

Coalescence between Adjacent Drops Lying on the Interface of Two Liquids

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This paper is aimed to the study and characterization of the coalescence of two adjacent drops lying on, or under (depending on the different densities), the macro-interface of two immiscible liquids. Experiments have been performed and coalescence times measured by using an oil-water system. A mechanistic model of coalescence is proposed. The comparison with experimental data is satisfactory.

1. Introduction

Some industrial processes involve in their operations two or more immiscible liquid phases. The dispersed drops are surrounded by a continuous phase. The drops tend to coalesce with adjacent drops or to join their mother phase separated by an interface. These kinds of phenomena occur in many industrial operations as well as in environmental processes. The liquid-liquid foams behavior is connected to them.

Literature has devoted some attention to the problem, mainly for the case of coalescence of a single drop through a planar surface. Charles & Mason, 1960, studied the effect of temperature, drop size, diffusion and contamination on coalescence time. They tried to explain partial coalescence and observed up to eight steps in a coalescence cascade. They also observed that the first step gives a smaller drop size ratio than the following steps. A correlation was proposed for describing the cascade of coalescence that is reliable in describing the first step but not satisfactory for the following ones. Hartland, 1967, in three different papers experimentally described drop shape, film thickness and rupture of a single drop at liquid-liquid interface. Davies et al., 1971, studied the separation of clusters of drops and single layers and found that their coalescence time is higher than the corresponding value of single drop. They affirm that the presence of adjacent drops seems to increase the rest time by disrupting the drainage process. They tried also to propose a correlation to relate the mean coalescence time to the system properties. Drop/drop coalescence time has been found to increase with viscosity and drop size. Their observation are qualitative and no experimental data related to drop/drop coalescence are reported.

Zulfaa & Longmire in 2004 focused the attention in the study of the vorticity generated in the collapsing fluid and developing in a vortex ring straddling the upper drop surface. Chen et al., 2006 reported experiments with low-viscosity fluids expanding the knowledge on the partial coalescence process to finite values of Bo (Bond number $\Delta\rho g D_s^2 / \sigma$ also known as Eotvos number E_o) and Oh (Ohnesorge number $= \mu_1 / \sqrt{(\rho_1 + \rho_2)\sigma D}$).

They defined two other regimes of partial coalescence strongly influenced by viscosity and gravity, and tried also to deduce the drop size ratio between daughters and mother drop after partial coalescence. They proposed a correlation for the evaluation of this ratio that is not completely satisfactory even if a correct trend is obtained. Aryafar & Kavehpour, 2006, expanded the investigation over a wide range of fluids to fully investigate the effects of physical properties of fluids on coalescence. They found that for $Oh > 1$ drops fully coalesce, and for $Oh < 1$ partial coalescence occurs with a resulting daughter drop. They also developed a relationship between the drop ratio and the Oh number obtaining good agreements with their data even if at small Oh numbers a large spreading of data is reported. Blanchette F., T.P. Bigioni, 2006, experimentally investigated coalescence of drops at the interface with their mother phase in air. Bozzano & Dente in 2011 proposed a mechanistic model for vertical coalescence taking into account Van der Waals attractive forces and, consequently, Hamaker constants.

Regarding coalescence of adjacent drops the literature is less abundant, also because during experiments vertical coalescence often occurs before lateral one develops. Chen & Pu, 2001, performed experiments in an artificially gravity system studying the coalescence of two pendant drops maintained flanked. Gravitation minimized nearly to zero allowed to overcome drop deformation. Any external force out of the drops was avoided, when one liquid drop goes near enough to be tangential to another. They connected the coalescence driving force directly to the chemical potential difference of the coalesced drops (oil in water) and defined a binary coalescence time as the time between the touch of two perfect sphere liquid drops and the rupture of the interposed film. They also studied the effects of the surfactant on the binary coalescence process: the surfactant hinder the coalescence by creating a repulsive barrier.

Zdravkov et al., 2003 aimed their experimental work to the validation of the existing theoretical models in the limiting cases of immobile and of partially mobile film drainage. They investigated the PEO(polyethylene oxide)/PDMS(polydimethylsiloxane) systems and found that the drainage is very sensitive to the film radius increase and the effect was attributed to a depletion of the adsorbed polymer molecules from the drop interfaces in the film. They reported data on the minimum film thickness variation during coalescence.

The present work reports the results of some experiments performed in a water-in-oil system. The coalescing drops (Figure 1) have been captured by means of a camera and the coalescence time measured. A model has been proposed and compared with the experimental data. The attention is focused on the relevant importance of the Van Der Waals/London intermolecular attraction forces and the effects of the deformation of the interface area contained between the two drops are described.



Fig.1 Two adjacent water in oil drops relying at the interface of two liquids

2. Methods

The very simple experimental equipment is described in figure 2, reporting a picture of the system. A microscope was positioned over a beaker containing two immiscible phases for better observing the phenomenon. The two phases was water and oil. The water is demineralized and the oil is vegetal oil. The properties of both the phases have been measured and are reported in table 1. The two drops have been colored with ink of different colors in order to better observe the coalescence phenomenon.

The experiments have been performed by gently depositing by means of syringes measured volumes of water at the interface between the two phases, forming two drops. Many tests have been realized in order to study the relation between coalescence time and drop volume (drop volumes ranged from 0.025 to 0.8 mL). All the tests have been recorded with a high speed camera allowing extracting the pictures of coalescence sequence. Some of the tests have been repeated because the coalescence with the underlying interface was anticipated.

Table 1: properties of the two phases

	Density (kg/m ³)	Surface Tension (kg/s ²)	Viscosity (Pa/s)	Refractive index (at 589 nm)
Vegetal oil	912.02	0.032	0.12	1.47
Dem. Water	996.96	0.0726	0.001	1.33

The Ohnesorge number of the experiments is ranging from to 0.0014 to 0.0019 and the Bond number is ranging from 0.27 to 3.15. The interfacial tension is 0.04 kg/s². The selection of a viscous system for the continuous phase allows to have longer coalescence times and to better observe the phenomenon.



Figure 2: picture of the experimental apparatus

3. Model description

First of all, it is essential to describe the phenomenological aspects of the process justifying the model equations. The two drops, after their arrival at the interface, approach one to the other and rest there. The gravity drives the drops towards their mother continuous phase and, coupled with the resistance of the interface separating the two phases, induces drops deformation. A thin film of continuous phase is interposed between them and drained until final coalescence occurs. The shape of the drops interfaces in the region containing the draining film is also deformed as showed in figure 3.

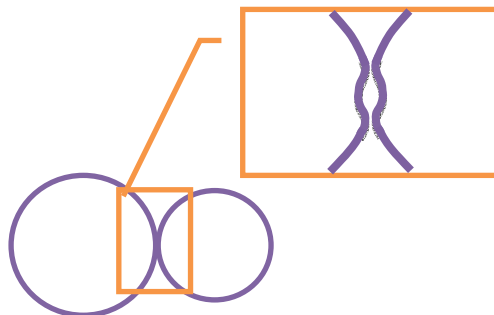


Figure 3: Schematic representation of the area contained between the two drops and containing the draining film

The lying drops assume initially a shape similar to an oblate spheroid with a major axis “a” and a minor axis b (see figure 4)

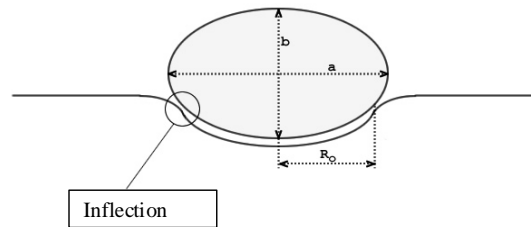


Figure 4: assumed single drop shape

This shape changes along film drainage. Each drop is elongated towards the other until coalescence occurs. Thanks to the use of colored ink it has been possible to observe the stages of coalescence in which the two drops initially doesn't mix each other. The coalescence time is assumed as the time starting from the drop rest and the interface breakage, i.e. the coalescence time is the time required for film drainage. The macro-interface is deformed for supporting the weight and shows an inflection line around each leaning drop. Also below each drop a film of continuous phase is present so that sometimes it has been difficult to observe transversal coalescence because one of the drops coalesced with the beneath mother phase. The viscous flow of the liquid enclosed into the progressively thinning film, produces a dissipative force that hinder the coalescence and, as will be described in the following, depends on an inverse power of the average film thickness. Of course the component of the gravity of the approaching drops, depending on to the inflection of the surface supporting the drops, is constant along the time and cannot overcome the viscous resistance as soon as the drainage proceeds. Then, only the Van der Waals attractive energies can constitute the driving force for the ultimate deformation of the drops (see figure 5) and the final drainage of the interposed film.

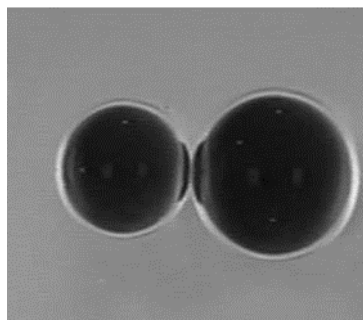


Figure 5: Drops deformation during film drainage

These energies can be estimated for instance by using the Lennard-Jones potential energy. The final rate of drainage (= coalescence) depends also on several physical and geometrical properties: worth to say, it is proportional to the viscosity of the drained phase and to the drop size. After film drainage, the interface of contact is disrupted and the drops coalesce producing a larger new drop. This final step is extremely fast compared to the time required for film drainage. The new drop, subsequently, can coalesce with its mother phase (by restoring the continuity of the macro-interface between the two bulk phases). Following the described phenomena, the coalescence can be shared in two main steps. In the first one the two drops approach having assumed the shape of oblate spheroids, in the second one the interposed film is drained out and coalescence occurs.

3.1 Stage of drops approaching and deformation of the underlying interface

The macro-interface among dispersed and continuous phase is deformed by the presence of the drops (see figure 6) and inflection lines are generated. The meniscus presents an enhanced deformation in the area between and around the drops. This results in an inclination with respect to of the horizon. This inclination promotes the movement of the drops one towards the other. The equatorial plane of the two drops declines of an angle ϕ that can be evaluated by using the expressions reported in Bozzano & Dente (2011) related to drop and underlying surface shape calculation. The shape of the macro-interface is approximated thank to a linearized expression introduced into the Young-Laplace equation:

$$\frac{d^2y}{dr^2} + \frac{1}{r} \frac{dy}{dr} - \frac{\Delta\rho g y}{\sigma} \cong 0 \quad 1)$$

where , σ is the interfacial tension, g the gravity acceleration, $\Delta\rho$ the density difference between the two phases, y the direction of drop sinking.

This linearization allows the superposition of the deforming effects of the two (or more) drops over the macro-interface.

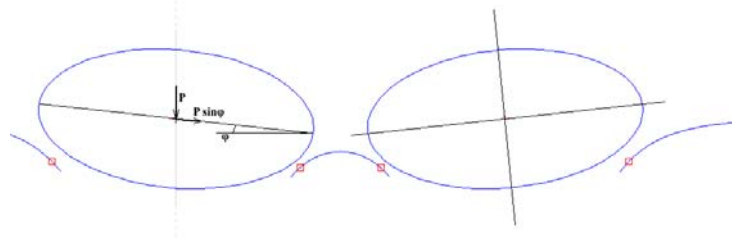


Figure 6: qualitative sketch of the drops lying over the macro-interface

In order to enter in touch, the two drops need to drain out the interposed film of the continuous phase. The mechanical energy equation governing this phenomenon can be described, with an excellent approximation, by the following expression that takes into account the involved dissipation and the mass of dispersed phase adherent to the drop:

$$\frac{d}{dt} \left(\frac{1}{2} (\rho_c + 0.5\rho_d) \cdot \vec{v}^2 \right) \cong -\mu_c \Phi_v \quad 2)$$

where: \vec{v} = approaching velocity

$\hat{\Phi}_v$ = dissipation function

μ_c = viscosity of the continuous phase

ρ_c = density of the continuous phase

ρ_d = density of the dispersed phase

The dissipation function essentially depends on the velocity field between the drops and, then, on their size. The power that is dissipated during this stage varies with the inverse of the third power of the distance between the drops, resulting in a drastic decrease of the velocity during the approach. The evaluation of the dissipation function can be performed by estimating a parabolic velocity profile inside the film (justified by its extremely reduced thickness and by the viscous flow, see figure 7).

The velocity profile inside the fluid contained between the two drops is then given by:

$$v_x(y) = \frac{4v_{x,max}}{h} \left(y - \frac{y^2}{h} \right) \quad 3)$$

The maximum velocity $v_{x,max}$ can then be related to the average film velocity:

$$v_{x,\max} = \frac{3}{2} \langle v \rangle \quad 4)$$

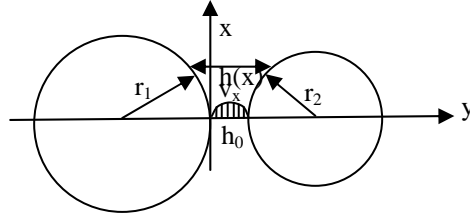


Figure 7: velocity profile of the draining film

The average film expulsion velocity can be easily evaluated by means of volumetric balances and results in:

$$\langle v \rangle = \frac{x \cdot \left(-\frac{dh_0}{dt} \right)}{h(x)} \quad 5)$$

Then the total dissipated power is given by:

$$\dot{E}_{\text{diss}} = \frac{3 \cdot \sqrt{2} \cdot \pi \cdot \mu_c}{h^{3/2} \cdot \left(\frac{1}{R_{c1}} + \frac{1}{R_{c2}} \right)^{3/2}} \left(\frac{dh}{dt} \right)^2 2\pi R_0$$

And in the case of twin drops ($R_{c1}=R_{c2}=R_c$):

$$\dot{E}_{\text{diss}} = \frac{3 \cdot \pi^2 \cdot \mu_c R_c^{3/2} R_0}{h^{3/2}} \left(\frac{dh}{dt} \right)^2 \quad 6)$$

The resulting final thickness corresponding to the final stop of the two drops (h_0) and starting from which drainage starts, is then given by:

$$h_0 = 0.37 \left(\frac{\rho v_\infty}{\mu_c R_0 R_c^{3/2}} \right)^{2/5} \quad 7)$$

where R_0 is the distance between the center of the drop and the inflection point of the interface, R_c is the radius of curvature at the inflection point (about half of the radius of the equivalent sphere), v_∞ is the asymptotic approach velocity, i.e. dh/dt .

The viscous (dissipation) force depends on the viscosity of the continuous phase and on the local radius of curvature of the drops when their distance approaches the minimum one:

$$F_{\text{visc}} = \frac{3 \cdot \pi^2 \cdot \mu_c R_c^{3/2} R_0}{h^{3/2}} \frac{dh}{dt} \quad 8)$$

The estimation of these parameters has been already proposed in a previous paper (Bozzano & Dente, 2011) and are here reported:

$$\begin{aligned} a &= R_s \cdot z^{-1/3} \\ b &= R_s \cdot z^{2/3} \end{aligned} \quad 9)$$

where a and b are the major and minor axes of the drop, related to the variable $z=b/a$ that can be deduced from the Bond number through the following expression:

$$Bo = 4 \cdot \frac{(1-z)(1+z+2z^2)}{z^{7/3}} \quad 10)$$

Then, starting from the system properties it is possible to evaluate Bo and therefore, z. The distance between the center of the drop and the inflection point of the interface, R_0 , is then given by:

$$R_0 = \frac{R_s \cdot z^{-1/3}}{\sqrt{1+6z^{1/3}/Bo}} \quad 11)$$

3.2 Attractive intermolecular forces

The nature of these forces is related to Van der Waals-London forces and their importance is particularly relevant for very short distances. In fact, the attractive potential is described by equation 12, where the intensity of the attractive energy depends on the inverse of the sixth power of the distance:

$$dE_{att} = -A \frac{dV_1 dV_2}{d^6} \quad 12)$$

Where dV_1 e dV_2 are the elementary volumes of the two particles, d is the distance, A is the Hamaker constant. The Hamaker constant for drops separated by a media can be calculated following Mahanty and Ninham (1976):

$$A = \frac{3\pi^2}{2} \left\{ \frac{\mu_1^2}{2l_1} + \frac{\mu_0^2}{2l_0} - \frac{2\mu_0\mu_1}{l_0 + l_1} \right\} \quad 13)$$

$$\text{where: } \mu_i = \alpha_i \rho_i l_i = \frac{\varepsilon_i - 1}{4\pi} \cdot l_i$$

$$l_i = \hbar \omega_0^{(i)}$$

$$\varepsilon = n^2, \quad n = \text{refractive index}$$

$$\hbar = h/2\pi$$

$$\omega_0 = 2\pi c/\lambda \quad \text{Absorbance frequency } (\lambda \text{ is the wave length, } c \text{ in the light velocity)}$$

$$h \text{ is the Planck constant } (= 6.6242 \cdot 10^{-34})$$

For performing the integration of equation 12), the two facing surfaces have been described as two toroids. The approximated integration provides the attractive force between the two drops:

$$F_{att} = \frac{\pi}{8} A \frac{R_0 R_c \frac{1}{2}}{h_0 \frac{5}{2}} \quad 14)$$

3.3 Forces Balance

It is now possible to propose a forces balance, from which the drainage time is calculated. All the contributions to the film drainage (component of the net-weight, viscous resistance and attractive force) are taken into account:

$$\left(\frac{8}{3}\pi R_s^3 \Delta\rho g \cdot \cos\vartheta\right) + \left(\frac{\pi}{8} A \frac{R_0 R_c^{\frac{1}{2}}}{h_0^{\frac{5}{2}}}\right) = \left(\frac{3 \cdot \pi^2 \cdot \mu_c R_C^{3/2} R_0}{h^{3/2}} \frac{dh}{dt}\right) \quad (15)$$

($\Delta\rho$ the density difference, g the gravitational force per unit mass). The integration of equation 15) can be analytically performed by assuming h_0 as infinite. This is a good approximation because the function is very restricted around its maximum and this simplification allows to reduce the problem to the integration of an improper integral which solution can be found for instance in the book of Jahnke and Emde. The following expression results:

$$t_{\text{coal}} = 19.6\mu_c \left(\frac{R_0^4 R_c^7}{A(\Delta\rho g)^4 R_s^{12} (\cos\vartheta)^4}\right)^{\frac{1}{5}} \quad (16)$$

Some considerations can rise from the analysis of the obtained expression: the coalescence time is proportional to the continuous phase viscosity; it depends also on the equivalent spherical radius with a power greater than one, so that the time increases with the drop size. The coalescence time decreases with the interfacial tension contained in R_0 . These results are in agreement with the ones obtained also by other researchers (see for instance Chen & Pu, 2001) and with the experimental observation. The analysis of the different contribution of equation 15) also explains what obtained. The force required for the film drainage needs to overcome the viscous resistance. The increase of drop size from one side increases the gravity force, but, from the other side, increases drop deformation with a consequent larger surface contact. This produces a decrease of the inflection of the surface interposed between the two drops. The $\cos\vartheta$ can be evaluated by means of the equation that characterizes the shape of the interface. However, a satisfactory, simplified, expression can be proposed:

$$\cos\vartheta = 0.4165 - 0.0176 \cdot \text{Bo}^2 - 0.055 \cdot \text{Bo} \quad (17)$$

3.4 Superface Energy Dissipation

The surface of the newly formed drop is reduced with respect to that of the two separated drops, and the same happens for its superficial energy. Being the surface area of each drop given by:

$$A_s \cong 2\pi \left(\frac{b^2 + a^2 \arctan h(\sin(\psi))}{\sin(\psi)}\right) \quad (18)$$

$$\text{with: } \psi = \arccos\left(\frac{a}{b}\right) = \arccos\left(\frac{1}{z}\right)$$

and the volume:

$$V_d = \frac{4}{3}\pi a^2 b$$

The volume of the new drop is:

$$\hat{V}_d = \frac{4}{3}\pi(a_1^2 b_1 + a_2^2 b_2) \quad \text{or} \quad \hat{V}_d = \frac{4}{3}\pi \hat{R} s^3 = \frac{4}{3}\pi \hat{a}^2 \hat{b} \quad (19)$$

Where the symbol ' $\hat{}$ ' indicate the new formed drop. It is possible to demonstrate that:

$$\frac{A_s}{V_d} - \frac{\hat{A}_s}{\hat{V}_d} > 0$$

The reduction of the surface releases a part of the surface energy and it has been experimentally observed a relaxation of the new drop after coalescence. This energy released generate capillary waves propagating in the surrounding continuous phase.

4. Results and Comparisons

The water drops have been differently colored (red and black) in order to better observe the process. The pictures reported in the following figure are extracted from the taken movie and start from a time zero equivalent to the start of the final film drainage that is very fast. It is possible to observe that, during final coalescence no mixing is occurring between the drops and a relaxation of the new drop is present generating also waves over the surface. The final coalescence process is extremely fast.

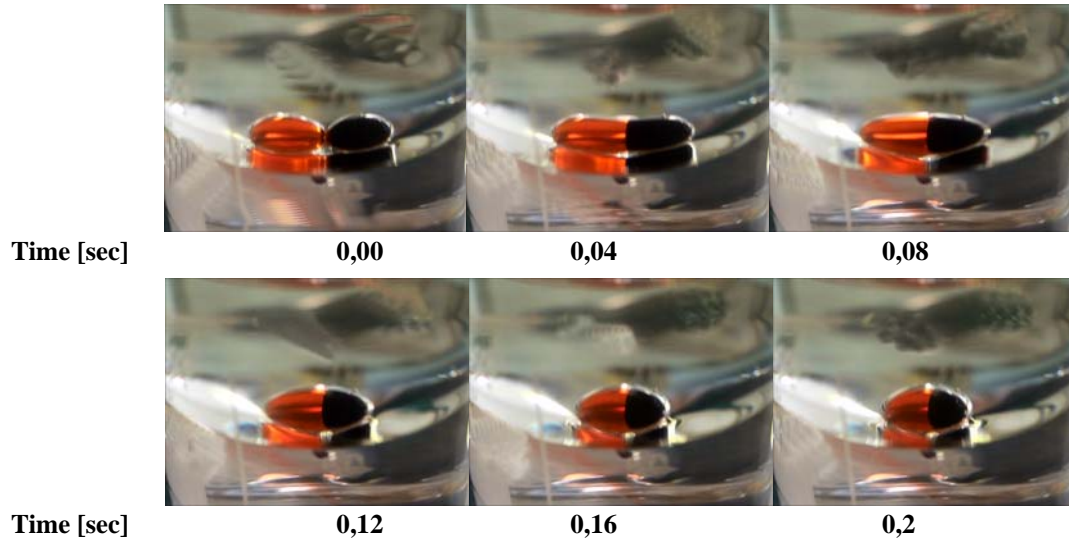


Figure 8: some photograms of the coalescence process (from 1 to 6)

Figure 9 shows the comparison between calculated coalescence times and some experimental data. In this case the time zero corresponds to the beginning of coalescence process that starts from the end of the initial approach. The agreement is satisfactory taking also into account the simplifications that have been adopted.

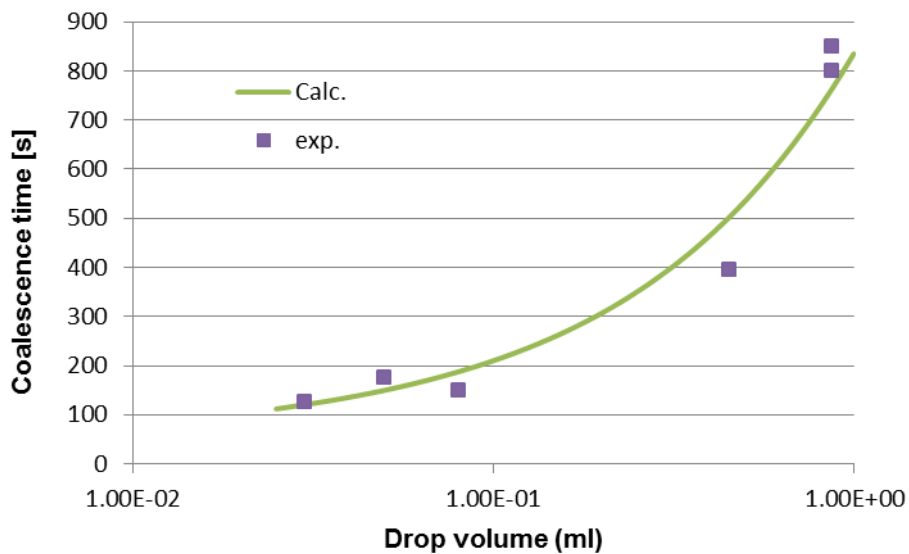


Figure 9: comparison of experimental data with coalescence model

5. Conclusions

In this paper an original model for the transversal coalescence of drops is proposed. The model is compared with some experimental data obtained by the authors. The comparisons are quite satisfactory. The study can constitute the basis for the analysis of more complex (multi-drops) systems like liquid-liquid foams that can be of great importance into many types of equipment.

Acknowledgments

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