

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. A mechanistic model of coalescence is proposed. The comparison with experimental data is satisfactory.

1. Introduction

Some industrial processes, in their operations, involve the presence of two 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 kind of phenomena occur in many industrial operations as well as in environmental processes. The liquid-liquid foams behaviour is connected to them. Literature has devoted some attention to the problem of drop coalescence, mainly for the case of coalescence of a single drop through planar surface (Charles and Mason, 1960; Hartland, 1967; Davis et al., 1971; Zulfar and Longmire, 2004; Chen et al., 2006; Aryafar and Kavehpour, 2006, Blanchette and Bigioni, 2006).

Some research has been also devoted to the coalescence of adjacent drops (Chen and Pu, 2001; Zdravkov et al, 2003). This work reports the results of some experiments performed in a water-in-oil system. The coalescing drops (Figure 1) has been captured by using a camera and the coalescence time measured. A model has been proposed and compared with the experimental data. The reported approach concentrate the attention on the relevant importance of the Van Der Waals/London intermolecular attraction forces and describes also the effects of the deformation of the interface area contained between the two drops.



Figure 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. Two phases are present: a water phase and an oil phase. The water is demineralized and the oil is a vegetal oil. The properties of both the phases have been measured and are reported in Table 1.

The experiments have been performed by gently injecting 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 0.125 mL). All the tests have been recorded with a high speed camera allowing to extract the pictures of coalescence sequence. Some of the test have been repeated because the coalescence with the underlying interface was anticipated.

Table 1: Properties of the two phases

	Density (kg/m ³)	Surface (kg/s ²)	Tension	Viscosity (Pa/s)	Refractive index
Vegetal oil	912.02	0.032		0.12	1.47
Dem. Water	996.96	0.0726		0.001	1.45

The two drops have been coloured with ink of different colours in order to better observe the coalescence phenomenon.



Figure 2: Picture of the experimental apparatus

3. Model description

First of all it is important to give a description of what has been observed in order to characterize the phenomena that are occurring. The two drops, after their formation approach one to the other at the interface and rest there until final coalescence occurs. The shape of the oblate spheroidal drops changes along the time (that in the present paper is assumed as the coalescence time); the macro-interface is deformed for supporting their weight and shows an inflection line around each leaning drop. Even if the two drops seem to be completely at rest, during this stage the very thin film of the continuous phase interposed between (and under) them is drained out. The viscous flow of the liquid enclosed into the progressively thinning film, produces a dissipative force that hinder the coalescence. It depends on the inverse square 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 molecular attractive energies that can be estimated by Lennard-Jones potential energy, can constitute the driving force for the ultimate deformation of the drops and the final drainage of the interposed film. The drainage (= coalescence time) depends on several physical and geometrical properties: worth to say, it is proportional to the viscosity of the drained phase. At the end, the interface of contact is disrupted and the drops coalesce producing a larger new drop. This final step is extremely fast with respect of 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).

The coalescence mechanism can be therefore divided in two main steps. In the first one the two drops approach, in the second one the interposed film is drained out and coalescence occurs. Also coalescence with the beneath mother phase can occur. In this work the coalescence time reported in the experiments will refer only to film drainage that starts when the drops, after their approach, rest at the interface till the final coalescence into a single drop.

3.1 Stage of drops approaching

The macro-interface among water and oil is deformed by the presence of the drops (see figure 3). 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 and Dente (2011) related to drop and underlying surface shape calculation. The shape of the macro-interface is approximated thank to a linear expression introduced into the Joung-Laplace equation:

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

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

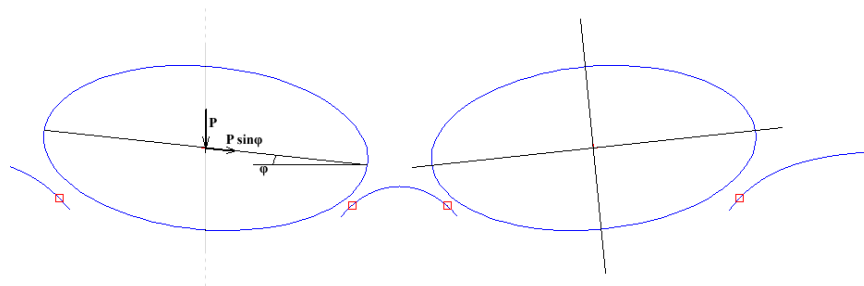


Figure 3: Qualitative sketch of the drops lying over the macro-interface

In order to enter in touch, the two drops have to drain out the interposed film of the continuous phase. The indefinite equation of the mechanical energy governing this phenomenon can be described, with an excellent approximation, by the following expression:

$$\frac{d}{dt} \left(\frac{1}{2} \rho_c \bar{v} \right) \cong -\mu_c \hat{\Phi}_v \quad 2)$$

where: v = approaching velocity

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

μ_c = viscosity of the continuous phase

ρ_c = density of the continuous phase

The dissipation function is essentially a function of the velocity and, then, of the volume of the drops. 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 estimated by assuming a parabolic velocity profile inside the film (due its extremely reduced thickness); it allows to evaluate the viscous dissipation force that results to depend on the viscosity of the continuous phase and on curvature radius of the drops where their distance in the minimum one:

$$F_{diss} = \frac{3}{2} \pi \mu_c \frac{R_o R_c^{\frac{3}{2}}}{h_o^{\frac{3}{2}}} \frac{dh_o}{dt} \quad 3)$$

In expression 3, h_0 is the thickness reached by the interposed film to drain out, R_0 is the distance between the centre of the drop and the inflection point of the interface, R_c is the radius of curvature at the inflection point. The calculation of this parameters has been already proposed in a previous paper (Bozzano and Dente, 2011).

3.2 Attractive intermolecular forces

The nature of this 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 3, where the intensity of the force depends on the inverse of the sixth power of the distance:

$$dE_{\text{att}} = -A \frac{dV_1 dV_2}{d^6} \quad (4)$$

where V is the particle volume, d is the distance, A is the Hamaker constant. The Hamaker constant for drops separated by a media is calculated following Mahanty and Ninham (1976):

$$A = \frac{3\pi^2}{2} \left\{ \frac{\mu_1^2}{2l_1} + \frac{\mu_0^2}{2l_0} - \frac{2\mu_0\mu_1}{l_0 + l_1} \right\} \quad (5)$$

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

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

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

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

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

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

For performing the integration of equation 4), the two facing surfaces have been described as two toroids . The results of the approximated integration produced the attractive force between the two drops:

$$F_{\text{att}} = \frac{\pi^3}{8} A \frac{r_0 R_c \frac{1}{2}}{h_0 \frac{5}{2}} \quad (6)$$

3.3 Forces Balance

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

$$\left(\frac{4}{3} \pi R_s^3 \Delta \rho g \cdot \cos \vartheta \right) + \left(\frac{\pi^3}{8} A \frac{R_0 R_c \frac{1}{2}}{h_0 \frac{5}{2}} \right) = \left(\frac{3}{2} \pi \mu_c \frac{R_0 R_c \frac{3}{2}}{h_0 \frac{3}{2}} \frac{dh_0}{dt} \right) \quad (7)$$

(R_s is the equivalent spherical radius of the drop, $\Delta \rho$ the density difference, g the gravitational force per unit mass). Integrating equation 8):

$$t_{\text{coal}} = 19 \mu_c \left(\frac{R_0^4 R_c^7}{A (\Delta \rho g)^4 R_s^{12} (\cos \vartheta)^4} \right)^{\frac{1}{5}} \quad (8)$$

Making reference to the previous paper by Bozzano and Dente (2011), it is possible to re-write equation 6) as:

$$t_{\text{coal}} = \mu_c \left(\frac{R_0^4 R_c^7}{A (\Delta \rho g)^4 R_s^{12}} \right)^{\frac{1}{5}} \cdot 19z \frac{z^{-\frac{32}{15}} [1 - (1 - z^2)u^2]^{\frac{5}{2}} u^{\frac{4}{5}}}{(1 - u^2)^{\frac{2}{5}}} \quad (9)$$

where: $u = \frac{R_0}{a} = \frac{1}{\sqrt{1+6z^{1/3}/Eo}}$, $z=b/a$, a is the major axis the oblate spheroid representing the drop undisturbed shape (see figure 4), Eo is the Eötvös number ($Eo = \Delta\rho g D_s^2 / \sigma$), σ the interfacial tension.

By approximating the radius of curvature as follows :

$$\frac{1}{R_c} \cong \frac{1}{2} \left(\frac{1}{\infty} + \frac{1}{2a} \right) \cong \frac{1}{4a} \quad (10)$$

The following expression results for the evaluation of coalescence time:

$$t_{\text{coal}_{\text{bal}}} = 109\mu_c z^{-2.133} \left(\frac{R_s^7}{A\sigma^4} \right)^{\frac{1}{5}} \quad (11)$$

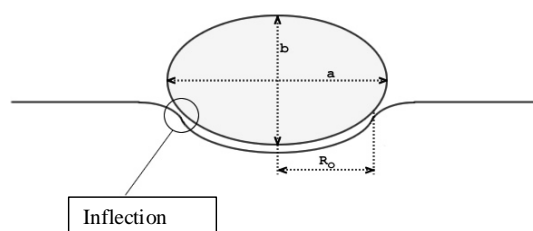


Figure 4: Assumed single drop shape

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 dimension. The coalescence time decreases with the interfacial tension. This results are in agreement with the ones obtained also by other researchers (see for instance Chen and Pu, 2001) and with the experimental observation.

The analysis of the different contribution of equation 6) also explains what obtained. The force required for the film drainage has to overcome the viscous resistance. The increase of drop size from a side increases the gravity force, but, from the other side, increases drop deformation with a consequent major surface contact. This produce a decrease of the inflection of the surface interposed between the two drops. The obtained result is related to a “balanced approach” where the two drops have the same volume (indicated by the index bal). When the two drops have a different volume (index unbal), expression 12) can be modified in (R_s is estimated as the geometric average of the equivalent spherical radius of the two drops):

$$t_{\text{coal}_{\text{unbal}}} = 83\mu_c z^{-0.733} \left(\frac{R_s^7}{A\sigma^4} \right)^{\frac{1}{5}} \quad (12)$$

4. Results and Comparisons

In order to better observe the coalescence process the water drops have been differently coloured (red and black). The pictures reported in the following figure are extracted from the movie and start from a time zero equivalent to the end of the initial approaching time. Table 2 reports the times (in seconds) corresponding to the different sequences. From the pictures 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.



Figure 5: Some photograms of the coalescence process (from 1 to 6)

The final coalescence process is extremely fast.

Table 2: times related to sequences of Figure 5

[s]	1	2	3	4	5	6
Time	00.00	00.04	00.08	00.12	00.16	00.20

Figure 6 shows the comparison between calculated coalescence times and some experimental data. The agreement is satisfactory taking also into account the simplifications that have been adopted.

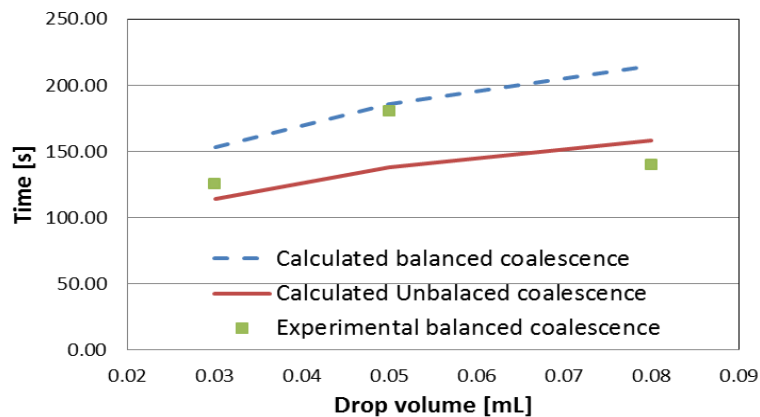


Figure 6: Comparison of experimental data with coalescence model

5. Conclusions

In this paper an original model for this kind of transversal coalescence mechanism is proposed. The model is compared with some experimental data obtained by the authors. The comparisons are quite satisfactory. The study of single drop coalescence 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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