Dynamics of drops — Formation, growth, oscillation, detachment, and coalescence

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Abstract

Single drops or bubbles are frequently used for the characterization of liquid—fluid interfaces. Their advantage is the small volume and the various protocols of their formation. Thus, several important methods are based on single drops and bubbles, such as capillary pressure and profile analysis tensiometry. However, these methods are often applied under dynamic conditions, although their principles are defined under equilibrium conditions. Thus, specific attention has to be paid when these methods are used beyond certain limits. In many cases, computational fluid dynamics (CFD) simulations have allowed researchers, to extend these limits and to gain important information on the interfacial dynamics. Examples discussed here are the capillary pressure tensiometry used for short time and profile analysis tensiometry for long time dynamic interfacial tension measurements, the oscillating drop methods for measuring dilational visco-elasticity. For measuring the coalescence of two drops the liquid dynamics of the subsequently formed liquid bridges have to be considered. In this paper, a thorough review of important experimental and computational findings, related to the dynamics of drops, including its formation, growth, oscillation, detachment, and coalescence is presented. Emphasis is however on some selected important developments. In addition, the paper tries to predict the main directions of advancement in interfacial research for the near future.

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1. Introduction

In the past decades, a wide range of experimental investigations have been conducted in order to study fluid–fluid interfaces. However,
because of their simplicity, and at the same time their complexity, single drops/bubbles having different types of interfaces, have been the main concern of both numerical and experimental investigations for many years. In several of such studies, most dynamic effects have been neglected and thermodynamic equilibrium has been assumed. However, these studies have led to reliable, and at the same time relatively, simple and important theories.

More recently, it seems that emphasis has turned to interfaces in which dynamic effects play the main role. Especially, the complicated dynamic behaviors existing in both phases (e.g., inside and outside bubbles/drops) have attracted much interest in fundamental and applied research works. This for example has led to studying the mechanism of drops/bubbles formation and detachment from a capillary tip, which under certain conditions are of great interest.

To study the dynamics of interfacial layers, the interfaces are not necessarily in equilibrium conditions and considering hydrodynamic effects usually becomes very crucial. The complexities of fluid–fluid interfaces are mostly related to the mutual interactions between the interface and its adjacent bulk [1]. In addition, any change in the properties of the interface may directly affect the flow field in both phases. This includes interrelations between the physico-chemical properties and hydrodynamics, which usually make interfacial dynamics considerably complicated. Such mutual interactions are of course more complicated in systems containing surface active molecules (as the mechanism of transport of surfactant molecules to and from the interface). On the other hand, the quantitative understanding of the mutual dynamical bulk–interface interactions is the main challenge in studying the stability of many systems (like foams and emulsions). Thus, the properties of the adsorbed layers depend on rather complex mutual bulk–interface interrelations.

Various protocols and experimental techniques have been applied for such investigations. Among different available experimental techniques, the most recently developed capillary pressure technique (CPT) [2–5] and profile analysis technique (PAT) [6–9] represent the leading edge of the experimental investigations on dynamics of single drops and bubbles. Furthermore, these techniques have also the potential to be applied to study the bubble/drop coalescence and splitting processes [10,11]. Note, oscillating drop and bubble experiments are also very essential for studying rheological properties of interfacial layers [6,12,13]. A variety of other experimental techniques and protocols were developed to study the dynamics of interfacial layers, also based on single drop and bubble manipulations [11,14]. This is true also for rising drops and bubbles in surfactant solutions the rising velocity values of which depend strongly on the structure of the dynamic adsorption layer formed at the drop/bubble surface (see reference [15] for more details).

Challenges in fluid–interface interactions are more complicated to be understood via experimental investigations alone and thus their comprehensive studies also need special attempts from the computational fluid dynamics (CFD) community. In about the past three decades, detailed CFD simulations have provided necessary insight required for understanding the actual flow properties and the mechanisms of transfer of mass and momentum in the bulk and at the interface. Of course, recent CFD simulations (validated with accurate experimental measurements) have also been effectively used to describe some of the complexities in the bulk–interface interactions [16].

Even though there has been a great deal of experimental and computational efforts in this field, the complete complex dynamics of most fluid–fluid interfaces is not yet fully understood. The main objective of this paper is to highlight some selected challenges involved in the two-way coupling of complex liquid–fluid interfaces. More specifically, this paper mainly deals with the latest progress in experimental and computational studies of drop formation and drop surface behavior (under different dynamical conditions). In addition, new findings on dynamical drop formation and detachment, drop oscillations and growth, direct drop/drop interactions, liquid bridges, and drop coalescence are discussed in details.

2. Drop profile analysis for growing drops

The shape analysis of pendant drops or buoyant bubbles (originally called axisymmetric drop shape analysis — ADSA [17]) is nowadays a routine tool for measuring the surface tension and other interfacial properties. The curvature of an interface corresponds to the physical properties of the interface as well as the dynamic interaction between the two adjacent phases. Therefore, a big advancement in the analysis of drop or bubble profiles has been performed so that modern commercial drop profile analysis tensiometers are available now for fundamental and industrial studies in interfacial science. There are many advantages with the profile analysis techniques, when compared to traditional methods like Wilhelmy plate, Du Nouy Ring, and drop volume tensiometry. The drop/bubble profile analysis technique is easy to handle and requires less amount of liquid for measurements. In addition, tracking the changes in the drop profile with time allows studying the dynamics of interfacial properties.

The process of drop formation and growth is one of the most important research fields because of the enormous number of scientific and industrial applications, like in food industry, extraction technology and petrochemical industry, pharmacy and biotechnology. Therefore, many investigations are performed with growing drops (e.g. [18–20]). In addition, this is an interesting field of fundamental research for interfacial science [21,22]. During drop formation, the interface is getting out of equilibrium due to hydrodynamic effects. This allows deducing dynamic interfacial properties from the profile analysis technique (PAT), however, beyond interfacial properties and gravity as the body force, inertia force, and the drag force during drop growth at the tip of a capillary also contribute in the local drop curvature. According to literature, there are many experimental and numerical studies conducted on growing drops/bubbles, to the aim of studying the role of different contributions in drop and bubble surface deformation [3,9,16].

The basis of PAT is an equilibrium force balance as given by the Gauss–Laplace equation. The parametric form of the equation can be presented as [8]:

\[
\frac{dx}{ds} = \cos\theta
\]

\[
\frac{dz}{ds} = \sin\theta
\]

\[
\frac{d\theta}{ds} = 2 \frac{\Delta \varphi gz}{R_0 \gamma} - \frac{\sin\theta}{x}
\]

Here \(\Delta \varphi\) is the difference of the densities of the two fluids, and \(g\) is the acceleration due to gravity. Fig. 1 shows the definition of the coordinates and other parameters used in the fitting of the Gauss–Laplace equation to an experimental axisymmetric drop profile.

To obtain the surface tension \(\gamma\), the Gauss–Laplace equation is fitted to the experimental drop profile coordinates, as described in detail in [23,24]. As the technique is commonly in use, several attempts are performed to assess and to extend its capability to different experimental conditions or applications. For example, in [25] overviews on the limitation of surface tension measurements with PAT are discussed. However, most of the work is concerned with the use of the technique for equilibrium or very slow dynamic conditions. Only recently, the profile analysis technique was used at rather dynamic conditions where the obtained dynamic profiles of growing drops are analyzed by fitting the Gauss–Laplace equation [9]. In this study, the applicability of this technique is examined for growing drops of water in air and in hexane, in a broad range of flow rates and drop sizes. For this aim, the values of the standard deviation of fitting the Gauss–Laplace equation to the dynamic drop profiles are obtained. The obtained surface tension values
are apparent values and were used to describe hydrodynamic contribution to the drop surface deformation, as shown in Fig. 2. From the apparent surface tension values, one can see a deviation from physically accepted values caused by hydrodynamic effects on the drop surface.

3. Capillary pressure technique for growing drops

For the characterization of the liquid interfaces under dynamic conditions fast changes of the surface/interfacial area within a short time are required in order to bring the interface far out of equilibrium and monitor subsequently the kinetics of adsorption. Growing drop protocols are one of the most relevant techniques for this purpose. It is not a difficult technique to inject the liquid under study through a capillary and create a fresh liquid surface. However, drop profile analysis under conditions of fast injection faces instabilities of the profile needed for the determination of the surface tension. Therefore, measurements of the capillary pressure P provide an extra parameter for this purpose. This technique was developed for fast dynamic conditions starting from a basic design [5,26,27] for static or quasi-static conditions [1,3,4]. Fig. 3 shows the schematic view of a capillary pressure tensiometer (CPT) setup that can be applied for growing drop experiments via flow injection by syringe pump (0.1 to 1000 mm³/s) or via a piezo drive for very accurate small volume changes (0.01 to 1 mm³). This setup can be also applied to generate oscillations of drops and bubbles as it is the case for the Oscillating Drop Bubble Analyzer (ODBA) for measuring the interfacial dilational rheology in the frequency range of 0.1 to 200 Hz (discussed in the next section). Capillary pressure tensiometry is also an important technique for systems of low density difference and for microgravity conditions [28] where other density based surface tension measurements do not. This is also an applicable technique for measuring interfacial properties under instability conditions such as shaking drop caused by Marangoni convection [22]. For the condition of low flow injection and negligible hydrodynamic effects, the surface or interfacial tension is calculated according to the Laplace equation \( \gamma = P/(2/r) \), where \( r \) is the radius of curvature. However, when the hydrodynamic contribution is significant it has to be estimated (experimentally or theoretically) and recalculated as \( \gamma = (P_{\text{total}} - P_{\text{hydro}})/(2/r) \). The hydrodynamic pressure losses \( P_{\text{hydro}} \) are a function of capillary tip size and capillary geometry, the flow path line through the pressure chamber, fluid properties and the applied flow rate [4,29].

Fig. 4 shows a constant interfacial tension measured during a growing drop experiment for a pure water drop in pure hexane at a low flow rate of \( Q = 0.85 \) mm³/s. In Fig. 5 the corresponding measured values of capillary pressure and drop radius are shown. For higher flow rates, such as \( Q = 2 \) mm³/s, a slight increase in the interfacial tension values of about 1 mN/m is observed which is due to the hydrodynamic pressure loss inside the capillary tip (Fig. 6). The corresponding experiment for a surfactant solution (\( 10^{-5} \) mol/l aqueous Span80 solution in hexane) is shown also in Fig. 6. It is observed that this growth rate is fast enough for this system to achieve a fresh interface after a short experimental time. However, this depends on the concentration and surface activity of the surfactant and higher injection and faster growth rates for the drop are required [3,4].

4. Oscillating drops

In many works on multiphase flow systems involving liquid surface phenomena, just the dynamic surface tension or in some cases even constant tension values are considered for the system characterization. However, also the interfacial rheology parameters can play a significant role for the characterization of the liquid interfaces. This is true for example for the formation and stabilization of foams and emulsions. Set-ups for interfacial shear and dilational rheology experiments have been developed for this purpose. The deformation of the interface can be done in various ways [30]. The dilatational elasticity modulus as the main rheological parameter is defined as the change in surface or interfacial tension \( \delta \gamma \) with the relative interfacial area \( \delta \ln A \):

\[
E = \frac{\delta \gamma}{\delta \ln A}.
\]

For solutions at low concentrations of highly surface active compounds, such as proteins, low frequency experiments via profile analysis tensiometry (PAT) are applicable [31,32]. However, for many solutions of traditional surfactant of a significant surface activity experiments are hard to be performed with PAT from a certain concentration on (e.g. higher than \( 10^{-4} \) for SDS at the water/air interface). The reason is that the kinetics of adsorption reaches the equilibrium adsorption state within a few seconds and even faster, in adsorption time shorter than a millisecond. The shape of a drop/bubble under fast growth or oscillation condition is not suitable for such studies because the acquired profiles are not Laplacian [33]. The capillary pressure setup ODBA presented in Fig. 3 is a tool for fast dynamic interfacial tension measurements and interfacial rheology studies in a broad range of frequencies [4,12,13,34–36]. In addition to the usual injection facility (syringe pumps) used for the standard PAT set-ups, it contains also a piezo drive for the exact size control of very small droplets (0.01 to 1 mm³) with the accuracy of \( \pm 0.0001 \text{ mm}^3 \) (\( \pm 100 \) pl) in the frequency range of 0.1 to 300 Hz. For oscillation experiments the volume amplitude

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**Fig. 1.** Definition of the coordinate system for a pendent drop; coordinate points with fitted Laplace profile.

**Fig. 2.** Surface tension vs. drop volume \( V_D \) for growing drops of water in air at different Re (varied by different flow rates only); according to Karbaschi et al. [9].

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can be selected in the range between 0.0005 and 0.075 mm$^3$ with an accuracy of 0.0001 mm$^3$ (100 pl). During the oscillations the pressure variations can be recorded (in the range between 1 and 10$^4$ Pa) via an accurate pressure sensor as a function of time. The data acquisition board is able for a sampling rate of $2 \times 10^5$ per second, i.e. 5 $\mu$s per reading. Each signal contains the capillary pressure contribution along with hydrodynamic effects. The hydrodynamic effects are negligible for low frequencies, however, it can be very significant for the higher frequencies depending on the applied piezo amplitude, fluid viscosities, tip size and geometry of the capillary [4,29,36].

The most reliable way of testing the highest reliable frequency for oscillation experiments is to perform experiments with pure solvents. The observed changes in the capillary pressure $P(t)$ should be compensated by the changes in the radii of curvature $r(t)$ such that the final surface tension value $\gamma(t)$ is time independent, i.e. the visco-elasticity of the liquid interface should be zero. The results of interfacial tension and capillary pressure during oscillating of an aqueous drop of a 10$^{-4}$ mol/l CTAB solution in hexane are shown in Fig. 7 along with the result for the pure system [4,36]. The obtained data for a frequency of 10 Hz show how the interfacial tension variations are considerable for the CTAB solution as compared to the pure system, where we can observe negligible variations. The hydrodynamics of the oscillatory flow inside the capillary tip at high frequencies can be more complex than for constant continuous flow rates in growing drop experiments [12,13,29,34–36]. Fig. 8 shows simulation results of the velocity profiles at the moment of maximum pressure loss for an oscillatory flow with $dV = 0.01$ $\mu$L in a capillary with the diameter of 0.45 mm for different frequencies 5 to 100 Hz [29]. Therefore, in addition to the discussed regular hydrodynamic effects, extra phenomena and related limitations such as the hydrodynamic relaxation time $\tau_h = r_c^2/\nu$ and the phase shift between the hydrodynamic
pressure loss and the main capillary pressure signal should be considered. Here $r_c$ is the capillary tip radius and $\nu$ is the kinematic viscosity of the fluid in the capillary.

For very high frequencies also due to inertia, viscosity and gravity effects, drops might start to oscillate in a deformed shape, out of a radial oscillation mode with overtones so that a clear analysis of the measured pressure signal becomes very difficult. The frequency limits depend strongly on the properties of the liquid bulk and the interface, the absolute drop size and the geometry of the capillary. Therefore, the optimization of the drop size and volume amplitude for a given capillary is a very important issue for studies of a certain solution at high frequencies. Fig. 9 illustrates reasonable monotonic drop shape oscillation at up to 80 Hz for a drop of an aqueous $10^{-3}$ mol/l CTAB solution in hexane (interfacial tension of about 10 mN/m), while for oscillating drops of the same solution in air, an acceptable oscillation is observed for up to 150 Hz.

5. Dynamics of drop–drop interaction

Another group of experiments deals with the contact of two single drops or bubbles, i.e. the stability of the respective liquid films. Such situations are important to forecast the stability of foams and emulsions. Foams and emulsions as liquid disperse systems are frequently used in various fields of application. They are common in foods, mineral flotation, water treatment, cosmetics, drugs, paving asphalt, paints, pulp and paper, detergents and so on. The stability of foams and emulsions is greatly affected by the dynamics of liquid films.

In literature, there are several studies on the rate of coalescence between drops and their mechanisms of interactions in a bulk system. In some systems, the rate of coalescence is determined via a drop size distribution analysis [37]. Other methods are proposed to measure the kinetics of coalescence between drops. For example, Håkansson et al. [38] developed a new evaluation method based on the Oil Transfer Technique proposed in [39], while Karbaschi et al. [40] proposed a new experimental method for studies of the kinetics of coalescence between drops of W/O emulsions, using colorimetry. In many of these studies, the stability of emulsion is measured in terms of the kinetics of coalescence between droplets in an emulsion.

According to literature, there are also attempts to directly study the interaction between drops or bubbles. For example, Bournival et al. [41] studied the process of coalescence between bubbles in surfactant solutions, measuring the coalescence time for different surfactant concentrations. Regarding the interaction between drops, Ata et al. studied the coalescence behavior of industrial kerosene oil drops [42].
measurements are performed for freshly prepared drops and at different aging times, to compare the dynamic behavior of aged and freshly prepared industrial emulsions.

To study the coalescence behavior of pairs of drops or bubbles, the Drop and Bubble Micro Manipulator (DBMM) (SINTERFACE Technology, Berlin) was developed as a new tool for a direct quantitative analysis of the interaction between two drops or two bubbles or even between a single drop and a bubble in a liquid medium [10]. It is an extension module of the Oscillating Drop and Bubble pressure Analyzer (ODBA) [4]. In brief, DBMM is made up with two identical cells; each of them consists of a special designed capillary, pressure sensor, piezoelectric translator for exact drop size control and precise drop oscillations and a rough syringe dosing system. As shown in Fig. 10, the two cells are mounted horizontally so that one cell has a fixed position to the PAT instrument while the second one can be manipulated in all directions by the xyz-stage. Loglio et al. have presented such an experimental tool in [43]. Other authors introduced qualitative set-ups only for the observation of the coalescence of two objects which has perpendicularly arranged capillaries [41, 42, 44–46]. In contrast, the DBMM allows not only a visual inspection of the interaction between drops or bubbles but also provides quantitative investigations with video registration and capillary pressure monitoring.

The DBMM has been used to determine the time of rupture of the liquid film between two air bubbles after a given aging time in β-lactoglobulin (BLG) solutions of different bulk concentrations. The use of the profile analysis tensiometer PAT1 has been used to compare the adsorption characteristics of BLG at the water/air surface with a complementarity technique. The combination of the two methods confirms that a respective amount of pre-adsorbed BLG at the bubble surface is required to prevent immediate bubble coalescence. The adsorbed amount of BLG was determined as a function of time and concentration and correlates with the observed coalescence behavior of the contacting bubbles. The minimum aging time becomes lower with increasing protein concentration. The longer the aging time above a threshold concentration of BLG the longer is the lifetime of the liquid film between the bubbles. The drop or bubble interaction is time dependent and therefore dynamic effects on different length scales have to be investigated with sufficient precision for a quantitative analysis.

6. Dynamics of liquid bridges

In the previous paragraph we discussed the coalescence of two separate drops due to drop–drop interactions. During this process a liquid bridge is formed between the capillary tips. In general liquid bridge is a specifically shaped volume of liquid being in contact with two solid surfaces in a short distance. Such liquid bridges can be surrounded by a gas or immersed in another immiscible liquid. Many applications involve liquid bridges e.g. printing, coating, heat and mass transfer. Their static and dynamic properties have been studied intensively since the 19th century [47, 48]. Such liquid menisci can be used as simple model of more complex fluid configurations. For experimental and theoretical studies it is normally assumed that a certain amount of liquid is hold between two solid circular rods in a certain distance. Apart from the density and viscosity of the liquid, its interfacial tension has an important influence on the stability and shape of liquid bridge. The liquid is hold mainly by intermolecular liquid–liquid forces and molecular solid–liquid forces. The first contribution is determining the interfacial...
tension and the latter one corresponds to wetting condition at the three phase contact line. Therefore a liquid bridge has a well-defined interfacial configuration which makes it possible to use them for the estimation of properties of the liquid's interface. Additional influences are gravity and other external fields. A conceptual understanding why a liquid bridge becomes unstable can be explained by the Gauss–Laplace equation. The interfacial tension is influenced by two separate radii of curvature. If the length of the liquid bridge with a certain volume exceeds a critical value (Plateau–Rayleigh limit) an imbalance between stabilizing and destabilizing effects occurs. In general the critical length depends on the volume of the liquid bridge, the density difference to the surrounding fluid, the fluid’s rheological properties, the interfacial tension and the radii of the solid ends between which the liquid bridges are formed.

The majority of publications deal with the stability of vertical liquid bridges in respect to stretching and breakup. For example in a computational study by Yildirim and Basaran [48] the deformation and breakup of Newtonian and non-Newtonian liquids have been investigated. Under the assumption that the fluids are held captive between two vertical solid rods which are separated from each other at a constant speed, a numerical simulation has been performed using different models. During the breakup of a liquid bridge a thin liquid thread connects the two larger liquid volumes which remain at the rods. The formations of such longer threads are the precursors of satellite droplets which are often unwanted in applications. The obtained results show that with a change of the rheological properties of the liquid, the location of neck breaking and the probability that satellite droplets are created can be influenced. The dynamics of non-cylindrical, axisymmetric, nearly unstable liquid bridges between two equal disks is analyzed for low viscosity liquids by Perales and Vega [49]. Under microgravity conditions the liquid bridge is cylindrical; an imbalance occurs at a critical length which is equal to its circumference. A non-linear response is sometimes obtained, if such liquid bridges are disturbed e.g. by sinusoidal perturbations. Martinez et al. reported about such experimental investigations [50,51].

Another often studied topic is shear-driven two phase flows. Gaponenko et al. [52,53] reported about experimental and numerical simulations for shear-driven two phase flows at vertical, cylindrical liquid bridges under normal gravity and microgravity conditions. The liquid bridge is held by solid cylindrical rods and the internal part is surrounded by a concentric gas channel. The liquid bridge is formed by a viscous liquid and kept in its position by the surface tension. The gas flow initiates a dynamic shear-driven flow of the initially quiescent liquid bridge. The Navier–Stokes equations for both liquids are solved numerically for the exact experimental geometry taking into account the interfacial deformation of the liquid bridge by gravity. A particular attention of the interfacial flow dynamics is focused on the effect of the free surface shape and the viscosity of liquid. Uguz et al. [54] reported about similar shear induced experiments with two liquids encapsulated in a cylindrical cavity. Depending on the flow direction the shearing flow can straighten out a bulging bridge suppressing deviations from a cylindrical interface. Depending on the viscosity differences the flow dynamics of the outer shearing liquid can stabilize the interface of a non-cylindrical bridge. The interfacial tension is estimated by image analysis and for the data analysis a modified Gauss–Laplace equation is used. The difference of the Bond and Capillary number describes the ability of flow to stabilize an otherwise unstable liquid bridge by reducing the effect of gravity. In the limits of small Capillary number flow induced dynamic free-surface deformations in thermocapillary liquid bridges were investigated numerically by Kuhlmann and Nienhäuser [55]. The wave magnitude and phase of the dynamic deformation of the interface relative to the magnitude of the temperature field of a hydrothermal wave are discussed. In another numerical study about thermocapillary convection in a liquid bridge when the interface is subjected to an axial gas flow was presented by Shevtsova et al. [56]. An experimental and numerical investigation of the accumulation of small mono-disperse particles in thermocapillary liquid bridges was presented by Kuhlmann et al. [57]. It is argued that due to the acceleration and deceleration of the tangential flow along the thermocapillary free surface, the interaction between the particles is the key importance for a fast particle accumulation.

An important property for wet granular systems is the action of liquid bridge forces between the wetted particles. Therefore in the past many mechanical models have been developed to express the volume and the force of the liquid bridge in terms of the liquid bridge profile. Chen et al. [58] presented a model to estimate the liquid bridge forces between two unequal-sized spheres or a sphere and a plane.

There are some attempts for the use of liquid bridges as a kind of diagnostic tool to estimate liquid or interfacial properties. A high speed visualization technique to observe the rupture of liquid bridges placed in a square cross section capillary tube was proposed by Wilinski et al. [59]. The process of rupture can be followed via the side and front views. It has been observed for such kind of experiments that the break-up of the liquid bridge is caused by drainage of liquid through the liquid filaments that were formed in the capillary corners. Another experimental technique using liquid bridges for a qualitative estimation of the rheological properties of a liquid was proposed by Bazilevski et al. [60]. The rheological parameters are determined from the filament thinning rate of a liquid bridge.

As mentioned before, the interfacial tension has an important influence on the stability of liquid bridges. Therefore it is surprising that only very few studies exist with liquid bridge formed from solutions of interfacial active compounds. Kostoglou and Karapantzos [61] presented a theoretical background for setting up a liquid bridge based model for the estimation of interfacial properties. This particular topic is devoted to liquid bridges made with electrically conducting liquids formed between two conducting solids for conductivity measurements. It is discussed that such a liquid bridge has an integral electrical conductivity which can be related to the specific shape of the liquid bridge. By this it seems possible to use the integral conductance as a shape descriptor instead of a conventional image analysis for the estimation of liquid interfacial tension.

In the previous paragraph a technique was discussed for studying direct drop–drop interactions. This capillary pressure technique is mainly devoted to drop coalescence studies. The interfacial properties can be estimated from the geometry of the drops and the corresponding capillary pressure. In the moment of coalescence a liquid bridge is formed between the two horizontal capillaries. Before the liquid bridge comes to rest, a certain oscillation can be observed and monitored by a high speed video technique [10]. Preliminary experiments show that the proposed technique also allows following the break-up of liquid bridge by slowly separating the capillaries to a certain distance. In the moment of break-up two drops are again formed at the capillary tips. Fig. 11 shows the protocol of such experiment for drops of water in air. After the formation of drops at the capillary tips (picture a), the drops are in a certain distance. For the water drops in picture (a), the drop sizes are 0.5 mm² and the distance 0.24 mm. While the position of the left capillary system is fixed, the right one can be moved via the xyz-stage. After a linear movement of the right drop, both drops touch each other as shown in picture (b). After a certain time elapse, a coalescence takes place and the liquid bridge is formed between the capillary tips (picture c). Due to the sudden change of the capillary pressure in both drops, the time elapsed between the contact of drops and their coalescence can be estimated precisely. In the presence of surfactant molecules this time depends strongly on the state of adsorption layer at the interface [62]. The pictures (d), (e) and (f) show the rough stages for the break-up of the liquid bridge. The red lines mark the same constant distance in all pictures. In (b) the right capillary is moved to the left side to decrease the distance between the drops. After coalescence the capillary tip is still in the same position. Due to the movement of the right capillary the system is brought back to the starting position while the liquid bridge starts to form a concave curvature (d). A much longer stretching is needed to bring the liquid bridge in a critical state, as
shown in (e). In this picture it is as well visible that the neck formation in the liquid bridge is not symmetric. Therefore, the drops have different sizes in their final state (f). Due to inertia both drops show initially oscillations right after the break-up. The fuzziness of the right drop picture is a hint of these oscillations. It needs longer time for the larger drop to come to rest. This makes it possible to detect the oscillations by standard video observations. From the geometry and very fast data recording of the capillary pressure, the amplitude and frequency can be estimated and the damping of the oscillation can be correlated to the interfacial and bulk rheological properties of the studied liquid.

7. Computational simulations of drop dynamics

Even though there has been a great deal of research conducted in this area of multiphase flow, the complete dynamics of such flows is not yet fully understood due to their complex interphase coupling, whereby different phases may strongly affect one another. Detailed numerical simulations are often computationally too intensive to predict many real life interfacial problems; however, they can provide necessary insight needed for modeling actual flow problems. In conventional CFD, three popular approaches for interface capturing exist: a) front tracking, b) VOF (volume of fluid), and c) level set.

In the past decade, new computational approaches, such as the Lattice Boltzmann Method (LBM) and Smoothed Particle Hydrodynamics (SPH) method have shown to overcome some of the difficulties with traditional computational approaches. Such methods are sometimes called meshless. In these approaches, the continuum assumption is removed by discretizing the fluid (instead of the media containing it). Then, the mathematical modeling is a bit similar to the one used in molecular dynamics (MD), wherein particle collisions are also taken into account. Note, the main difference between SPH and LBM is that the first one uses the Lagrangian form of the non-linear partial differential Navier Stokes (N.S.) equations, while the ordinary differential Boltzmann equation is used in the latter. It seems that LBM has been found to be more useful and thus has become more popular in simulating many fluid flow problems. Also, it has eased many of the difficulties people have been having before with conventional CFD. Even though LBM is not yet fully developed and has some drawbacks for certain flow physics, it seems at the present time that for interface capturing issues, it is a reliable tool.

Let us highlight the growth and detachment of drops as example for the hydrodynamic challenges involved in the two-way coupling of complex fluid–fluid interfaces. Zhang and Stone in 1997 numerically studied drop formation in viscous low Reynolds number flows at a vertical capillary tube [63]. They found that for very small viscosity coefficients, break-up occurs at shorter times, there is no detectable thread between the detaching drop and the remaining pendant fluid column, and thus no large satellite drops are formed. They also studied the effect of external uniform flow on the drop growth and detachment and found that it leads to smaller drop sizes (when the flow is viscosity dominated).

In 1998, Jones et al. presented a dynamic model of drops detaching from a gas metal arc welding electrode [64]. Interestingly enough, they observed a drop impulsive response in the process of detachment. This event had been observed before, but not enough logical explanations had been presented for it (e.g. Fainerman and Miller [65]). In their model, two centers of mass were simulated for a necking drop in order to capture both common and differential modes of motion of the upper and lower parts of the drop.

Lau and Mashayek [66] developed a model for the dynamics of oscillating drop with thermocapillary effects and showed that the most obvious feature of thermocapillary flows is demonstrated by vortices whose number and strength vary with the mode of temperature disturbance. These vortices tend to modify the amplitude of oscillations and enhance the kinetic energy.

Davidson and Cooper-White [67] numerically predicted shear thinning drop formation, using the VOF method to capture the interface. In their article, the evolution of predicted drop shape, drop thickness and length, and the configuration at pinch-off are discussed for various shear thinning parameters. They also performed their studies for different Ohnesorge numbers.

In 2004, Cramer extensively studied continuous drop formation at a capillary tip and drop deformation in a flow channel [68]. He suggested that there are basically five important dimensionless numbers related to the physics of such problem, namely: Reynolds number, Capillary number, Bond number, Ohnesorge number, and viscosity ratio. He also emphasized the old finding that, depending on the flow rate, there are two regimes of dripping and jetting of the flow. In addition, Cramer studied the periodic dripping dynamics mentioned above [64], and argued that when a drop breaks up from a needle, a residual fluid is left at the needle which rebounds and oscillates. These mechanical vibrations are then transferred to the new growing drop and affect its growth and detachment. Of course, this explanation was also found in previous works (e.g. [69]).

Fawehinmi et al. [70] performed a combined experimental and computational fluid dynamics analysis of the dynamics of drop formation. In their numerical work, they implemented the VOF approach in both CFX and FLOW-3D commercial CFD codes. They emphasized that for low flow rates and viscosity, their CFD predictions were found, in general, to be poorer with the issue of free surface smearing introduced by the VOF method. Most of their numerical results were compared with their own experimental data, performed as a relatively complete and detailed study of all different events occurring in such flows.

Later in 2006, Chao et al. numerically simulated the hydrodynamics of drop formation, using the level set method [71]. In their work, the shape of a drop growing at a capillary tip and the flow field inside the
drop were predicted. They claimed that the level set approach is effective in simulating the formation process of a pendant drop, something that is a big challenge in such CFD predictions. Soleymani et al. [72] also numerically studied drop formation in a single hole in solvent extraction. They clearly detected different drop formation periods, which were essentially different for straight and conical holes. Also, they showed that the shape of the hole has a considerable effect on the size of the drop.

In addition, Timgren et al. [73] both numerically and experimentally investigated the effect of cross-flow velocity, capillary pressure, and oil viscosity on oil-in-water drop formation from a capillary. They also used VOF for their interface capturing and found out that an increase in cross flow, oil viscosity, and capillary pressure displaces the position of necking and drop detachment away from the capillary opening, which has a decreasing effect on the final size of the drop. One of the shortcomings of this work was the use of a first order time discretization.

A year later, these same authors presented a model for drop size prediction during cross-flow emulsification [74], where they also used the VOF approach. Note, the results predicted in this work were not much better than their previous ones, however, credit should be given to the important physics they studied.

As mentioned earlier, in the last decade, attention has been moved toward meshless CFD approaches. As an example, in 2011 Haghsenas performed a detailed computational simulation of drop formation and detachment, using the LBM [75]. In this work, he tried to prove that this method has many advantages compared to the conventional CFD. Especially, since it is a meso-scale approach (compared to a macro-scale one in conventional CFD), it better deals with interfacial problems.

Interests toward using LBM for the numeric simulations of interfacial problems have been growing more and more since then.

However, the use of conventional CFD for interfacial problems has not stopped and some researches are still producing valuable results. A good example is the work of Olgac et al. who performed a DNS (direct numerical simulation) of an oscillating drop in partial contact with a substrate [76]. They used the famous Tryggvason’s front tracking method and obtained relatively accurate results. As far as the frequency of the detached drop concerns, they showed that it mainly depends on drop radius, drop density, and surface tension (something previously predicted by Strani and Sabetta [77]).

Another interesting work using classical CFD is the complementary research performed by Dieter-Kissling et al. in 2014, which is based on experimental and computational investigations [16]. Using a kind of interface tracking approach for capturing the interface, they obtained relatively accurate results, which then were compared with experimental data using PAT. Interestingly enough, they were able to also simulate the details of the flow inside the drop. Their main finding was that due to strong hydrodynamic effects, the evolution of surface tension by fitting into the Gauss Laplace equation is not valid for dynamic drop formation conditions. Of course, new techniques are being developed, which may be proven to be reasonable alternatives (e.g. see Saad and Neumann [78]).

8. Critical drop size and dynamics of its breakup

The process of detachment and liquid breakup is widely studied for many years due to its applications in various technical and industrial fields like inkjet printing or sprays. In addition, the behavior of drops during detachment is important for many interfacial studies [79]. Here, we want to present and discuss the most recent advancement in the study of drop detachment and dynamics of breakup.

Once the volume of a pendant drop formed at the tip of a capillary reaches its critical value, the drop becomes too heavy to be kept at the edge of the capillary by the acting surface tension. As the drop begins to stretch away from the orifice circumference, it develops a region of a stretching volume referred to as necking or bridging. Because the fluid flow continues to be pumped into the hanging drop, it accumulates mass while the detachment is proceeding. There is also internal flow within the separating drop that may contribute to the drop mass at separation.

With regard to the quest for the critical drop volume (the maximum drop size for a drop formed infinitely slowly), the first attempt was to empirically relate the volume of small drops to a function of time while the drop was in the finite process of detachment (e.g. [80,81]). However, this function of separation time was later shown by Miller et al. [82] to also include various parameters that might affect the hydrodynamic effects of separation, such as surface tension, density difference, and capillary size.

Only recently with the great advancement in the relevant experimental techniques and numerical simulations, a good progress in the analysis of the drop detachment process was achieved. For example, in an experimental study performed by Kuznetsov et al. [83], the process of detachment of drops from a metal wire by a novel annular laser beam was studied. In this study, several drop detachment regimes are presented and analyzed. In another study by Lexmond et al. [84], the effect of fluid flows on the detachment of liquid drops from the edge of a vertical plate was experimentally investigated. According to the literature, most of the works dedicated to the experimental study of drop detachments are performed for special applications and therefore, the results are not very useful for a fundamental analysis. In a recent study presented by Karbaschi et al. [85], the process of drop formation and growth from the tip of a circular capillary was studied experimentally using the profile analysis tensiometry equipped with a fast video camera technique (Sinterface Technologies, Berlin). Here, dynamic drop profiles of drops of water in air growing at different flow rates at a 0.45 mm circular capillary were analyzed. Drops are formed at the outer edge of the capillary (OD = 0.71 mm). From the drop images recorded at 3000 f/s, the dependency of the defined dynamic contact angle on the drop volume is obtained and the results are presented in Fig. 12. This contact angle is the angle between the tangent of the drop profile and the x-axis where the liquid–air interface meets the capillary tip, as shown in this figure. Note, all the flow rates considered for this study are beyond the flow rate of transition to a jet flow regime, and therefore correspond to the dripping flow regime. From the results, one can see that the process of detachment (the sharp increase in the contact angle values) is independent on the flow rate. However, the total drop volume at the onset of detachment goes through a maximum at 16.7 mm³/s. Thus, with any further increase in the flow rate, the maximum drop volume would decrease. For a further understanding of these complexities, more efforts from numerical simulations and experiments on dynamics of drops are required. The obtained drop profiles are also used to study the structure of the neck during detachment and its functionality from different parameters.

Regarding the mechanism of drop detachment, there are still many more complexities which are not well understood. For example, in the experimental study presented by Fainerman et al. [65], the formation time of drops at a circular tip of a capillary is measured and reported with high precision. With a continuously changing flow rate and for capillaries of different diameters, for the drop formation times lower than 1 s, stable intervals as well as regions of high scattering are observed. Fig. 13 shows the scattering results of measured drop formation times for growing water drops in air at 70 mm²/s flow rate of from the tip of a 2 mm circular capillary (the corresponding drop volume is 52 mm² at the onset of detachment).

In literature, there are also several works dedicated to the numerical study of the drop detachment process. For example, in a numerical work presented by Garzon et al. [86], the pinch-off process of a non-viscous liquid is analyzed using a hybrid level-set and boundary integral method. The results show the capability of the implemented method in the prediction of complex satellite drop structures observed experimentally. In another study, the VOF computational technique is used to predict the dynamic drop formation behavior. The numerically predicted drop shapes are well compared to experimental ones [87]. Then, the
validated code is used to predict the behavior of drops during detachment at different Reynolds and Weber numbers.

9. Conclusion and outlook

It was shown that all methods frequently used for the characterization of liquid–fluid interfaces based on single drops and bubbles are applicable also under non-equilibrium conditions. The corresponding limits of all the discussed methods are essentially defined by the dynamics of the fluids involved. When going beyond the limits one risks to obtain physically wrong data. Thus, as shown in Fig. 2 the surface tension of pure water can erroneously be measured to be 20 mN/m rather than correctly 72 mN/m at room temperature. Something similar is true for example when using the oscillating drop tensiometry. At too high frequencies even pure water could show a dilational visco-elastic surface behavior, although both the elasticity and the viscosity must be zero [33].

Considering the viscous flow, inertia and other hydrodynamic effects quantitatively, a significant extension of many experimental methods appears feasible. A complete description of the growth process of a liquid drop via the adequate N.S. equations with the proper boundary conditions including the transport of surfactants inside the drop and adsorption at the drop surface would allow getting the actual surface tension from video images of a growing drop. Due to the enormous amount of required computer time such a method is not feasible at present. However, attempts of modifying the Gauss Laplace equation such that it includes also hydrodynamic effects would extend the application limits of PAT significantly.

CFD appears to be a useful tool not only for analyzing the limits of experimental methods. Some experimental protocols are so complex that obtained experimental data can be interpreted only on the basis of respective simulations. Otherwise, experiments end up with only effective values for physical quantities, sometimes even beyond any physical sense.
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References


