Chapter II

2. Literature Review

2.1. Flow in capillaries

Two-phase flow through capillary channels is considerably different from two-phase flow through larger channels: viscous \((\mu u/d)\) and interfacial \((\gamma/d)\) stresses, both inversely proportional to the diameter, are more important than inertial \((\rho u^2)\) and gravitational \((\rho g H)\) stresses.

A reasonable definition of the term capillary might be obtained by requiring the dominance of surface tension forces over buoyancy. It has been shown analytically (Bretherton, 1961) that the rise velocity of an elongated bubble in a sealed liquid phase capillary vanishes for

\[
Bo = \frac{\rho g d^2}{\gamma} < 3.368 \quad (1)
\]

This definition of a threshold diameter has the advantage of taking the effect of some fluid properties into account, but is still imperfect: it lacks viscosity as a parameter and for non-axisymmetric duct geometries, the constant in Eq.1 changes. A froth created over a fritted glass from separate gas liquid feed is used to feed the gas and liquid phases to the channels of the monolith. A chemical reaction occurs on the walls of the individual square channels where the catalyst is deposited. The characteristic of the flow field inside the liquid slug in individual square capillaries affect the overall mass transfer rate and liquid-phase residence time distribution inside the reactor. The co-current movement of air bubbles and liquid slugs has received considerable attention since the pioneering work of Fairbrother and Stubbs who used bubbles to measure the velocity of liquid inside capillaries. The primary observation was that the indicator bubble was always surrounded by a thin liquid film, hence the bubble moved faster than the average liquid velocity. The relative velocity between the bubble and liquid, \(W = (U_b - \nu_b)/U_b\) where \(U_b\) is the bubble velocity and \(\nu_b\) is the average liquid's velocity, is proportional to the square root of the capillary number of flow, \(N_{ca} = \mu U_b/\sigma\) where \(\mu\) is the viscosity of liquid and \(\sigma\) is the interfacial
tension. Taylor extended Fairbrother and Stubbs experimental results for $N_{ca}$ up to 2, found that film thickness approaches an asymptotic limit at the highest range of $N_{ca}$, and gave a rough sketch of the possible streamline patterns in the liquid phase in front of the bubble.

### 2.1.1. Flow regimes

Many flow patterns have been described for two-phase flow in capillaries. Although objective methods, e.g. based on void fraction measurements (Dowe and Rezkallah, 1999) are under development, this is usually done by visual observation, and the discrimination of the different patterns is rather subjective. Most researchers present “representative” pictures of the observed flow pattern (Fig. 1) for a schematic example. Typically with the aforementioned limitations in mind the number of different flow patterns may be reduced to the following five.

1. At very low liquid superficial velocities, typically in the order of a few mm/s, a film flow pattern is feasible, in which the liquid flows downwards on the walls of the channel and the gas flows through the centre, either upward or downward.

2. In bubbly flow, the non-wetting gas flows as small bubbles dispersed in the continuous, wetting liquid. This pattern is observed for low gas fractions at moderate velocities, i.e., those conditions in which coalescence is minimal.

3. Taylor flow, sometimes called plug flow, slug flow, bubble train flow, segmented flow or intermittent flow is the flow pattern of large long bubbles that span most of the cross-section of the channel. The relevant lengths are mainly determined by the inlet conditions, as was demonstrated by Kreutzer et al. (2003), who were able to obtain a wide variety of bubble and slug lengths by varying the inlet conditions alone.

4. At higher velocities, small satellite bubbles appear at the rear of the slug, and the slugs eventually are aerated (Reinecke and Mewes, 1999). The chaotic flow pattern that emerges when the velocity is increased even further is called churn flow.

5. At high velocities and low liquid fraction, the annular flow pattern exists of a thin wavy liquid film flowing along the wall with a mist of gas and entrained liquid in the core.
2.1.2. Flow transitions

Typically, so-called flow maps are constructed of liquid superficial velocity versus gas superficial velocity. In these maps, experimentally determined flow patterns are plotted with distinct markers, and the boundaries, i.e., the transitions of one flow pattern to the other, are plotted by lines. Which flow pattern actually occurs in a given capillary channel depends on the gas and liquid properties ($\rho_G$, $\mu_G$, $\rho_L$, $\mu_L$, $\gamma$), duct geometry (at least $d$) and gas and liquid velocities ($u_{Ls}$, $u_{Gs}$). The number of relevant dimensionless groups is large, and most experimental flow maps in the literature are applicable only to the specific systems in which they were obtained. Most of the transitions depend on a disturbance to grow, and the amplitude of the disturbances introduced has a profound effect on the flow map.

This was already pointed out by Satterfield and Ozel (1977), who reported that the boundary between falling film flow and slug flow is in fact a broad region where the observed flow pattern depends on the method of introduction. Galbiati and Andreini (1992) demonstrated that a smooth introduction of gas and liquid into the capillary channel resulted in stratified and dispersed flow. By introducing only a single thin wire into the water feed of the channel, these flow patterns vanished completely and only slug flow and annular flow were observed. The same effect was
observed by using an extremely long calming section that allowed even the smallest disturbances to grow. While most flowmaps are presented without attempting to account for the effect of fluid properties and channel diameter, some noticeable exceptions exist. Suo and Griffith (1964) performed experiments using octane, heptane and water as liquids and helium, nitrogen and argon as gases. No significant changes were found for the different gases and the groups $\left( \frac{\mu_G}{\mu_L} \right)$ and $\left( \frac{\rho_G}{\rho_L} \right)$ were eliminated from consideration. A transition from slug flow to churn flow was given by $ReWe=2.8\times10^5$, which agrees more or less with aeration of the slugs at the development of turbulence, see Fig. 2. Zhao and Rezkallah (1993) (later updated with new literature data by Rezkallah (1996)) showed that three distinct regimes may be identified: (1) a surface tension dominated regime with bubbly and slug flow, (2) an inertia dominated regime with annular flow and (3) a transitional regime in between with churn flows. Then, the boundary between the regimes is determined by the Weber number, which they based on gas properties and gas superficial velocity ($WeGs=\frac{\rho_Gu^2Gs}{\gamma}$). Roughly, the surface tension dominated regime was delimited by $WeGs<1$ and the inertial regime was delimited by $WeGs>20$. Jayawardena et al. (1997) extended the models of Rezkallah by incorporating viscous effects, based on microgravity experiments alone. In a plot of $\left( \frac{ReGs}{ReLs} \right)$ versus $\left( \frac{ReLs}{Ca} \right)$, the boundaries for a large set of experimental data, obtained using different fluids and geometries, could be accurately predicted, see Fig. 3(a-b). For raw experimental data in dimensional form the interested reader is referred to Satterfield and Ozel (1977), Triplett et al. (1999), Fukano and Kariyasaki (1993), Mishima and Hibiki (1996), Akbar et al. (2003), Wolk et al. (2000), Gunther et al. (2004), Cubaud and Ho (2004).

![Flowmap from Suo and Griffith, 1964.](image)
2.1.3. Influence of surface tension and viscosity

An increase of the gas slug length with gas velocity was observed whatever the viscosity value in the range tested (Fig. 4 from Michiel T. Kreutzera, Freek Kapteijna, Jacob A. Moulijna, Johan J. Heiszwolf (2005)). Moreover, for a definite value of $U_{gas}$, an increase of the liquid viscosity seemed to lead to a slight decrease in the mean air slug length. As was observed before, the mean liquid slug length decreased when $U_{gas}$ increased and, in the same way as for the gas slugs, for a
definite value of $U_{\text{gas}}$, liquid slug length seemed to decrease when viscosity increased. Fig. 5 gives $\langle L_{\text{gas}} \rangle$ versus gas superficial velocity for systems characterised by different surface tensions.

![Image of figure 4: Influence of liquid viscosity on $\langle L_{\text{gas}} \rangle$](image4.png)

**Fig 4** Influence of liquid viscosity on $\langle L_{\text{gas}} \rangle$

![Image of figure 5: Influence of liquid surface tension on $\langle L_{\text{gas}} \rangle$](image5.png)

**Fig 5** Influence of liquid surface tension on $\langle L_{\text{gas}} \rangle$
2.2. Taylor flow

As one of the dominant two-phase flow patterns in microchannels, Taylor flow is characterised by periodic occurrence of elongated capsular bubbles with an equivalent diameter several times that of the channel. The bubbles are separated by liquid slugs while only a thin liquid film (usually a very small percentage of the channel diameter) exists between them and the channel wall. Because the liquid phase is interrupted by the bubbles the flow pattern in the liquid slugs is modified to form toroidal vortices, which affect hydrodynamics and mass and heat transfer within the liquid significantly. The primary advantages offered by Taylor flow are the greatly reduced axial (Salman et al., 2004) and improved radial mixing (van Baten and Krishna, 2004), which can augment two- or three-phase reactions (Vandu et al., 2005) or enhance liquid–liquid mixing (Gunther et al., 2005). In addition, the diminished channel dimensions in microchannels result in laminar flow which renders the modelling of Taylor bubble systems easier. A number of investigations have shown that Taylor flow hydrodynamics and mass transfer performance are slug length dependent (Irandoust et al., 1992; Kreutzer, 2003). From inlet gas and liquid flowrates, the slug to bubble length ratio can be determined (Thulasidas et al., 1995). Their absolute values, however, will depend on the dynamics of the two-phase contacting at the inlet. Inlet geometry, fluid physical properties and operating conditions will determine the bubble formation mechanism. Single bubble formation from gas nozzle or orifice in a pool of Newtonian fluid has been studied by many investigators (for example see Kumar and Kuloor, 1967; Kim et al., 1994; Bhunia et al., 1998; Nahral Henry and Kamotani, 2000; Gnyloskurenko et al., 2003). A force balance analysis during the formation process characterised most of these works and two sets of forces, namely detaching and attaching forces, were identified. Factors affecting bubble formation and corresponding forces as proposed by the literature include gas-flux, buoyancy, bubble inertia, liquid inertia, shear-lift, pressure, surface tension and liquid drag (Kim et al., 1994; Bhunia et al., 1998; Nahral Henry and Kamotani, 2000). Their relevant importance is determined by the scale of the system and the flow regime. For example, the attaching effect of surface tension could be predominant at small scales.
or reduced gravity, while the effect of liquid drag force could be significantly different in a fast flowing compared to a quiescent liquid. Accordingly, various bubble formation models have been developed and the bubble volume was defined. In the single-stage model of Walters and Davidson (1963), the detaching force was considered to be in a continuous balance with the attaching force. Kumar and Kuloor (1967) disagreed with this static model and proposed a dynamic two-stage model, in which a force balance was only achieved at the end of the first stage. The two stages defined were bubble expansion and detachment. During the expansion stage, bubbles reside on the nozzle while during the detachment stage they “lift off” and form a neck connecting them to the nozzle tip. The two stage model is frequently adopted for the investigation of bubble formation (Kim et al., 1994; Bhunia et al., 1998; Nahal Henry and Kamotani, 2000). Gnyloskurenko et al. (2003) investigated bubble formation from a 1mm diameter orifice at very low gas flowrates of 2 ml/min \(U_{GS} = 0.042 \text{ m/s}\) and presented a multistage model, in which the stages of bubble nucleation, under critical growth, critical growth and necking, were identified. By equating the detaching and attaching forces, bubble volume can be calculated. At intermediate and low gas flowrates (<104 ml/s), the effect of the inertia force diminishes (Kumar and Kuloor, 1967), while the effect of surface tension has to be included to balance the buoyancy force. The fact that the discrepancy between model predictions and experimental data increased with decreasing gas flow rate (Gnyloskurenko et al., 2003) suggests that other parameters, apart from surface tension, play a role. In the study of Byakova et al. (2003), bubble volume at low gas velocity was found to depend on wettability. By increasing the equilibrium contact angle, i.e. worsening the liquid wettability on the gas nozzle wall, the bubble volume was found to increase by more than 50%. Taylor bubble sizes in microchannels, however, cannot be predicted accurately by models based on force balance. On one hand, Taylor bubbles deform significantly as they grow and approach the channel wall, deviating from the spherical shape assumed by most force balance models. On the other hand, at the low Reynolds numbers encountered in microchannels viscous forces are important and have to be taken into account.
Some correlations based on both experimental data and numerical simulations have been suggested in the literature (Fig. 6).

Laborie et al. (1999) correlated experimentally bubble and slug lengths in 1–4 mm capillaries to Reynolds and Eötvös numbers as given by Eqs. (2) and (3), respectively. A porous membrane was used to form the dispersed phase. Based on the experimental data by Heiszwolf et al. (2001) in a 200 cpsi monolith reactor, where a distributor was used for the liquid phase, Kreutzer (2003) suggested Eq. (4) for slug length in square channels. Liu et al. (2005) used the dependence of mass transfer coefficient on slug length (Bercic and Pintar, 1997) to derive an empirical correlation (Eq. (5)) from their experiments in capillaries ranging from 0.9 to 3 mm ID and with a T-inlet. The predictions seemed to be good but the comparison with Eqs. (3) and (4) was poor. Eq. (5) was further modified by Akbar and Ghiaasiaan (2006) to include gas holdup (Eq. (5)) by fitting their numerical results and the data by Liu et al. (2005) and Laborie et al. (1999). The agreement was satisfactory with a standard deviation of 19.5%. In another numerical study of Taylor bubble and slug lengths, Qian and Lawal (2006) correlated their 148 set of data obtained by Computational Fluid Dynamics 2D simulations in a microchannel with 1 mm width and T-inlet with different dimensions to derive the length of a unit cell (one bubble and one slug) (Eq. (7)). Bubble and slug lengths can be obtained by multiplying the equation with the respective phase holdup. The correlation showed that the bubble and slug lengths depend mainly on the phase holdup and slightly on Reynolds and Capillary numbers. Garstecki et al. (2006) suggested a scaling law (Eq. (8)) to determine bubble size formed via a T-junction in a rectangular microchannel of width w. The value of \( \alpha \) is of the order of 1, depending on the geometry of the T-junction, but is independent of the fluid properties (flow rates and two-phase superficial velocities are between 0.01–1 µl/s, and 0.1–1.1 m/s, respectively). In contrast to Garstecki et al. (2006), Xiong et al. (2007) reported for fluids that joined in parallel at the inlet that viscosity and surface tension affected bubble size and proposed to replace the channel width w in Eq. (8) by bubble width \( w_B \). In their study \( \alpha \) was equal to 1. Cubaud et al. (2005), using a cross-flow inlet, also found a correlation similar to Eq. (8) where \( \varepsilon_L^{-1} \) was used instead of \( 1 + Q_G/Q_L \) but without the coefficient \( \alpha \).
The above correlations show the dependence of bubble and slug sizes on operating conditions and fluid properties. The lack of agreement between correlations suggests that other parameters also affect the sizes. Qian and Lawal (2006) found significant dependence of bubble and slug lengths on the inlet geometry. By varying T-junction orientation and size of inlet channels as well as the degree of premixing of the two fluids in their numerical simulations, the slug length was found to vary up to 300% under the same operating conditions. In general, small mixing zones and good premixing at the inlet favoured short bubble and slug lengths. Bubble size distributions at constant operating conditions have also been observed, e.g. experimentally by Mantle et al. (2002) and theoretically by Qian and Lawal (2006), who attributed them to the toroidal vortices that are generated at the inlet and propagate throughout the channel length. Kreutzer et al. (2005) bounded the occurrence of uniform slug and bubble sizes to $0.25 < \frac{U_{LS}}{U_{GS}} < 2$. Systematic experimental investigations on the effect of inlet conditions on Taylor flow were carried out by Amador et al. (2004). Taylor bubble formation was found to follow three mechanisms: formation of a gas chamber at the top of the gas nozzle with the bubble detaching from the end of it; formation of a meniscus at the nozzle that leads to pressure built up behind it until the gas finally erupts to form a bubble; the third mechanism is similar to the two-stage model known in the literature. Bubble lengths, formed at T- and Y-junction and co-flow configurations with various gas/liquid inlet
dimensions, were found to depend significantly on the ratio of gas to liquid superficial velocities and gas inlet diameter for any given geometry. According to Garstecki et al. (2006) under typical conditions in microchannels (widths and heights of the order of 10–100 µm, flow rates of the order of 0.01–1 µl/s and Ca < 10⁻²), where interfacial forces dominate shear stresses, bubble break-up is controlled by the pressure drop across the bubble. A “squeezing mechanism” was suggested to describe the process: the expansion of gas phase to the entire cross section of the main channel confines the liquid phase to the film region, and builds up pressure upstream the liquid that leads to the “squeezing” of the bubble neck until complete bubble breakage. However, the model is only appropriate when the width to the height ratio of the main channel is larger than 1 and the gas inlet to the main channel width ratio is larger than 0.5. Bubble size was found to be determined by the ratio of the volumetric flowrates of the two phases and the T-junction geometry (see Eq. (8)), which agreed with Amador et al. (2004). Haverkamp et al. (2006) characterised gas–liquid flow in single and multiple rectangular microchannels by using two inlet mixing geometries. For both of them the gas-feed was flanked by two equal liquid inlets, but the channel connecting to the main channel had different designs. In the T-mixer, the width of the connecting channel followed a two-stage reduction while in the smooth mixer the width of the channel was smoothly reduced. The mixer design was reported to affect the flow pattern map and the bubble formation mechanism. In the smooth mixer bubble sizes were reduced and the bubble size distribution was narrower compared to the T-mixer.

2.2.1. Influence of shape

Experimental data and fitted correlations are available for round channels, and to a lesser extent also for square channels. In monoliths in particular and coated microchannels in general, the corners are rounded to some extent by the coating process, and for rounded corners no film thickness correlations are available. Moreover, the rounding of the corners is sometimes not perfectly symmetrical, so defining a general film thickness correlations is going to be impossible unless we accurately describe the channel geometry. Here, we discuss the results for round and square channels, which gives a lower limit (round channels) and a upper limit (square channels).

2.2.1.1. Round capillaries

For round capillaries, numerous experimental correlations of the film thickness are available (e.g. Chen, 1986; Irandoust and Andersson, 1989a; Thulasidas et al., 1997; Aussilous and Quere, 2000).
Most of these correlations tend to zero for vanishing $Ca$, and most exhibit a smaller slope on a graph of $\log(\delta/r)$ vs. $\log(Ca)$, than the lubrication value of $2/3$. The change in slope can be attributed to the increasing importance of Marangoni effects at small $Ca$. Typically slopes between 0.5 and 0.66 are reported: Fairbrother and Stubbs (1935) found 0.5, Irandoust and Andersson (1989a) found 0.54, Halpern et al. (1998) found 0.52, etc. All these correlations give the same order of magnitude for the film thickness. The correlation of Aussilous and Quere (2000) for round capillaries,

$$\frac{\delta}{d} = \frac{0.66 Ca^{2/3}}{1 + 3.33 Ca^{2/3}}$$

has the benefit of accounting as best as possible for high $Ca$ values and agrees with the data of Bretherton and Taylor for $10^{-4} < Ca < 100$.

### 2.2.1.2. Square capillaries

For square capillaries, most correlations give comparable results for the film thickness in the corners. For the film far away from the corners, however, there is no such agreement. Kolb and Cerro (1991) measured the shape of the liquid film for different capillary numbers in the directions $AA'$ and $BB'$ (see Fig. 7). Note that the channel diameter is defined in the direction $BB'$, so in the direction $AA'$ the maximum bubble size is $\sqrt{2}$ times the channel diameter. Thulasidas et al. (1995a) measured the film thickness in the direction $AA'$ using optical methods for a wide range of capillary numbers. Hazel and Heil (2002) computed the shape of bubbles in square capillaries using a finite-element free surface formulation, similar to Heil (2001).

![Fig 7 The shape of the liquid in square capillaries](image)
In Fig. 8, the experimental data (Kolb and Cerro, 1991; Thulasidas et al., 1995a) and numerical data (Hazel and Heil, 2002) are plotted against the capillary number. The data presented in Fig. 6 are for horizontal flow. In square capillaries, the influence of gravity on the film thickness is more pronounced than in circular capillaries. For the diagonal (AA’) direction, the agreement between all the data is good. For $Ca \to 0$, the dimensionless bubble diameter approaches 1.2. In other words, even at low velocities the film does not vanish completely in the corners. Note that the upper limit is based on the data of Thulasidas et al. alone. For $Ca \to \infty$, the dimensionless bubble diameter approaches a value of 0.7. For $Ca > 0.04$, the bubble diameter in both directions is the same and the bubble is axisymmetric, while the results in Fig. 8 show that for $Ca < 0.04$ the bubble diameter in the BB’ direction is virtually independent of $Ca$. Using the asymptotic values of 1.2 and 0.7, the dimensionless bubble diameter in the diagonal direction can be correlated against the Capillary number as

$$\frac{d_{\text{square}}}{d_{\text{channel}}} = 0.7 + 0.5e^{-2.25Ca^{0.445}} \quad (10)$$

which is also plotted in Fig. 8. For monoliths, the region of interest is $Ca < 0.04$. Here the bubble diameter in the direction BB’ is close to the width of the channel. From the data of Hazel and Heil, a value of $d_{\text{bubble}}/d_{\text{channel}} = 0.99$ is obtained, while the experimental data of Kolb and Cerro is somewhat lower, $d_{\text{bubble}}/d_{\text{channel}} \approx 0.95$. 

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**Fig 8 film thickness versus Ca in square capillaries**
2.2.2. Mass transfer

For the development of microreactors to carry out liquid-liquid processes, mass transfer coefficients must be consistently estimated to obtain a reliable process design. Few works focused on liquid-liquid mass transfer using slug flow in microchannels: Burns and Ramshaw (2001) studied the titration of acid acetic which was controlled by the acid transfer from kerosene to a basic aqueous solution. This reaction was carried out in a square microchannel of 380 µm depth using slug flow. They obtained an increase of the global mass transfer coefficient with the flow velocity. Dummann et al. (2003) observed the same tendency while carrying out the nitration of single ring aromatics in circular capillaries of 0.5 and 1.0 mm diameter. However, no model was suggested to estimate mass transfer coefficients in such systems. Nevertheless, two cases have been intensively studied as described afterwards: (1) liquid-liquid mass transfer in macrochannels and (2) gas-liquid mass transfer in microchannels. For liquid-liquid mass transfer in macrochannels, numerous empirical correlations to predict dispersed phase mass transfer coefficients \( k_d \) have been established (Knudsen et al., 1998; Slater, 1994). However, in order to approach microchannel flow conditions, we should focus on circulating droplets, i.e. with internal recirculation loops, with non-oscillating interface (Kashid et al., 2005). An empirical correlation was proposed by Skelland and Wellek (1964):

\[
\text{Sh}_d = \frac{k_d d_d}{D_d} = 31.4 \text{Re}_d^{0.371} \text{Ca}_d^{0.371} \text{Fo}_d^{-0.338} \text{Sc}_d^{-0.125}
\]

(11)

where \( d_d \) is the diameter of a sphere with the same volume than the droplets, \( D_d \) the molecular diffusion coefficient of the solute in the dispersed phase. The dimensionless numbers are particle numbers, calculated with a characteristic length equals to \( d_d \). In the case of gas-liquid system in microchannels, we can distinguish two types of models: the first one based on empirical correlations, and the second one based on theory. Both of them allow the estimation of continuous phase mass transfer coefficients since the resistance to the transfer in the gas phase is negligible compared to the one in the liquid phase. Berčič and Pintar (1997) proposed to estimate liquid volumetric mass transfer coefficient \( k_{d,a} \) using the following correlation
where $U_d$ represents the bubble velocity, $\varepsilon_G$ the gas hold-up, and $L_{UC}$ the unit cell length (Figure 9). They deduced this correlation from experimental results obtained in circular capillaries of 1.5 to 3.1 mm diameter. As it can be seen in Eq. 12, it does not consider the influence of the channel diameter $w_C$ on the mass transfer coefficient.

\begin{equation}
   k_L a = \frac{0.111 \cdot U_d^{1.19}}{((1-\varepsilon_G) \cdot L_{UC})^{0.57}}
\end{equation}

(12)

Fig. 9 Illustration of a unit cell for slug flow in a microchannel

Irandoust et al. (1992), Kreutzer (2003) and van Baten and Krishna (2004) used a more fundamental approach to estimate $k_L a$ in monolith reactors with circular channels. They consider that gas-liquid mass transfer in those devices was the result of two contributions: from the gas phase to the liquid film surrounding the bubbles $k_{L,\text{film}} a_{\text{film}}$, and to the liquid slugs through the two bubble caps $k_{L,\text{cap}} a_{\text{cap}}$:

\begin{equation}
   k_L a = k_{L,\text{cap}} a_{\text{cap}} + k_{L,\text{film}} a_{\text{film}}
\end{equation}

(13)

$k_{L,\text{cap}}$ is then calculated according to Higbie penetration theory, which leads to the following equation in circular channels:
This model assumes that the film is very thin compared to the channel diameter. Therefore, the slug diameter $w_d$ can be approximated by the channel diameter $w_c$. Van Baten and Krishna (2004) estimated the film contribution by referring to the modeling of mass transfer from a bubble to a laminar falling film. Mass transfer coefficient in this case can be written in terms of Eq. 15 or Eq. 16 according to Fourier number $F_{film}$ given by Eq. 17., film stands for the contact time of a fresh liquid element at the film interface (Eq.19).

\[
\begin{align*}
  k_{L,\text{film}} &= 2 \sqrt{\frac{D_c}{\pi \cdot t_{*f,\text{film}}}} \frac{\ln(1/\Delta)}{1 - \Delta} & F_{film} < 0.1 \text{ (short contact)} \\
  k_{L,\text{film}} &= 3.41 \frac{D_c}{\delta_{\text{film}}} & F_{film} > 1 \text{ (long contact)} \\
  F_{o,\text{film}} &= \frac{D_c}{t_{*f,\text{film}} \cdot \delta_{\text{film}}^2} \\
  \Delta &= 0.7857 \cdot \exp(-5.121 \cdot F_{o,\text{film}}) + 0.1001 \cdot \exp(-39.21 \cdot F_{o,\text{film}}) + ... \\
  t_{*f,\text{film}} &= \frac{L_{\text{film}}}{U_d}
\end{align*}
\]

Finally, the film interfacial area $a_{film}$ can be written in terms of Eq.20.

\[
\begin{align*}
  a_{\text{film}} &= \frac{\pi \cdot w_d \cdot L_{\text{film}}}{L_{\text{UC}} \left(\pi \cdot w_c^2\right)/4} \approx \frac{4L_{\text{film}}}{w_c L_{\text{UC}}}
\end{align*}
\]

Van Baten and Krishna compared these correlations with gas-liquid mass transfer simulations in circular capillary. They obtained good predictions of $k_{L,a}$ over a wide range of parameters values.
(\(w_C = 1.5, 2\) and 3 mm; \(L_{UC} = 0.015 \) to 0.05 m; \(U_d = 0.15 \) to 0.55 m/s; \(\varepsilon_G = 0.136 \) to 0.5). Vandu et al. (2005) fitted experimental results obtained with air and water in circular and square capillaries with van Baten and Krishna model: they showed that the film contribution was the major contribution to mass transfer with their operating conditions (\(w_C = 1, 2\) and 3 mm; \(L_{UC} = 0.005\) to 0.06 m; \(U_d = 0.09\) to 0.65 m/s). Indeed, they neglected the caps contribution and obtained a reasonable agreement between the model and their experiments when \((U_d/L_d)^{0.5} > 3 \, s^{-0.5}\) which corresponds to short contact times. Regarding liquid-liquid systems in microchannels, the hydrodynamic of the dispersed phase seems more complex compared to gas-liquid flows. Sarrazin et al. (2007) showed that the flow structures developed in droplets was strongly influenced by the Reynolds and the capillary numbers (internal velocity profiles, number of recirculation loops). This may lead to different behaviours in terms of mass transfer. The influence of various flow parameters and the channel size on the mass transfer coefficient is considered in order to obtain a better understanding and prediction of this transport mechanism at such scale. The reliability of the existing models that are likely to estimate mass transfer coefficients in the system we studied is discussed.

### 2.2.2.1. Methodology for the identification of the mass transfer coefficient

The code developed for the computation of the solute transport from the dispersed phase to the continuous phase allows the calculation of the local solute concentration all along the microchannel. The computed concentration profiles as a function of the residence time in the three volumes representative of slug flows: (1) the droplet, (2) the interval, which is the volume between two successive droplets, (3) and the film. The division of the continuous phase into two distinct volumes is pertinent since the concentrations in the interval and the film are very different: the film saturates faster than the interval. Moreover, it can be noticed that the concentration in the film can temporary overpass the steady state concentration. This phenomenon is particularly important for the case where the interval volume is high compared to the sum of the film and the droplet volumes (Figure 10(a)). This is due to the time the interval requires to enrich in solute: if this interval is important compared to the droplet and the film, it takes a long time for this volume to be charged insolute compared to the saturation time of the film. Therefore, the homogenisation of the concentration in the film and the droplet occurs before the interval is totally charged. Then, the homogenisation
over the all unit cell leads to a decrease of the film and the droplet concentrations to the final steady state concentration.

![Mean concentration profiles in the three volumes identified in a unit cell](image)

**Fig10** Mean concentration profiles in the three volumes identified in a unit cell

A local mass transfer coefficient $k_{d,\text{simu}}$ is identified from the computed concentration field. It is obtained from a mass balance in a droplet, where the flux through the interface is modelled using this coefficient, the mean solute concentration in the droplets and the final concentration $C_d^*$ obtained for an infinite time (Eq.21). $V_d$ and $V_{UC}$ respectively correspond to a droplet and a unit cell volume. The integrated formulation of Eq.21 directly leads to the mass transfer coefficient (Eq.22).

\[
V_d \frac{\partial \overline{C_d}}{\partial t} = -k_{d}a_{d,\text{simu}}V_{UC}(\overline{C_d} - C_d^*)
\]

\[
\ln \left( \frac{C_d^0 - C_d^*}{C_d - C_d^*} \right) = \frac{k_{d}a_{d,\text{simu}}V_{UC}}{V_d} \cdot t
\]

To obtain $k_{d,\text{simu}}$, the specific interfacial area $a_d$ is calculated according to the capillary number $Ca$. Infact, Sarrazin et al. (2007) showed that the cross section shape of a droplet in square microchannels dependes on this number: for $Ca$ higher than 0.04 the droplets body can be considered as cylindrical, while for $Ca$ lower than 0.04 the dispersed phase tends to cling to the
channel walls. This tendency was also suggested by Kreutzer et al. (2005) for gas-liquid slug flow. We consider the caps of the droplets have a spherical shape in both cases. Consequently, ad is estimated using the following equations:

\[
a_d = \frac{\pi \cdot w_d \cdot (L_d - w_d) + \pi \cdot w_d^2}{L_{UC} \cdot w_C^2} \quad \text{for } Ca > 0.04
\]  

\[
a_d = \frac{4 \cdot w_d \cdot (L_d - w_d) + \pi \cdot w_d^2}{L_{UC} \cdot w_C^2} \quad \text{for } Ca < 0.04
\]

2.2.2.2. Model for mass transfer coefficient

In order to study the relationship between the droplet side volumetric mass transfer coefficient and the flow parameters, it is assumed that this coefficient could be modelled in terms of Eq.25, where \(d_d\) is the droplet volume equivalent diameter defined by Eq.26 and \(\varepsilon\) the ratio between the volume of a droplet and a unit cell \((\varepsilon = V_d / V_{UC})\).

\[
k_d = \alpha \cdot U_d^{p_1} \cdot w_C^{p_2} \cdot d_d^{p_3} \cdot \varepsilon^{p_4} \cdot \sigma^{p_5} \quad \text{(25)}
\]

\[
d_d = 2 \cdot \sqrt[3]{\frac{3}{4\pi} V_d} \quad \text{(26)}
\]

The parameters \(\alpha\) and \(p_i\) are identified to fit the simulation results. It lead to Eq.27, where the term \(k_d d_d\) can be related to a Sherwood number, \(U_d w_C\) to a Reynolds number and \((U_d / \sigma)\) to a capillary number. The term \((w_C / d_d)\) shows the positive impact of the confinement on mass transfer. The power 0.69 that illustrates the dependency of Reynolds number on mass transfer is in the good order of magnitude. Indeed, we can relate it to the common dependency of discontinuous phase mass transfer coefficient in particle Reynolds number, where the power equals 0.371. The proposed correlation shows that the mass transfer coefficient decreases when the capillary number increases. This tendency can be explained by the influence of this number on the flow structure in the droplets. In fact, for low values of the capillary numbers, Sarrazin et al. (2007) show that very small recirculation loops appear at the front of the droplets. This effect tends to increase the mixing efficiency in the dispersed phase, to the benefit of the mass transfer (reduction of the resistance to
the transfer in the droplets). Nevertheless, regarding the dependency of the term \((U_d / \sigma)\) on mass transfer, this effect has a minor influence compared to the Reynolds number and the confinement impact. The parameter \(\alpha\) is equal to \(2.77 \times 10^{-04}\). However, this value is obtained by fitting 2D results, and would have probably been different if we had carried out 3D simulations. Moreover, this parameter value depends on the fluid properties.

\[
 k_d d_d = \alpha \cdot e^{0.17} \cdot (U_d w_c)^{0.69} \cdot \left(\frac{U_d}{\sigma}\right)^{-0.07} \cdot \left(\frac{w_c}{d_d}\right)^{0.75}
\]  

(27)

Figure 11 shows that this correlation allows a good fitting of the simulation results as far as the hydrodynamic behaviour of the droplets correspond to flow structure (a). Indeed, the correlation underestimates mass transfer for structure (b), and it overestimates it for structure (c). This can be explained by: (1) the recirculation nodes in flow structure (b) that increase the transfer by enhancing the mixing in the dispersed phase and (2) the lack of recirculation loops in the continuous phase in flow structure (c) that slows down the solute transport in that phase compared to the transport phenomenon in flow structure (a). However the global trends of the curves obtained for all flow structures are roughly the same. This means that mass transfer evolves with the flow parameters in the same way whatever is the flow structure. The main difference in the mass transfer coefficient estimation will be the value of the parameter \(\alpha\).

Fig11 simulation results fitting with Eq.27
Finally, it is compared the simulation results with the coefficients obtained from the models. Regarding the correlation suggested by Skelland and Wellek, the difficulty is to use the pertinent characteristic parameters to calculate the dimensionless numbers. In order to have a correlation easy to be applied, we focused on parameters that can simply be estimated. Therefore, mass transfer coefficient with this correlation has been estimated using the following formulation of Eq.28:

\[
\text{Sh}_d = \frac{k_d d_d}{D_d} = 31.4 \left( \frac{\rho_d U_d d_d}{\mu_d} \right)^{0.271} \left( \frac{\mu_d U_d}{\sigma} \right)^{0.271} \left( \frac{4 D_d \cdot (L_d - w_d + \pi w_d / 2)}{d_d \cdot U_d} \right)^{-0.538} \left( \frac{\mu_d}{\rho_d D_d} \right)^{0.125}
\]  

where the particle Fourier number \( \text{Fo}_d \) depends on a contact time defined as the ratio between a contact length and the droplets velocity \( U_d \). The contact length has been estimated as the length of the interface travelled by a fluid element of the droplets as shown in Eq.29 (i.e. a fluid element of the vortex external streamline). The characteristic length used is half a droplet diameter which represents the characteristic length of diffusion inside the droplets.

\[
\text{Fo}_d = \frac{D_d}{t_e (d_d/2)^2} \tag{29}
\]

\[
t_e = \frac{(L_d - w_d) + \pi w_d / 2}{U_d} \tag{30}
\]

As illustrated in Figure 13, this formulation leads to two different trends for low and high values of mass transfer coefficients. In fact, this correlation is used to model mass transfer within circulating droplets: it does not consider the difference in flow structure. Moreover, it was proposed for macrochannels where the droplets are not constrained by the channel wall while we noticed an enhancement of mass transfer with the confinement factor. The model of van Baten and Krishna suggested for gas-liquid slug flow leads to a good global trend. However, it allows the calculation of continuous phase side mass transfer coefficients. Therefore, it could possibly be used when the resistance to transfer in the droplets is negligible compared to the resistance in the continuous phase (flow structure (b) with high recirculation motion). Finally the correlation proposed by Bercic and Pintar leads to a high scattering when trying to fit the simulation results. Nevertheless, their correlation, which was suggested from experiments in channels of more than 1 mm diameter,
is independent of the channel size while Vandu et al. (2005) shows the importance of this parameter on mass transfer.

![Comparison of the mass transfer coefficient obtained by simulation and with literature models](image)

**Fig 12** Comparison of the mass transfer coefficient obtained by simulation and with literature models

### 2.2.3. Pressure drop

In multiphase monoliths, the predominant flow pattern is a bubble-train flow of elongated bubbles. The theory of these elongated bubbles is a classical problem in fluid mechanics, referred to as Bretherton’s problem or Taylor Flow. The pressure drop in Taylor flow is indeed very low compared to randomly packed beds of similar geometric surface area. Furthermore, it has been shown that the hydrodynamics of Taylor flow allow for good mass-transfer rates from the bubbles to the liquid, and spectacular mass transfer from the bubbles to the wall. Increasingly, the benefits of Taylor flow are recognized outside the field of monoliths, especially in the microfluidics and microreactor community.

There are several reasons why such a model is highly desired. The most obvious one, the prediction of the pressure drop over a reactor column so compressors and pumps for that reactor may be designed, is the least important. The pressure drop over the column is low (or even zero), so the design of pump and compressors is not critical, and one might be contented with the less accurate models that are available. This work was motivated by other considerations, which are:
Taylor flow can exhibit highly undesired dynamic oscillations that may grow to significant instability. The behavior can be predicted if the gradients of pressure drop versus gas and liquid flow rate are accurately known, and stability criteria for monoliths can be then formulated. Monoliths can be operated in a loop reactor configuration, where a compressor can be eliminated and the gas circulation is induced by the suction of the downward bubble train flow. Now the pressure drop is approximately zero, and a pressure drop model is required to predict the gas circulation flow rate.

Horvath et al. demonstrated that the pressure drop in flow depends on the slug length. The slug length is an important parameter in predicting the mass transfer rate and physical intuition predicts that more bubbles per unit channel length (that is, shorter slugs) will result in a higher pressure drop. Then, because this effect is apparently significant, pressure drop measurements can be used to obtain the slug length.

A model for the residence time distribution in monoliths may be constructed from the notion that in all the channels, the pressure drop must be the same. For all these considerations, we need an accurate model for the pressure drop. For an order-of-magnitude estimate of the pressure drop in two-phase flow in randomly packed reactors, the approach of Lockhart and Martinelli, or a homogeneous model approach is most frequently used. Surface tension effects, which are quite naturally absent in single phase pressure drop, are always missed by approaches like Lockhart-Martinelli that estimate two-phase pressure drop from single phase results. Chen et al. collected sets of literature data for two-phase pressure drop in small diameter tubes, and found that even if surface tension was included in the model by a Weber number or a Capillary number, neither Lockhart–Martinelli models nor homogeneous pressure drop models accurately predicted the data. Both the homogeneous model and the Lockhart–Martinelli model use little information about the two-phase flow pattern. The advantage is that no specific knowledge of the flow pattern is required to predict the pressure drop, and the related and obvious disadvantage is that no information about the flow pattern can be obtained from experimental pressure drop data. In Taylor flow, the information that is specific to the flow pattern is the amount of bubbles per unit length of channel, that is, the bubble frequency. The average bubble and slug length may be obtained from the bubble frequency in a straightforward manner. In Taylor flow, the slugs are sealed between the bubbles, preventing coalescence, and the length of a slug formed at the entrance of the channel remains constant over the entire length of the channel. The same holds for the bubble length, and the two-phase Taylor flow pattern in a capillary is fully characterized and determined by the bubble frequency, the liquid superficial velocity, the gas superficial velocity and the fluid properties. The aim of this work can thus be reformulated as: the development of a pressure drop model for Taylor flow in capillaries that takes the slug and bubble length into account and allows the slug length to be determined from experimental pressure drop data.
Gas-liquid hydrodynamics in Taylor Flows with complex liquids

Chapter II

The second paper, by Bretherton (1961), pioneered the use of a lubrication analysis for the transitional region where the film is formed, between the spherical front of the bubble and the flat film far behind the front. Lubrication theory was originally developed to explain why no solid to solid contact occurs in bearings due to the motion of a lubricating viscous fluid. Although in Taylor flow the thin film prohibits gas-to-solid contact rather than solid-to-solid contact, the same mathematical treatment of the equations of fluid motion as developed for the bearings by Reynolds (1886) may be used. The full analysis of Bretherton is lengthy, but thorough. Here only a condensed scaling analysis from Aussilous and Quere (2000) is given. The front of the bubble may be regarded as spherical with radius $r$, so the Laplace pressure difference across the gas–liquid interface is given by $\Delta p = 2\gamma/r$, provided the film thickness is small $(\delta \ll r)$. In the region of constant film thickness, the curvature in the axial direction vanishes, and the Laplace pressure difference is given by $\Delta p = \gamma/r$. A balance of the viscous force and the pressure gradient in the transitional region yields

$$\frac{\mu u}{\delta^2} \sim \frac{1}{\lambda} \frac{\gamma}{r},$$

(31)

where $\lambda$ is the length of the transitional region between the spherical and flat interface. The length $\lambda$ is unknown, but we can estimate it by requiring that the Laplace pressure is continuous at the interface or, in other words, that the curvature of the spherical part matches the curvature at the end of the transition region.

$$-\frac{\gamma}{r} - \frac{\gamma \delta}{\lambda^2} \sim \frac{2\gamma}{r},$$

(32)

or $\lambda = \sqrt{\delta/r}$, which yields upon substitution into Eq.32 the now classical scaling rule $\delta/r \sim Ca^{2/3}$.

The more rigorous analysis of the full Navier–Stokes equations in the transition region at the front and the back of the bubble by Bretherton results in

$$\frac{\delta}{d} = 0.66Ca^{2/3}.$$  

(33)

The method developed by Bretherton also gave an expression for the pressure drop over the bubble. In fact, the excess bubble velocity, film thickness and pressure drop are all related.
The theory of Bretherton agrees nicely with experimental data for low Capillary numbers. Fig. 14 shows how well the theoretical predictions, which contain no fitted parameters, agreed with experiment. However, for $Ca < 10^{-4}$ and for $Ca > 10^{-2}$, the Bretherton analysis breaks down.
2.2.3.1. **Marangoni effect**

As Taylor flow is dominated by surface tension effects, it is no surprise that small amounts of contaminants have a huge impact. Impurities on the gas–liquid interface change the surface tension and gradients of the concentration of these impurities lead to a gradient in the interface pressure. The usual no-shear boundary condition for the gas–liquid interface then breaks down. Ratulowski and Chang (1990) showed that taking into account these surfactant effects, also known as Marangoni effects, explains the difference between theory and experiment for very dominant surface tension (low \( Ca \)). The largest concentration gradients are found near the stagnation rings on the bubble, see Fig. 15. At the nose, surfactants are swept from this ring to the axis of the channel or to the film separating the bubble and the wall. On the ring at the rear, surfactants are desorbed to the bulk liquid. The maximum impact of the Marangoni effects may be modelled by assuming no-slip on the interface. Bretherton (1961) showed that using no-slip in the transition regions increases the film thickness and the pressure drop over the bubble by a factor \( 4^{2/3} \). Most of the experimental on film thickness is indeed bounded by Brethertons “clean” and “hard” limits. The full solution of the interplay of bulk diffusion, surface adsorption and convection of surfactants is much more complex, and the interested reader is referred to the works of Ratulowski and Chang (1990), Park (1992), Stebe and Barthes-Biesel (1995), Waters and Grotberg (2002), Severino et al. (2003) and Ghadiali and Gaver III (2003).

![Fig15 Schematic representation of the surface concentrations and the interaction with fluid flow](image)

2.2.3.2. **Inertial effect**

In experimental work the Capillary number is usually varied by increasing the viscosity of the liquid, and keeping the velocity low for ease of observation. As a consequence, most of the experimental data was obtained at low Reynolds numbers for which simplification to Stokes flow seemed justifiable. The effects of inertia may in a first analysis be ignored in small capillaries.
Bretherton proposed $\text{We} \ll 1$ as a suitable criterion. In monolith channels, where $Ca = O(10^{-2})$ and $Re = O(10^2)$, the Weber number ($\text{We} = Ca\text{ Re}$) readily approaches unity and inertia should probably be considered. Numerically, the effect of inertia was first included by Edvinsson and Irandoust (1996). They found that the rear spherical caps were flattened and the amplitude of the ripples increased as the Reynolds number increased. Giavedoni and Saita (1997, 1999) found a slight decrease in film thickness up to $Re = 100$. Heil (2001) reported noticeable changes in film thickness and pressure drop when inertia was taken into account in a numerical analysis for Reynolds numbers up to 280. Kreutzer et al. (2005b) simulated entire bubbles and slugs for $Re$ up to 900, using a hybrid upwinding scheme that introduced minimal amounts of numerical diffusion. All numerical investigations agree that the film thickness decreases slightly from $Re = 0$ to $10^2$, and from then on increases monotonically with increasing $Re$. Experimental data at high Reynolds numbers were recently reported by Aussilous and Quere (2000), who measured film thickness at high velocities using low viscosity liquids. A noticeable increase in film thickness was found and explained using a scaling analysis, see Fig. 16.

![Fig16 Effect of liquid viscosity on the film thickness](image)

2.2.3.3. Gravitational effect

The effect of gravity in Bretherton’s problem is very limited. Hazel and Heil (2002) studied the impact of gravity on the film thickness and pressure drop and found only a small difference for $Bo = \pm 0.43$ (the sign of the Bond number indicates up-flow or downflow). Edvinsson and Irandoust (1996) performed several calculations for $Re = 200$ and $-2 < Fr < 2$. The effect of gravity on the film...
thickness was significant for $Bo > 1$. In square capillaries, the influence of gravity on the film thickness is more pronounced than in circular capillaries: for up-flow smaller bubble radii are reported, and the reverse effect was observed experimentally and numerically for down flow.

### 2.2.3.4. Evaluation of pressure drop

For fully developed Hagen–Poiseuille flow of a single phase in a tube, the pressure drop is given by

$$\frac{\Delta p}{L} = \frac{16}{Re} \left( \frac{1}{2} \rho U^2 \right) \frac{4}{d} \text{ or } \frac{\partial p^*}{\partial z^*} = -32$$

(35)

Far away from the bubble, the pressure drop per length is constant and has a value that is consistent with Hagen–Poiseuille flow. In the region of constant film thickness, the shear of the gas is negligible, and Figure 17 shows that the pressure at the wall is constant. The pressure drop over the entire bubble, however, is not zero, and the pressure difference over the frontal transition region is higher than the pressure drop over the rear transition region. The large oscillation at the rear of the bubble is caused by the presence of an inundation on the gas–liquid interface. The total pressure drop over the entire computational domain can be decomposed into the frictional pressure drop of the liquid slug, and the pressure drop over the bubble.
where $\Delta p^*$bubble describes the effects near the bubble, and is a function of $Re$ and $Ca$. Note that in Eq. 36, the term $\Delta p^*$bubble now includes all the effects on the pressure drop over the bubble, including the effect of circulation in the slug and interfacial contributions. Because the frictional pressure drop is dominated by the slug region, we can model the effects of the bubble as part of the pressure drop in the slug to obtain

$$\Delta p^* = -32L^*_{{slug}} + \Delta p^*_{{bubble}}(Re, Ca)$$  \hspace{1cm} (36)$$

The function describes how the pressure drop is affected by the presence of bubbles. The parameter $L^*_{{slug}}$ now appears in the functional form of , because with increasing slug length, the relative contribution of to the overall friction in the slug decreases. In fact, for infinitely long slugs, the effects of bubbles vanish.
For a train of bubbles in a capillary, the dimensional pressure drop is then given by the pressure drop over the slugs alone

\[ \frac{\Delta p}{L} = \beta_L f_{\text{slug}} \left( \frac{1}{2} \rho U^2 \right) \frac{4}{d} \]  

(39)

where \( \beta_L \), the dynamic holdup of liquid in the channel, is the fraction of channel length occupied by the slugs. Here, the slug friction factor is given by

\[ f_{\text{slug}} = \frac{16}{Re} \left[ 1 + \xi(Re, Ca, L_{\text{slug}}^*) \right] \]  

(40)

In other words, an accurate model for pressure drop must include the bubble length perhaps in the form of the bubble frequency as a parameter. Experimentally, a wide range of slug lengths can be created in a given setup. The slug length is mainly determined by the hydrodynamics and geometry near the inlet of the channel, because once a volume of liquid is trapped between two bubbles, it cannot escape the slug it forms between the two sealing bubbles on either side. As a result, different slug lengths (or bubble frequencies) will be found in different setups, and this probably explains the spread in experimental data for capillary tubes in correlations based on homogeneous or two-phase multiplier (Lockhart–Martinelli) models. The function \( \xi \) in Eq. 41 depends on \( Ca \) and \( Re \). For low values of both of these dimensionless groups, that is, for \( Ca \ll 1 \) and \( Ca^*Re = We \ll 1 \), the Stokes-flow lubrication solutions may be used, and we rewrite Bretherton’s result as

\[ f_{\text{slug}} = \frac{16}{Re} \left[ 1 + \frac{7.16(3Ca)^{2/3}}{32L_{\text{slug}}^*Ca} \right] \]  

(41)

In the remaining discussion of the numerical results, we will first validate the work with theory at low \( Re \), and then continue with the simulations for higher Reynolds numbers to explore the effect of inertia on the pressure drop.
2.2.4. Gas and liquid slug properties

2.2.4.1. Gas Length

Fig. 19 represents log(L_gas/D) versus log(Re_{Vs}/E_0), the Reynolds number being expressed as a function of the gas slug velocity and noted Re_{Vs}. The dimensionless number is defined as:

\[
\frac{Re_{Vs}}{E_0} = \frac{V_s \rho_L \gamma_L^2}{\mu_L (\rho_L - \rho_g)^2 D^2 g^2}
\]

(42)

This number represents the ratio:

\[
\frac{\text{inertia forces (interfacial forces)}^2}{\text{viscosity forces (gravity forces)}^2}
\]

(43)
A linear function was observed between the logarithm of the two parameters, with a correlation coefficient of 0.84. We can then write:

\[
\frac{L_{\text{Gas}}}{D} = 0.0878 \left( \frac{Re_{(g)}}{Eo^2} \right)^{0.63} = 0.0878 \frac{Re_{(g)} \cdot Eo^{0.26}}{Eo^{1.26}}.
\]

This correlation allows a first empirical description of gas slug length versus a dimensionless number characteristic of the flow and of the fluid properties. Results of the previous analysis can be found again in this correlation, i.e. gas slug length decreases when the capillary diameter and the viscosity increase. Moreover, an increase in the gas superficial velocity leads to an increase in the ratio \( L_{\text{Gas}}/D \). On the other hand, the influence of liquid superficial velocity does not appear in the empirical global correlation.

![Fig 19 The variation of \( L_{\text{Gas}}/D \) with \( Re \) and \( Eo \) from T. C. Thulasidas](image)

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Chapter II

Gas-liquid hydrodynamics in Taylor Flows with complex liquids
2.2.4.2. Liquid Length

The same approach was used for the ratio $L_{\text{liq}}/D$. Another dimensionless number was found to describe the influence of operating parameters on liquid slug length. This number includes the Eotvos number $Eo$ and the Reynolds number defined as a function of the gas superficial velocity and noted $Re(U_{\text{gas}})$.

$$\frac{1}{Re(U_{\text{gas}})Eo} = \frac{\mu L}{U_{\text{gas}}(\rho_L - \rho_G)\rho_L D^2 g}$$

(45)

This dimensionless number represents the ratio:

$$\frac{\text{viscosity forces(interfacial forces)}}{\text{inertia forces(gravity forces)}}$$

(46)

Fig. 20 plots $\log(L_{\text{liq}}/D)$ versus $\log(1/Re(U_{\text{gas}})Eo)$. A linear relationship is observed between the logarithm of the two parameters, the correlation coefficient is 0.82:

$$\frac{L_{\text{liq}}}{D} = 3451 \left(\frac{1}{Re(U_{\text{gas}})Eo}\right)^{1.2688} = 3451 \left(\frac{Re(U_{\text{gas}})}{Eo^{1.27}}\right)^{1.27}$$

(47)

This relationship expresses the influence of the gas superficial velocity on the liquid slug length observed in the previous study, i.e. an increase of $U_{\text{gas}}$ leads to a decrease of $L_{\text{liq}}$. Moreover, the parameter $U_{\text{liq}}$ does not appear in the correlation (47), which is in accordance with the results of the previous study. In this case too, this correlation is just a first approach to the global description of the liquid slug length. It is interesting to note that the dimensionless Eotvos number appears with the same weight ($Eo^{1.27}$) in correlations to describe both the slug lengths. On the contrary, the Reynolds number, expressed with different velocities, appears differently for each kind of length.
Numerous researchers have studied the motion of a single elongated bubble in stagnant liquid analytically and experimentally. Usually, the asymptotic cases are considered: inertial flow, viscous flow and capillary flow. The ranges of these regimes were determined experimentally by White and Beardmore (1962). The drift velocity is determined by the three-dimensional flow at the front of the bubble. For the case of inertial flow (where both interfacial and viscous effects are negligible) the fluid is assumed to be immiscible. Dumitrescu (1943) and Davies and Taylor (1950) performed an analysis based on potential flow for the vertical case and obtained the following expression for the drift velocity:

\[ U_0 = k\sqrt{gD}. \]
Dumitrescu (1943) found that the value of the coefficient $k$ in Eq. (48) is equal to 0.351, while Davies and Taylor (1950), who used a less accurate solution, obtained $k \approx 0.328$. Measurements show that the value of $k$ is in the range of $0.33 \pm 0.36$ (Nicklin et al., 1962; Goldsmith and Mason, 1962; Clift et al., 1978). For a Taylor bubble rising in a moving liquid, Nicklin et al. (1962) suggested that the translational velocity of the bubble is a superposition of its rise velocity in stagnant liquid $U_0$ and the contribution due to the mean liquid velocity $U_L$:

$$U_t = C U_L + U_0.$$  \(49\)

They also measured the velocity of the bubble nose in stagnant liquid under different cases of hydrostatic expansion; i.e. when liquid is removed below or above the bubble. If the bubble is allowed to expand downward, the velocity of the bubble nose remains the same as the bubble rise velocity in a pressurized tube. When the bubble expands upward, its velocity increases linearly, and the rate of acceleration is related to the pressure gradient. In this case, the coefficient $C$ in Eq. (49) was found to be not zero but 1.48, in spite of the fact that the liquid was initially at rest. Griffith and Wallis (1959) showed that for continuous slug flow, the liquid velocity $U_L$ in Eq. (8) should be replaced by the mixture velocity:

$$U_t = C U_M + U_0.$$  \(50\)

where $U_M = U_{LS} + U_{GS}$ is the total mixture velocity, $U_{LS}$ and $U_{GS}$ are the liquid and gas superficial velocities, respectively. The value of the factor $C$ in Eq. (59) depends on the velocity profile in the liquid ahead of the bubble, and can be seen as the ratio of the maximum to the mean velocity in the profile. Hence, for turbulent flows, $C \approx 1.2$, while for laminar pipe flow, $C \approx 2$ (Nicklin et al., 1962; Collins et al., 1978; Grace and Clift, 1979; Bendiksen, 1985). Shemer and Barnea (1987) performed a visualization of the velocity profiles behind Taylor bubbles in vertical and horizontal slug flows. They found that the tip of the trailing bubble in the wake of the leading one follows the location of the maximum instantaneous velocity in the wake. Tung and Parlange (1976) and Bendiksen (1985) analyzed the influence of surface tension on the bubble velocity in the inertial regime, first in stagnant liquid and then in upward flow.
2.3. Rheology

The measurements of rheological surface characteristics are important for studying versatile systems, ranging from pure liquids to colloidal systems and polymer solutions. However, it should be emphasized that, in the majority of cases, the objects for investigation in 2D rheology are interfacial layers of surfactants, including proteins and surface-active polymers. Interfacial layers are either organized spontaneously at liquid interfaces due to adsorption of surfactants from solution or formed mechanically by depositing insoluble surfactant layers on the surface of a liquid phase. The thickness of these interfacial layers of surfactants does not exceed a few nanometers, which allows these layers to be referred to as two-dimensional systems. The aim of measuring the rheological characteristics of interfacial layers, as well as any measurements of quantitative characteristics of a material, is their comparison with the composition and internal structure of this material in order to eventually predetermine the choice and optimization of its composition for some applications. Definitions of parameters subjected to measurements in 2D rheology are related to the analogous notions and definitions used in classical rheology. However, notions and definitions were reformulated because we deal here with surface (two-dimensional) rather than bulk (three-dimensional) properties. Thus, fundamental characteristics in our discussion are stress, which is understood as the force referred to a unit length (albeit not to unit surface area as in continuum mechanics), and strain $\gamma$, which, as usual, represents the relative change in the distance between two infinitely close point in the continuum. Then, surface shear viscosity is expressed, in full keeping with the classical Newton law, as,

$$\eta_s = \frac{\tau}{\gamma},$$

(51)

where $\gamma$ is the strain rate. The dimension of the value of surface (or 2D) viscosity has the form of $[(N \text{ s})/m]$ not $[(N \text{ s})/m^3]$ as in the rheology of bulk materials. The notion of the existence of surface viscosity was probably introduced into science for the first time by Plateau and the fundamental term of surface elasticity was formulated by Gibbs. In addition to shear viscosity $\eta_s$, a substantial significance in the theory of surface properties belongs to so called surface dilational viscosity $\eta_d$, which is analogous to longitudinal viscosity (the viscosity measured in expansion, but not in shear) in the rheology of bulk media. However, as a rule, this parameter in 2D rheology is considered to include the deformation of a two dimensional surface rather than a uniaxial stretching deformation. We should additionally mention that, in the theory of viscous Newtonian liquids, there is an rigorouscorrelation between shear viscosity $\eta$ and longitudinal (so-called Trouton) viscosity $\lambda$, which is absent in the theory of surface flow. The $\eta_s$ and $\eta_d$ parameters are considered to be independent rheological surface characteristics that is probably not entirely
correct. Regimes of periodic deformation, which in rheology are usually called dynamic regimes, are used in the study of viscoelastic interfacial layers in the region of linear viscoelasticity (as it is done in the study of three dimensional bodies). Shear deformation applied to a surface changes with time $t$ according to harmonic law:

$$\gamma(t) = \gamma_0 \sin(\omega t). \quad (52)$$

The response of a surface to harmonic changes in deformation is expressed in the appearance of a harmonic shear stresses delayed in phase relative to the generating deformation:

$$\tau(t) = \tau_0 \sin(\omega t + \delta), \quad (53)$$

where $\gamma_0$ and $\tau_0$ are amplitudes of deformation and stress, respectively; $\omega$ is the oscillation frequency; and $\delta$ is the phase angle (the lag angle or mechanical loss angle). In this case, the main characteristic of an interfacial layer is the complex 2D elastic modulus measured in shear, whose value defined as:

$$|G_s^*| = \frac{\tau_0}{\gamma_0}. \quad (54)$$

### 2.3.1. Non Newtonian fluid

During my work I used ludox solution which is a non Newtonian fluid, but this solution is used diluted so all solutions with ludox are considered Newtonian like water. To give a completely idea of all kinds of fluid, I put this short chapter about non Newtonian fluid. The cornerstone work by Reynolds on laminar-turbulent transition in flow through tubes is perhaps the most disseminated evidence of the enormous usefulness of analyzing fluid mechanics problems in dimensionless form. The discovery of this powerful tool is due to Stokes. Since then, it has been employed extensively to help unveiling the physics involved in a wide variety of fluid mechanics situations. For given geometry and initial conditions, the main benefit of analyzing a fluid mechanics problem in dimensionless form is the reduction of the number of governing parameters. The dimensional governing parameters are grouped into dimensionless parameters which govern a whole family of dynamically similar flows. However, this grouping procedure is not unique, and the degree of success of dimensional analysis depends on how well represented by the dimensionless groups are the physics of the situation at hand. In the process of reducing a non-Newtonian fluid mechanics
problem into its dimensionless form, it is customary to follow the same procedure employed in Newtonian fluid mechanics. It is argued that this practice can generate unsuitable non-dimensional formulations of non-Newtonian fluid mechanics problems. Then a different procedure is proposed and its features are discussed. This procedure has been recently used successfully for flows of viscoplastic liquids. The non-dimensionalization of a fluid mechanics problem generally starts with the selection of a characteristic velocity. For internal flows, the typical choice is an average velocity at some representative cross sectional area $A$:

$$v_c = \frac{1}{A} \int_{A} |v \cdot n| \, dA$$  \hspace{1cm} (55)$$

where $n$ is the unit vector normal to the cross sectional area.

Alternatively, a characteristic viscosity can be constructed by a combination of characteristic values of the pressure gradient, and length. For external flows, the far-away fluid velocity relative to the solid boundary, $V_{rel}$, is the usual selected characteristic velocity:

$$v_c = V_{rel}$$  \hspace{1cm} (56)$$

Examples of internal and external flows are given in Fig. 21. Because for the flow of non-Newtonian fluids the stress depends non-linearly on the flow kinematics, the deformation rate is a key quantity in the analysis of these flows. Thus, a characteristic deformation rate $\dot{\gamma}_c$ is needed, and it is usually defined as the ratio of a previously selected characteristic velocity to a characteristic length $L$:

$$\dot{\gamma}_c = \frac{v_c}{L}$$  \hspace{1cm} (57)$$

When the flow is predominantly a shear flow, the characteristic length $L$ is a length measured perpendicularly to the flow direction, while in predominantly extensional flows $L$ should represent
a length in the main flow direction. It is clear that the characteristic deformation rate chosen should always fall within the range of deformation rate actually observed in the flow. Moreover, the relevant rheological information must correspond to the same deformation rate range. For periodic flows, it is generally convenient to employ the inverse of a characteristic frequency as characteristic time. For other flows, a characteristic time may be defined as the inverse of the characteristic deformation rate, namely, \( t_c = 1/\dot{\gamma}_c = L/v_c \). By definition, this is the time that a fluid particle at speed \( v_c \) takes to travel a distance equal to the characteristic length \( L \). Characteristic values of other important flow quantities are also derived from the ones already selected. The characteristic viscosity is obtained by evaluating the viscosity function \( \eta(\dot{\gamma}) \) at the characteristic deformation rate,

\[
\eta_c \equiv \eta \left( \frac{v_c}{L} \right) \tag{58}
\]

A characteristic stress is constructed by multiplying the characteristic viscosity by the characteristic deformation rate, \( \tau_c = \eta_c v_c / L \). Other characteristic quantities that may be needed can also be defined in a similar manner. For incompressible materials, the mass conservation equation is written as

\[
\nabla \cdot \mathbf{v} = 0 \tag{59}
\]

where \( \mathbf{v} \) is the velocity vector field. The linear momentum conservation principle requires that

\[
\rho \frac{d\mathbf{v}}{dt} = -\nabla p + \nabla \cdot \mathbf{\tau} + \rho \mathbf{g} \tag{60}
\]

where \( \rho \) is the mass density, \( d(\cdot)/dt \) the material time derivative, \( p \) the pressure, \( \mathbf{\tau} \equiv \mathbf{T} + \rho \mathbf{1} \) the extra-stress tensor field, \( \mathbf{T} \) the stress tensor field, \( \mathbf{1} \) the unit tensor, and \( \mathbf{g} \) is a field of external forces (e.g. gravity). The next step of the non-dimensionalization procedure is to employ the selected characteristic quantities to obtain a dimensionless version of the conservation equations. To this end, the following dimensionless variables are defined:

\[
\begin{align*}
    t^* & \equiv \frac{v_c}{L} t; \quad \mathbf{v}^* \equiv \frac{v}{v_c}; \quad \nabla^* \equiv L \nabla; \quad p^* \equiv \frac{pL}{\eta_c v_c}; \\
    \tau^* & \equiv \frac{\tau L}{\eta_c v_c}
\end{align*} \tag{61}
\]

\[
\begin{align*}
    (59)
\end{align*}
\]
The dimensionless version of the conservation equations is
\[ \nabla^* \cdot \mathbf{v}^* = 0 \]  
(63)

\[
Re \frac{\mathrm{d}\mathbf{v}^*}{\mathrm{d}t^*} = -\nabla^* p^* + \nabla^* \cdot \mathbf{\tau}^* + Ga \frac{\mathbf{g}}{g}
\]  
(64)

where \( g = |\mathbf{g}| \). Two dimensionless groups arise, namely, the Reynolds number, \( Re \), and the Galilei number, \( Ga \). The Reynolds gives the importance of inertia forces relative to viscous forces in the flow:

\[ Re \equiv \frac{\rho v_c L}{\eta_c} \]  
(65)

The Galilei number gives the importance of the external forces relative to viscous forces in the flow:

\[ Ga \equiv \frac{\rho g L^2}{\eta_c v_c} \]  
(66)

Other dimensionless groups may arise in the boundary conditions. For example, in flows with free or moving boundaries, the capillary number may arise:

\[ Ca \equiv \frac{\eta_c v_c}{\sigma} \]  
(67)

where \( \sigma \) is the surface tension. The above definitions are given solely to serve as an example of the non-dimensionalization procedure. It is clear that they are not unique, and that other characteristic and dimensionless quantities are also employed, depending on the specific problem. The correct choices ensure that the dimensionless variables and related derivatives appearing in the conservation equations are order one (\( O(1) \)). Hence, the order of magnitude of the terms in these equations is the same as the one of the dimensionless groups appearing as coefficients. Additional dimensionless parameters appear in the dimensionless version of the constitutive equation. For liquids that obey the generalized Newtonian liquid model,

\[ \mathbf{\tau} \equiv \eta(\dot{\gamma})(\nabla \mathbf{v} + \nabla \mathbf{v}^T) \]  
(68)
dimensionless groups appear in the non-dimensional version of the viscosity function. For polymeric liquids, a widely used viscosity function is the Carreau equation,

\[
\eta(\dot{\gamma}) = \eta_0 + (\eta_0 - \eta_\infty) \left\{ 1 + \left[ \frac{\dot{\gamma}}{\dot{\gamma}_1} \right]^2 \right\}^{(n-1)/2}
\]

where \(\eta_0\) is the zero-shear-rate viscosity, \(\eta_\infty\) the infinite-shear-rate viscosity, and \(n\) is the power-law or behavior index. Its dimensionless form is given by

\[
\eta^*(\dot{\gamma}^*) \equiv \frac{\eta(\dot{\gamma})}{\eta_c}
\]

\[
= \eta_0^* + (\eta_0^* - \eta_\infty^*)[1 + Cu^2\dot{\gamma}_1^2]^{(n-1)/2}
\]

\[
Cu = \frac{\nu_c}{\dot{\gamma}_1 L} ; \quad \eta_0^* = \frac{\eta_0}{\eta_c} ; \quad \eta_\infty^* = \frac{\eta_\infty}{\eta_c}
\]

The parameter \(\dot{\gamma}_1\) is the shear rate at which it occurs the transition from low-shear rate Newtonian plateau to the power-law region
Fig 22 The Carreau viscosity function.