF's front or its potential fragment meets an attached droplet, the direction of sliding is affected and mainly causes a deviation from the strict axial direction. This in turn causes a transversal displacement of sequent potential sub-rivulet fragments. As the wall coverage with the attached droplet is rather high, the above process appears to occur frequently leading to the transformation of a LASRF into an array of rivulet fragments where any one of them appears to possess an individual trajectory (Fig. 21).

4.4. Sub-rivulet fragmentation due to sinuous instability

This kind of instability is well-known for free jet (Fig.8) [72] and replaces the Rayleigh instability with a further increase in jet velocity. The next image (Fig. 22) demonstrates a sub-rivulet in the state of sinuous instability during the separation process of a sub-rivulet fragment. It is obvious that due to the spontaneous transversal displacement, the separation of rivulet fragments is easy.

4.5. Surfactant stabilizes sub-rivulets

For free jet, it is well known that surfactants may suppress Rayleigh waves and that the jet becomes more stable due to Marangoni stress [108]. As neck formation is normally accompanied by local stretching of the liquid-air interface, this stretching leads to a local decrease in the surface concentration of the surfactant which in turn results in a local surface tension gradient. This situation causes Marangoni flow towards the stretched sections where neck formation would be possible. Based on these scenarios, it is obvious that the dynamics of surfactant adsorption, i.e., the dynamic surface tension, is manifested in this stabilization mechanism.

An extreme manifestation of the suppression of Rayleigh instability is the formation of long sub-rivulets without any features of instability when some surfactants are used, as shown in Fig. 22(a,b,c), where neither periodic necks nor sub-rivulet fragments are present. This is in striking contrast with the pure water case (Section 4.6) where many images demonstrate sub-rivulet fragments while the sub-rivulet itself was not detected.

4.6. Peculiarities of rivulet fragment flow of pure water

With pure water, the separation of a sub-rivulet from a rivulet occurs rather infrequently. On the other hand, the frequency of sub-rivulet fragmentation is rather high. Although few images demonstrate the presence of some rivulet fragments (RFs), the sub-rivulet itself was not detected in the majority of images [23]. This indicates that the lifetime of a sub-rivulet is rather short, and as a consequence, a larger number of images had to be inspected to detect the presence of sub-rivulets.

Interestingly, RFs have no tails and almost no linear droplet arrays were present in the water case. This indicates that sliding of RFs occurs in the meniscus regime which promotes the preservation of their integrity. Two factors prevent the transition to the meniscus regime of sliding RFs. The equilibrium contact angle for water on Teflon® is rather high, about 101° . Although the receding contact angle is much smaller, the receding meniscus preserves. The not so large sliding velocity is favorable in the preservation of the receding contact angle as well. The latter is not high because the height of RFs is small in the pure water case. This restricts the magnitude of the aerodynamic drag force which affects the sliding velocity.

4.7. Surfactant influence on the evolution of rivulet fragment

When the contact angle decreases due to the presence of a surfactant, a large decrease in the receding contact angle occurs and this facilitates the transition to the film regime of a sliding entity. However, as was discussed in Section 2.7, the receding meniscus may attain the shape inherent in the cornered droplet case. This is observed in the majority of images, for example, the image of Fig. 24. According to Fig. 6b, the corner transits into a micro-rivulet, which is very unstable. The elongated fragments of the unstable micro-rivulet are seen in Fig. 24, and their transformation into droplets is retarded due to the viscous stress on the wall. In addition, the fragments arising during atomization of a free jet are initially not spherical. However, this is not easily visible because their transition to the spherical shape is not retarded by the viscous interaction with the wall in contrast to our case.

As sliding of a sub-rivulet fragment is accompanied by the permanent loss of sliding droplets, it shrinks gradually in the axial direction and finally transforms into a sliding cornered droplet and into a linear array of smaller droplets, which may either slide or become immobile.

4.8. Surfactants classification on the basis of image analysis

Group I: Surfactants, hydrotropes and dispersants with behavior similar to that of pure water

—When the decrease in surface tension is rather small due to the addition of a surfactant in this group (from 72 to about 55 dynes/cm), there was no essential difference in the rivulet-droplet flow modes observed in comparison with the pure water case. The flow mode with the application of this group of surfactants is characterized by the features described in Section 4.6, and presented in Fig. 23. Examples of the surfactants of this group are listed in Table 1. The surface tension cannot be decreased below 55 dynes/cm when using these surfactants.

Group II: Low surface tension surfactants that stabilize Rayleigh waves and decrease sub-rivulet fragmentation

—In the opposite spectrum of surfactants, where it is possible to achieve low surface tension, there is an essential qualitative distinction in the features of two-phase flow modes, as described in Section 4.5. In this case, the Rayleigh waves are suppressed due to the Marangoni effect, which is enhanced with this kind of surfactants, and the sub-rivulets survive for a long time. Accordingly, the concentration of sub-rivulet fragments and sliding droplets is low in the presence of these surfactants. As the contact angle decreases in the presence of these surfactants, wall wetting predominates. This in turn suppresses rivulet meandering, which is considered the most important feature of the rivulet-droplet mode. Consequently, this class of surfactants is not the most interesting with respect to sub-rivulet fragmentation and to the creation of rivulet-droplet flow. Many of the surfactants tested in this group are listed in Table 2. The surface tension normally decreases below 35 dynes/cm when using these surfactants.

Group III: Intermediate surface tension surfactants with maximum sub-rivulet fragmentation

—The most interesting surfactants with respect to rivulet-droplet flow in long minitubes are those belonging to Group III, with examples provided in Table 3. The minimal surface tension achievable with these surfactants is in the range of 35–45 dynes/cm at 0.1% concentration. The application of surfactants in this group at the proper concentration (about 0.05%) simultaneously provides high frequency of sub-rivulet formation and results in significant sub-rivulet fragmentation. The use of these surfactants leads to the maximal coverage of the tube wall by sub-rivulet fragments.

Group IV: Low surface tension surfactants that lead to liquid film formation in minitubes

—These surfactants are characterized by very low surface tension and by a low HLB number. Solutions of such surfactants, even at low concentrations (0.05%), lead to the formation of an annular film which covers the majority of the tube surface. Members of this group overlap with those of Group II, but with a high tendency to stabilize the surface film, and this results in the formation of annular film. Examples of surfactants in this group are provided in Table 4.

Group V: Low surface tension surfactants that lead to excessive foam formation in minitubes

—Surfactants in this group are characterized by low surface tension and high hydrophilic-lipophilic balance (HLB) values. They tend to form stable foam which fills and covers the entire surface of minitubes during two-phase flow. Examples of the surfactants in this group are provided in Table 5.

5. Flow Regime Maps for Rivulet Droplet Flow in Long Minutubes

Analysis of the high-speed images acquired during the two-phase flow in minitubes (Section 4) allowed us to investigate the different sliding flow entities and to follow their evolution along the tube length. The information regarding the evolution of various surface flow entities along the tube was used to develop a qualitative model for this kind of two-phase flow and to represent its characteristics in the form of new informative flow maps. These flow maps are different from those used to characterize two-phase flow regimes (Figs. 2a and 2b) [50].

It turned out that the traditional characterization of two-phase flow maps [13,14], where the coordinates are superficial velocity for air (or its pressure) and superficial velocity for liquid, represents an oversimplified approach since the focus is mostly based on the nature of the core bulk flow inside the tube. Our flow maps which characterize the surface flow features along the tube length provide different information regarding the processes that determine the axial dependence on the development of the rivulet-droplet flow with emphasis on wetting and capillary processes and on related problems of instability.

As the evolution of rivulet-droplet flow is characterized by the sequence of qualitatively different stages, the axial dependence has to be an essential component in the characterization of this type of flow, and this information is well-captured in our flow maps. Taking this into account, we chose the distance to tube entrance and liquid flow rate as coordinates in our maps to better characterize rivulet-droplet flow in minitubes.

As to air pressure, there are constraints at low and high pressures. A rather low air pressure is not sufficient for the onset of rivulet meandering, while meandering is the valuable property of rivulets. Also, higher pressures are not acceptable because the transparent tubes are not rated for high pressures, and it becomes difficult to make visual observations during the flow. Hence, the visualization used to construct our flow maps was accomplished at the invariant pressure of 207 kPa (30 psi). Naturally, the large deviation from this pressure may lead to significant deviation from the generalizations made in this study, which was limited to pressures in the range of 207 – 345 kPa (30–50 psi).

In addition to the unusual strong axial dependence, the second peculiarity of rivulet-droplet flow is related to its high sensitivities to surfactants. Therefore, no universal map is possible which will cover the characteristics of two-phase flow for all surfactants. However, maps may be specified for the several groups of surfactants introduced in Section 4.8. To cover the overall picture of two-phase flow in minitubes, we only present maps of surfactants in Group III which provide, simultaneously, a large frequency of sub-rivulet formation and a large frequency of sub-rivulet fragmentation.

Visualization of two-phase flow in minitubes revealed a strong influence of tube diameter on rivulet meandering and on the corresponding flow regime. When the tube diameter exceeds 6 mm, a condition favorable to achieving high velocity with the concomitant onset of roll waves at the liquid-air interface, the annular-mist flow arises which complicates the detection of the rivulet downstream. When the tube diameter is much smaller than 0.6 mm, the large velocity necessary for the onset of rivulet meandering cannot be readily achieved at the 207 kPa (30 psi) air pressure. Hence, we do not present data for tubes with 0.6 mm diameter and smaller, a situation which requires special considerations.

The range of liquid flow rates used to prepare the two-phase flow used in different tube diameters was adjusted to provide approximately quality $\times$ about 1, i.e., WAVR about 1 to 1000. As the rivulet undergoes large and different transformations during meandering, and since these transformations depend on many parameters (liquid flow rate, surfactant nature/

concentration and the distance to the entrance), some of the important modes of the rivulet-droplet flow will need to be introduced. The analysis of the images and their dependence on flow rate and on the distance to tube exit allowed us to introduce five (5) modes.

In cases where a surfactant is likely to create an annular film (Group IV), the main bottom rivulet is generally wide and flat. Sub-rivulets do not readily branch off of the main rivulet. Instead they begin to break away from the main rivulet and “drag” the main rivulet with them creating something that looks like wave crashing on the lumen of the tube. This wave crashes back into the main rivulet, and after repeated “waves” and “crashes,” the main rivulet becomes wider and wider until there is an annular “wave head” which constitutes the leading edge of the annular film. This annular film is highly dependent on liquid and gas flow rates, surfactant type and surfactant concentration, as well as on the axial position in the tube. In general, we believe that the annular film is created in the middle-front to middle of the tube at higher concentrations of surfactants and at high liquid flow-rates. We have some but a very limited number of photographic evidence to support this theory. The main concern we have is that shifting parameters slightly in one direction can turn a surfactant “that creates annular film” into one that creates rivulet-droplet flow (RDF), as long as foam formation is not significant. There are very few surfactants that can sustain a “group” or “class” characteristic across a range of parameters. The “film forming Group IV” and the “long sub-rivulet without sub-rivulet fragment (Group II)” classes are highly specific, with very few if any surfactants achieving these conditions. It is easier to classify surfactants into the “water like,” the “intermediate” (RDF), and the “foam” classes.

The established dry/sparse mode corresponds to our experience in experiments with rivulet sliding along an inclined plane. At very small flow rate, sparse sliding droplets form, while the continuous rivulet forms only above a critical liquid flow rate.

For the onset of sub-rivulet separation from the main rivulet, two conditions are necessary: i) rivulet meandering, and ii) sufficiently high air velocity. Both conditions cannot be satisfied near the inlet section of the tube of the continuous rivulet formation. The onset of meandering occurs downstream, and at some critical air velocity, separation of sub-rivulet from the main rivulet occurs. This determines the location of the zone of the single rivulet along the tube axis.

Sub-rivulet fragmentation is a rather slow process because of the difficulty of separation of sub-rivulet fragments in the transversal direction. This is confirmed by the presence of images with sub-rivulets in the state preceding the separation of sub-rivulet fragments (Fig. 18). This mainly occurs in the middle zone of the tube where the sub-rivulet formation predominates; we call this the “ejection zone.”

The longer the distance from the inlet of the tube where air velocity becomes higher, the larger the amount of sub-rivulets produced by the meandering rivulet and the larger the amount of sub-rivulets transformed into sub-rivulet fragments and sliding droplets will be. This indicates that the concentration of sub-rivulet fragments and random droplets has to increase downstream, which is confirmed by visualization. This takes place within a zone along the tube (called “mixed zone”) because the sub-rivulets are present together with the products of their fragmentation. The formation of an annular film some distance from the exit due to rivulet meandering will be considered in the next section.

Although the evolution of rivulet-sub-rivulet-droplet flow is deterministic, the events are random because the evolution originates from different kinds of instabilities. In spite of this random feature of events, it was sufficient to make about 20 measurements for different combinations of positions along the tube (x) and flow rates to specify the location and the width for the strips. However, at least 100 strip positions and their width must be specified

to establish the boundary for one zone. This yields about 10^4 measurements to construct one flow map.

6. Discussion

6.1. Rivulet flow without surfactant

6.1.1. New hydrodynamic mode—While the study of rivulet flow down an inclined plate has attracted much attention (Section 2.4), to our knowledge, the rivulet in minitubes has been reported in only one publication [50]. Also, systematic studies of rivulet flow down an inclined plate are not sufficient to make reliable predictions to describe rivulet flow in minitubes. This is because the parallel streams of liquid and air conditions assumed in modeling the inclined plate cases are not valid for rivulet flow in minitubes. Although our visualization results, Section 4, revealed many common features of rivulet flow in minitubes and on flat surfaces (Section 2.4), new hydrodynamic modes were discovered in minitubes in addition to the one reported in [50]. In [50], either rivulet flow was observed or sub-rivulets were formed when the air velocity was increased above a critical value. The process of sub-rivulet formation was characterized in [50] as: “with higher gas velocity the rivulet breaks up into several rivulets.” In contrast to the latter statement, in our case both the rivulet and sub-rivulets were found to coexist in thousands of images during our investigations of the flow in minitubes. In our case, we found that the birth of a sub-rivulet occurs without the disappearance of the original rivulet. Some images (e.g., Fig. 13) document the initial stage of sub-rivulet formation, where the sub-rivulet is seen to branch out of the primary rivulet.

In minitubes, the separation of a sub-rivulet due to the aerodynamic drag force may be possible due to the abrupt change in rivulet direction and to the rapid variation in rivulet height in the vertical direction near its edge (Figs. 15 and 16). This branching off process may sometimes occur along the rivulet trajectory and may be qualified as a new mode of rivulet destabilization.

6.1.2. Main features of rivulet/sub-rivulet flow without surfactant—In the case of pure water (no surfactant), in spite of the separation of sub-rivulets, the rivulet exists along the entire tube length (about two meters). Within any cross-section of a minitube, the sub-rivulet mass flux is very small in comparison with the main rivulet mass flux, and there is no qualitative change in either rivulet or sub-rivulet flow downstream. In the absence of a surfactant, the range of sub-rivulet diameters is rather narrow, while there is a rather broad distribution in their length. As linear arrays of sub-rivulets are absent in this case, there is no basis for stating that a significant fragmentation process occurs after sub-rivulet separation from the rivulet.

6.1.3. Influence of air velocity, liquid flow rate and tube diameter—As the liquid flow experiences aerodynamic drag force, a critical velocity exists for the onset of rivulet meandering. In tubes with a diameter of about 6 mm, an air velocity of about 100 m/sec was achieved, and at this high velocity, the rivulet is directly destabilized by waves, a process that directly leads to mist formation. There is a first critical flow rate for the transition from dripping flow to the rivulet flow and a second critical flow rate for the onset of rivulet meandering. These regularities are common for rivulet flow along a flat surface (Section 2.4) and in minitubes (Section 4).

At air pressure of about 207 kPa (30 psi), the range of tube diameters when the rivulet/sub-rivulet flow takes place is $0.6 \text{ mm} < d_t < 6 \text{ mm}$. Although we observed rivulet flow in tubes with diameter 0.6 mm, the flow map generated was not very informative compared to the flow map for larger diameter minitubes.

6.2. Surfactant influence on rivulet flow

6.2.1. New hydrodynamic modes—In the presence of some specific surfactants, sub-rivulet fragmentation leads to the evolution of many forms of surface flow entities on the tube walls, including: linear arrays of sub-rivulet fragments (LASRF), separate sub-rivulet fragments, linear droplet arrays, cornered droplets and separate sliding droplets. The conditions for the onset of this new hydrodynamic mode in minitubes are characterized in our flow maps (Figs. 25a and 25b), and referred to as “mixed mode.”

6.2.2. Influence on rivulet meandering—When the frequency of sub-rivulet separation increases, the meandering of the main rivulet is altered downstream. Also, a larger influence on rivulet meandering is caused by the gradual formation of annular film downstream. This foam-film formation mode is enhanced by the presence of a surfactant and becomes visible if the surfactant used does not normally promote foam formation. Rivulet meandering may also be hampered because of the rheological properties of foam. This may be similar to the conditions arising from increasing the liquid viscosity, which also hampers meandering and associated sub-rivulet formation [57]. This may explain the reasons for the decrease in the amplitude of the meandering rivulet downstream that is observed in minitubes.

6.2.3. Influence on the frequency of sub-rivulet formation—If the liquid is characterized by minimal (low) surface tension, which can be provided by adding a surfactant, the influence on the frequency of sub-rivulet formation appears to be dependent on surface tension. This dependence is very similar to the one characterized in Fig. 4 for rivulet flow on a flat surface. The higher rate of sub-rivulet production is inherent to the Group III surfactants (intermediate surface tension), examples of which are listed in Table 3.

The larger coverage of the tube wall by SFEs and the larger portion of mass flow of SFEs characterize the frequency of sub-rivulet formation whose determination by direct observation is not easy. The higher level of these characteristics is also inherent to the Group III surfactants (Table 3).

6.2.4. Influence of surfactants on sub-rivulet stability—The sequence of “necks” inherent in varicose instability is seen in Fig. 17. The varicose mode, a form of Rayleigh instability, is discussed in the stability analyses of rivulets on a flat surface. However, the influence of surfactants on the varicose instability of rivulets is unknown.

6.2.5. Suppression of varicose instability by surfactants—While linear arrays of sub-rivulet fragments (LASRFs) are formed due to Rayleigh instability, the presence of very long sub-rivulets means that Group II surfactants (Table 2) are able to suppress the varicose instability. This is well known due to the systematic investigations of Levich [112]. There are few papers [105, 106] devoted to surfactant influence on rivulet formation. However, the present topic differs from surfactant influence on the stability of the existing rivulet.

6.2.6. Surfactant classification—Although the influence of tested surfactants on equilibrium surface tension is established, there is no available information regarding their dynamic surface tension, or their dynamic wetting properties. Although the importance of dynamic surface tension is obvious, we were forced to classify the tested surfactants according to their equilibrium surface tension. On the other hand, the surface elasticity resulting from the Marangoni effect is not a material parameter and is dependent on other difficult to measure parameters, including: Gibbs elasticity, diffusion in bulk, adsorption kinetics and other parameters.

6.2.7. Influence on rivulet/sub-rivulet interaction—Many subsequent acts of sub-rivulet separation from the main rivulet occur downstream in the minitubes. This means that the quantity/number of sub-rivulets has to increase if their fragmentation is absent. However, this is not the case, and the quantity/number of sub-rivulets in the images is not more than 2 or 3 at any $\times$ (distance to entrance) within rivulet ejection or mixed zone, as characterized on the maps (Figs. 10a, 10b, 22a, 22b and 22c).

If sub-rivulet fragmentation occurs, the quantity/number of SFEs has to significantly increase downstream. Indeed, the number of droplets within the linear droplet arrays and the random sliding droplets increase downstream; however, this increase is much less than would be possible if all the sub-rivulets transformed into droplets. The absence of the essential accumulation of SFEs downstream is caused by the continuous capture of SFEs by the meandering rivulet. This is likely the main mechanism that determines the distribution of SFEs during two-phase flow in minitubes.

Another complementary scenario is also possible when the amplitude of rivulet meandering decreases downstream; SFEs on the tube top may reach the tube exit. SFEs are observed on the tube top and the rivulet is observed near the tube bottom at a large distance to the tube exit. As the surfactant promotes the formation of annular film while it hampers meandering, the surfactant affects rivulet-sub-rivulet interaction. The meandering of the rivulet formed between two parallel plates was investigated in [107] in the presence of surfactant. The thin film formed near the rivulet three-phase contact line contributed to rivulet stabilization [107].

6.2.8. Surfactant influence on the formation of annular film—As long as the sliding occurs in the meniscus regime, it does not contribute to wall wetting. The sliding of cornered droplets appears to occur either in the meniscus regime or when a rivulet is formed and then transforms into a linear droplet array (Fig. 6b). One concludes that the last stage of SFEs evolution is the formation of immobile droplets which is manifested as linear droplet arrays (LDAs). These may accumulate during the experiment if the meandering amplitude decreases downstream. This occurs particularly downstream when the addition of surfactant promotes the formation of linear droplet arrays. When a sufficiently high coverage by sessile droplets is achieved, their phase lines may overlap which will cause their coalescence leading to the gradual formation of annular film near the tube exit. The lower contact angle, achieved due to the surfactant, promotes this process. However, this mechanism cannot explain the formation of the annular film not far from the entrance at a not low flow rate, which is seen on the maps.

During the sinking phase of a meandering rivulet inside the tube, its side meniscus recedes. As the meandering is a rather rapid process, the movement of the side three-phase line may occur in the film regime, which leads to annular film formation when the rivulet sinks. The smaller the contact angle is, the lower the critical velocity for the onset of film regime sliding will be. The presence of surfactants decreases the contact angle which contributes to the onset of the film regime of meniscus receding and to the formation of annular film.

6.3. Comparison of surfactant influence on the stability of free jet and of sub-rivulets in minitubes

6.3.1. Rayleigh instability—Drawing an analogy with free-jet destabilization is helpful in explaining the evolution in time of an air-driven sub-rivulet in minitubes. For both systems, the Rayleigh instability is of primary significance. The free jet finally transforms into a free droplet spray. The sub-rivulet in minitubes finally transforms into a sliding droplet array. However, there are many intermediate processes between the initial sub-rivulet and the sliding droplets in the latter case. Although a close analogy in Rayleigh

instability exists for both free jet and sliding straight sub-rivulet, a sub-rivulet fragment exists for a rather long time and this can be qualified as a new capillary hydrodynamic phenomenon, while the cylindrical fragment of free jet momentarily transforms into droplets.

To our knowledge, theoretical and experimental information regarding shear-driven surfactant-laden straight rivulet is lacking in the investigations of a rivulet on a flat surface. Perhaps the difference between the straight sub-rivulet sliding along the internal surface of a minitube and the shear-driven rivulet on a flat surface is not too large. If this is the case, the images obtained for the straight sub-rivulet in minitubes may be considered in predicting the behavior of a shear-driven straight rivulet on a flat surface.

The interaction of a sub-rivulet with the tube wall, which is absent in the case of a free jet, stabilizes the sub-rivulet and retards fragmentation due to Rayleigh waves. The shorter the dimensionless length of free jet L/d (d being the jet diameter) is, the stronger will be its instability. According to our observations, this ratio, where L and d are sub-rivulet length and diameter respectively, may be orders of magnitude larger compared to a free jet. This is the quantitative characterization of the hampering Rayleigh waves due to the wall-sub-rivulet interaction.

This interaction is the smallest when the contact angle equals 180° and the contact area with the tube wall is a straight line. Perhaps the Rayleigh theory for free jet is more or less valid for this hypothetical case. The smaller the contact angle is, the stronger the rivulet attraction to the tube wall will be, and correspondingly, the stronger the hampering Rayleigh waves due to surface wetting.

6.3.2. Sinuous instability—The transition from axisymmetric waves to sinuous waves occurs with the increasing velocity of free jet [72], and this leads to its momentary splitting into droplets (Fig. 8). On the other hand, the wall-sub-rivulet interaction hampers sinuous instability. The existence of a rather long sub-rivulet of sinuous-like and straight form is confirmed by inspection of the sequence of images, as illustrated by the image in Fig. 22. Similar to the linear array of SRFs, the sinuous array of SRFs is observed on many images. This means that the strong attraction of SRFs to the wall opposes their transverse displacements.

6.4. Hydrodynamic modes favorable for cleaning minitubes and channels

Based on our experimental results regarding the effective cleaning of minitubes, we found that the motion of the contact line of sliding flow entities on the dry regions of the tube surface to be the most important in creating the large hydrodynamic detachment forces sufficient to lift or dislodge strongly-attached contaminant particles from the tube surface. In order to realize this favorable hydrodynamic mode, the solid surface needs to be dry (no annular film) before the rivulet, sub-rivulet, sub-rivulet fragments, or drops move onto it to effect this high degree of cleaning. The role of surfactants has been found to be critical in obtaining high coverage of the tube surface with sliding surface flow entities provided that other conditions are satisfied. Therefore, tube surface hydrophobicity, liquid-to-air ratio, type and concentration of the surfactant, and air velocity all need to be selected to satisfy the conditions necessary to achieve high-level cleaning of minitubes, especially when high air pressure cannot be used such as in the case of flexible endoscopes.

In order to achieve high-level cleaning of minitubes, especially regarding the removal of highly-adhered micron and submicron contaminant particles from the tube wall, two opposing requirements have to be satisfied: i) the annular film has to be absent, and ii) the amount of sub-rivulet fragments has to be high. The second requirement is necessary to

sweep the entire tube surface by sub-rivulet fragments during the short time available for cleaning the endoscopes. The controversy between the above two requirements arises because the high amount and velocity of sliding surface flow entities is likely to lead to annular film formation.

Attention to the recent achievements in wetting dynamics (Section 2.6) and the systematic characterization of rivulet-droplet flow by the construction of new types of flow maps (Section 5) allowed us to overcome the above contradiction and to discover the optimal conditions needed to achieve advanced cleaning. This achievement has been possible due to two discoveries:

1. There is a sliding mode of sub-rivulet fragments similar to that of the sliding of cornered droplets (Fig. 6b) when either no annular film is formed or only a linear droplet array is formed (e.g., Fig. 24), and
2. There is a narrow range of flow rates of the surfactant solution when the coverage of the tube wall by linear arrays of sliding sub-rivulet fragments is not sufficient for the transition to annular film. The selection of special surfactants is necessary to satisfy these conditions.

Both discoveries could not be predicted because the phenomenon of sub-rivulet fragmentation was unknown and there is no quantitative model for the transition of two-dimensional droplet arrays to annular film. However, these discoveries were possible due to the planning of experiments based on the recent achievements in wetting dynamics (Section 2.6), rivulet flow (Section 2.4) and two-phase flow in narrow tubes (Section 2.1).

7. Future Directions

This research arose neither as the next problem in two-phase flow nor as an investigation of surfactant influence on rivulet flow on a flat surface which has been systematically investigated in fluid mechanics. While qualitative interpretation of our findings was possible taking into account the phenomena known in wetting dynamics and interfacial hydrodynamics (Marangoni stress, Rayleigh instability, forced wetting, meniscus regime of sliding, cornered droplets, etc.), the novel and most important phenomenon, namely sub-rivulet branching off of a meandering rivulet, is not completely understood. Although an explanation for this phenomenon (Figs.15 and 16) is proposed, it does not eliminate the possibility of alternate mechanisms.

The above phenomenon plays a role in the destabilization of meandering rivulets similar to the role of Rayleigh or sinuous instability in the collapse of a free jet. In distinction from a free jet, the sensitivity of a meandering rivulet on the presence of a surfactant and its nature is extremely significant. Neither the theory of meandering in a tube nor the theory of surfactant-laden rivulets on a flat surface has been previously reported. In the meantime, new understanding regarding the enhancement of sub-rivulet formation due to surfactant addition needs at least the combination of two theories, which do not as yet exist. The scientific significance of this new phenomenon is that the surfactants enhance the branching off of sub-rivulets, which is distinct from the known suppression of free jet decay due to surfactants.

Taking into account this broad gap between the experimental findings, the enhancement of branching off due to the surfactant, and the state of relevant theories, a proper next step would be the examination of the possibility of reproducing the branching-off phenomenon for a surfactant-laden rivulet meandering on a flat surface. If this phenomenon can be reproduced under simpler conditions (flat surface), the development of the theory would be possible.

It is remarkable that the splitting of the rivulet flowing down an inclined flat surface is known and even modeled [57]. However, the model of [57] differs from our experimental findings. First, the splitting is not branched off. Second, the shear-driven rivulet may be important in this case. On the other hand, the mechanism illustrated by Figs. 15 and 16 may be appropriate (or not) in the case of a flat surface as well. The example described in this review points to the necessity of an interdisciplinary approach.

The large success in annular flow achieved during the past 60–80 years is summarized in monographs [14, 38]. The strong influence of surface tension and tube wettability for narrow tubes was established in the 1990's, which led to the understanding of the possible influence of surfactants. Although the manifestation of this influence was revealed for other hydrodynamic modes, the selection of surfactants, which greatly enhances wetting dynamics, promoted the obvious formation of annular film, which in turn prevented rivulet formation [52].

In addition to this research, which has not promised any new interesting phenomena due to surfactants, the extreme difficulties in modeling became clear because they arose under much simpler conditions, namely, for a falling film, i.e., film sinking along an inclined surface. The further development in annular film flow and two-phase rivulet or sub-rivulet flow needs to account for the progress in liquid film stability [37], wetting dynamics [36] and interfacial rheology [93]. Perhaps the discovery of the strong influence of surfactants and their nature on sub-rivulet branching off will give new impetus to the investigation of surfactant influence on two-phase flow in narrow tubes, which is now identified as the rivulet/sub-rivulet/droplet mode. This should be an interdisciplinary investigation comprised of two-phase flow, wetting dynamics and interfacial rheology [93]. While the modeling must be accomplished by the methods of dynamics of wetting and stability of thin films, the surfactants need to be characterized by the methods of surface rheology [93].

Although the dynamics of adsorption [108] are accounted for in the equations for surfactant transport [106], this and other models regarding the role of surfactants on rivulet flow are greatly simplified and only consider the role of insoluble surfactants. In the meantime, Levich [112] emphasized that control of the concentration of insoluble surfactant under practical conditions is difficult. Accounting for surfactant solubility and convective diffusion is necessary because soluble surfactants promote sub-rivulet branching off.

In the current model of surfactant transport [106], adsorption on the water-air interface is accounted for, while recent investigations show that neglecting adsorption on the solid-air interface [109,110] and solid-water interface [111] is not always valid when the surface is hydrophobic.

Teflon is hydrophobic and the formation of annular film (Section 6.2.8) due to the accumulation of sessile droplets in linear droplet arrays depends on their spreading. Spreading over a hydrophobic surface becomes possible due to the adsorption of surfactant molecules in front of a moving triple line on a bare hydrophobic surface [110].

Both the accomplished visualization and general theoretical consideration show that almost all stages of rivulet evolution depend on the dynamic contact angle. Simultaneously, an essential change in the curvature of the contact line takes place. In the meantime, a recent investigation [111] has shown that the contact angle depends on the curvature of the three-phase line. This occurs not because of line tension but because of the adsorption at the solid-liquid interface [111]. This regularity may play a role regarding surfactant influence on rivulet flow in narrow tubes because of surfactant adsorption on the solid-liquid interface.

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Fig. 1.
Illustration characterizing different hydrodynamic flow modes [50].

(a)

(b)

Fig. 2.

Examples of flow modes in narrow tubes: a) Pyrex-water-air system ($\theta=34^\circ$); b) FEP fluoropolymer tube ($\theta=106^\circ$) [50].

Fig. 3.
a) Experimental setup used to study rivulet meandering [63]; b) Stationary meanders for $\alpha=32^\circ$, $Q=1.08$ ml/s for the left picture and $Q=1.40$ ml/s for the right one [63].

Fig. 4.
Effect of surface tension on stability domains [57].

Plan View of Process	Comments
Water comes out of the inlet hole and forms immediately into a rivulet which begins progressing downstream.
The rivulet progression stalls and the head of the rivulet begins to increase in size as it is fed by water flowing through the rivulet.
Aerodynamic load on the head becomes great enough to pull it away from the rivulet, forming a detached droplet.
The droplet elongates in the direction normal to the flow forming a roller. The roller gradually elongates and stretches in the middle.
The roller bifurcates in the middle into two smaller and slower-moving droplets, which quickly develop into smaller rollers.

Fig. 5. Typical sequence of droplet detachment and roller development and bifurcation for the terrestrial gravity experiments [64].

(a)

(b)

Fig. 6a

Fig. 6b

Fig. 6.

Fig. 6a. A plate being withdrawn from a bath of viscous liquid, with the contact line pinned at the edge of the plate: (a) Below the rivulet transition, the contact line forms a corner; (b) Above the transition, a rivulet comes out of the tip of the corner, and eventually decays into droplets [73].

Fig. 6b. Drops of silicone oil running down planes at increasing inclination. As the velocity increases, a corner first forms, which becomes unstable leading to the ejection of drops as the velocity increases [36].

Fig. 7a

Fig. 7b

Fig. 7.

Fig. 7a. Computer simulation of cornered drop formation and further ejection of droplets as a function of time [76].

Fig. 7b. Computer simulation of droplet array formation according to [76].

Fig. 8.
Image of free jet atomization: a) Fragmentation due to Rayleigh instability; b)
Fragmentation due to sinuous instability [72].

Fig. 9.
Experimental set up used to study rivulet-droplet flow in minitubes (this study).

Fig. 10a

Fig. 10b

Fig. 10.

Fig. 10a. Surface flow entities (SFEs) on the image are: sub-rivulets (A), sub-rivulet fragments (SRFs) (B), linear arrays of sub-rivulet fragments (LASRFs) (C) and linear droplet arrays (LDAs) (D) - Tube Diameter: 2.8 mm; Surfactant: Original Formulation (A 50% by weight mixture of AO-455 and Surfynol-485 -both obtained from Air Products); Liquid Flow Rate: 10 ml/min; Distance: 1.12 m.

Fig. 10b. Surface flow entities (SFEs) on the image are: rivulet, two sub-rivulets, LASRF, LDA and random droplets - Tube Diameter: 2.8 mm; Surfactant: Original Formulation; Liquid Flow Rate: 10 ml/min; Distance: 1.12 m.

Fig. 11.
Meandering rivulet and sub-rivulet - Tube Diameter: 2.8 mm; Surfactant: Original Formulation; Liquid Flow Rate: 10 ml/min; Distance: 1.12 m.

Fig. 12a

Fig. 12b

Fig. 12.

Fig. 12a. Sketch of meandering rivulet.

Fig. 12b. Illustration of kinematics of unstable meandering.

Fig. 13.
Sub-rivulet branch off of rivulet - Tube Diameter: 2.8 mm; Surfactant: Original Formulation; Liquid Flow Rate: 12 ml/min; Distance: 1.96 m.

(a)

(b)

Fig. 14.

Illustration of rivulet hydrodynamics: a) Velocity distribution over rivulet water/air interface at different distances to wall; b) rivulet edge and rivulet core.

Fig. 15. Illustration of the branching-off mechanism. Sinking velocity of rivulet edge in its top position is much smaller than that of rivulet core because the core is much thicker.

Fig. 16. Illustration of the branching-off mechanism. Sub-rivulet separates from rivulet during its sinking in its top position.

Fig. 17. Sub-rivulet and foamy rivulet. Six varicose necks are visible on sub-rivulet; they appear as darker pinched-off spots in the image - Tube Diameter: 2.8 mm; Surfactant: Original Formulation; Liquid Flow Rate: 12 ml/min; Distance: 1.96 m.

Fig. 18. Linear arrays of sub-rivulet fragments (LASRFs). The early stage of fragmentation - Tube Diameter: 4.5 mm; Surfactant: Original Formulation; Liquid Flow Rate: 32 ml/min; Distance: 1.23 m.

Fig. 19. LASRFs. The later stage of LASRF evolution. Tube Diameter: 2.8 mm; Surfactant: Original Formulation; Liquid Flow Rate: 12 ml/min; Distance: 1.12 m.

Fig. 20. LASRFs. Larger width of SRFs - Tube Diameter: 2.8 mm; Surfactant: Surfonic T-15 – 0.1%; Liquid Flow Rate: 19 ml/min; Distance: 1.46 m.

Fig. 21.
Random array of SRFs - Tube Diameter: 2.8 mm; Surfactant: Original Formulation; Liquid
Flow Rate: 18 ml/min; Distance: 1.46 m.

Fig. 22.

Stable sub-rivulets reproduced in many consecutive images: a) Tube Diameter: 2.8 mm; Surfactant: Surfynol 485 – 0.05% and Dynol 607 – 0.05%; Liquid Flow Rate: 12 ml/min; Distance: 1.25 m; b) Tube Diameter: 2.8 mm; Surfactant: Lutensol XL-40 – 0.1%; Liquid Flow Rate: 12.5 ml/min; Distance: 1.25 m; c) Tube Diameter: 2.8 mm; Surfactant: Lutensol XL-40 – 0.05%; Liquid Flow Rate: 14 ml/min; Distance: 1.25 m.

Fig. 23. Peculiarities of rivulet flow without surfactant. LASRFs, cornered droplets and LDAs are absent - Tube Diameter: 2.8 mm; Surfactant: Surfonic SX-40 – 0.1%; Liquid Flow Rate: 16 ml/min; Distance: 1.25 m.

Fig. 24.

Transformation of SRFs into LDA according to mechanism similar to that known for sliding cornered droplets (Fig. 6b). The fragments of microscopical rivulet formed near SRF corner have cylindrical shape. They transform into droplets which form LDA - Tube Diameter: 2.8 mm; Surfactant: Original Formulation; Liquid Flow Rate: 19 ml/min; Distance: 0.1 m.

Fig. 25. Flow Maps: a) Tube diameter = 1.8 mm; b) Tube diameter = 2.8 mm.

Table 1

Group I Surfactants/Hydrotropes/Dispersants – Similar to water

Commercial Designation	Chemical Name and Class	Surface Tension at 0.1% – 25°C (mN/m)	HLB	Solubility in Water
Surfonic SX-40 (Huntsman)	Xylene sulfonate (hydrotrope)	53 at 1%	N/A	Soluble
Witcolate D-510 (AkzoNobel)	2-ethylhexyl sulfate (hydrotrope)	50	N/A	Soluble
Sokalan CP5 (BASF)	Acrylic-maleic acid copolymer (MWt.=5kD)	~ 72	N/A	Soluble
Sokalan PA-30CL (BASF)	Anionic dispersant (MWt.=30kD)	~ 72	N/A	Soluble
Surfonic T2 (Huntsman)	Tallowamine ethoxylate (EO=2)	N/A	4.6	Insoluble
Surfonic T5 (Huntsman)	Tallowamine ethoxylate (EO=5)	N/A	9.0	Dispersible
Pluronic L61 (BASF)	EO-PEO copolymer	N/A	1 – 7	Insoluble

Table 2

Group II Surfactants – High surface activity (low surface tension and with stabilizing action of sub-rivulets)

Commercial Designation	Chemical Name and Class	Surface Tension at 0.1 % – 25°C (mN/m)	HLB	Solubility in Water
Tergitol TMN-3 (Dow)	Branched alkyl secondary alcohol ethoxylate (EO=3)	28	8.1	Partially Soluble
Lutensol XL 60 (BASF)	Branched alkyl secondary alcohol ethoxylate (EO=3)	27	12.5	Soluble
Lutensol XL 70 (BASF)	Branched alkyl secondary alcohol ethoxylate (EO=3)	27	12.5	Soluble
Lutensol XL 79 (BASF)	Branched alkyl secondary alcohol ethoxylate (EO=3)	27	13	Soluble
Lutensol XL 80 (BASF)	Branched alkyl secondary alcohol ethoxylate (EO=3)	27	13	Soluble
Lutensol XL 89 (BASF)	Branched alkyl secondary alcohol ethoxylate (EO=3)	27	14	Soluble
Lutensol XL 90 (BASF)	Branched alkyl secondary alcohol ethoxylate (EO=3)	27	14	Soluble
Lutensol XL 99 (BASF)	Branched alkyl secondary alcohol ethoxylate (EO=3)	27	14	Soluble
AG 6206 (AkzoNobel)	Alkyl glucoside	34	N/A	Soluble

Table 3

Group III Surfactants – Maximum fragmentation – Intermediate surface tension (34 – 50 dyne/cm)

Commercial Designation	Chemical Name and Class	Surface Tension at 0.1% – 25°C (mN/m)	HLB	Solubility in Water at 0.1%
Pluronic L31 (BASF)	EO-PEO block copolymer	47	3.5	Insoluble
Pluronic L43 (BASF)	EO-PEO block copolymer	47	10.5	Soluble
Pluronic L62D (BASF)	EO-PEO block copolymer	43	3.5	Insoluble
Pluronic L62LF (BASF)	EO-PEO block copolymer	39	3.5	Insoluble
Pluronic L31R1 (BASF)	Reverse Pluronic	34	3.5	Insoluble
Surfonic 25R2 (Huntsman)	Reverse Pluronic	38	N/A	N/A
Pluronic 10R5 (BASF)	Reverse Pluronic	51	18	Soluble
Surfonic LF-17 (Huntsman)	Ethoxylated and Propoxylated linear alcohol (C14)	33	13.7	Soluble
AO-455 (Air Products)	Amine oxide (Special composition) - Low foam	34	N/A	Soluble

Table 4

Group IV Surfactants – Low surface tension surfactants that lead to liquid film formation on Teflon mini-tubes

Commercial Designation	Chemical Name and Class	Surface Tension at 0.1 % – 25°C (mN/m)	HLB	Solubility in Water
Lutensol XL 40 (BASF)	Alkyl polyethylene glycol ether	26	7	Insoluble
Lutensol XL 50 (BASF)	Alkyl polyethylene glycol ether	26	9	Dispersible
Tetronic 1301 (BASF)	Tetrafunctional blade copolymer	33	1–7	Dispersible
Tetronic 150R1 (BASF)	Tetrafunctional blade copolymer	N/A	1–7	Dispersible
Surfonic CO-15 (Huntsman)	Castor oil ethoxylate	N/A	8.2	Dispersible

Table 5

Group V Surfactants – Low surface tension surfactants that lead to excessive foam formation in Teflon minitubes

Commercial Designation	Chemical Name and Class	Surface Tension at 0.1 % – 25°C (mN/m)	HLB	Solubility in Water
Lutensol XL 60 (BASF)	Alkyl polyethylene glycol ether	26	12	Soluble
Tergitol TMN-6 (Dow)	Branched alkyl secondary alcohol ethoxylate (EO=6)	27	13.1	Soluble
Tergitol TMN-10 (Dow)	Branched alkyl secondary alcohol ethoxylate (EO=10)	30	14.4	Soluble
Surfonic LF-17 (Huntsman)	Ethoxylated propoxylated C12-14 alcohol	33	N/A	N/A
Duomeen C (AkzoNobel)	Coco diamine	N/A	N/A	Slightly Soluble
Surfonic CO-25 (Huntsman)	Caster oil ethoxylate (EO=25)	N/A	10.7	Soluble