

# Size Dependence of the Stability of Emulsion Drops Pressed against a Large Interface

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In this work we study experimentally the lifetime of oil droplets pressed by buoyancy against a large oil/water interface, in a system containing protein (bovine serum albumin). The stability of the drops depends strongly on their size, which can be explained with the hydrodynamics of thinning of the gap region. Two distinct size intervals with different thinning regimes may be discerned: (i) Very small drops (below  $\sim 20 \mu\text{m}$ ). They remain practically nondeformed up to coalescence; in this case the lifetime diminishes with increase of the drop radius. The latter trend may be described qualitatively in terms of the Taylor law (or mixed Stokes–Taylor law) for viscous resistance. (ii) Large drops. They form films, and the lifetime rises with the increase of the size, which complies with the Reynolds law for the friction in the gap. The overall dependence of the lifetime on the drop radius passes through a shallow and broad minimum—here for the first time this is proved by direct measurement in a real system: only the drop size is varied with all other experimental conditions being the same.

## 1. Introduction

When a drop is pressed by an external force (e.g., buoyancy) to a large liquid interface or to another drop, different coalescence behavior is possible depending on the physicochemical characteristics of the system (type and concentration of surfactant, hydrodynamic regime, molecular interactions, magnitude of the pushing force, etc.). Especially important and relevant to practice is the dependence of the lifetime upon the droplet size. Some experimental evidence in this respect has been reported by a number of authors in the literature. Gillespie and Rideal,<sup>1</sup> Charles and Mason,<sup>2</sup> Hodgson and Lee,<sup>3</sup> Chakarova et al.,<sup>4</sup> and Burrill and Woods<sup>5</sup> have studied experimentally the coalescence of millimeter-sized oil drops at an oil/water interface. They have found that the larger the diameter, the more stable the drops against coalescence. On the other hand, Dickinson et al.<sup>6</sup> have observed exactly the opposite trend, performing similar experiments with micrometer-size emulsion droplets; i.e., in this case the larger droplets burst faster than the smaller ones. It seems that depending on the size range the coalescence behavior can change, which is manifested as a change in the functional dependence of the lifetime on the drop radius.

Recently, Ivanov and Kralchevsky<sup>7</sup> have put forward a theoretical prediction that the lifetime of drops approaching an interface should exhibit a minimum when plotted as a function of the radius. The reason for this is entirely due to the hydrodynamics of the flow in the gap between the two opposing fluid interfaces. The effect is connected

with the deformability of the drop surface. The viscous friction, and therefore the rate of thinning of the liquid layer between the drop and the large interface, is strongly affected by the existence of an intervening thin liquid film (and, more generally, by the geometry of the whole gap region). The functional dependence of the lifetime on the drop size is very different in the presence and in the absence of film,<sup>7</sup> and the film formation itself (i.e., the extent of drop deformation) is closely related to the drop diameter.

The purpose of this work is to check whether the experimentally measured lifetime of drops in a real system would obey the predicted dependence with a minimum at intermediate sizes. The shape of the curve for the lifetime can be of practical importance for understanding the properties of batch emulsions. For instance, one can expect a substantial decline of the emulsion stability in the medium drop size range (from dozens to hundreds of micrometers).

We study soybean oil droplets pressed by buoyancy against a large oil/water interface. The system is stabilized by bovine serum albumin (BSA). Proteins are frequently used in many food emulsions, so their performance as stabilizing agents is interesting from a practical point of view. An important feature, typical especially for globular proteins, is their ability to form adsorption layers which are essentially stiff (i.e., tangentially immobile), even at low bulk concentrations. This removes the necessity to account for a partial tangential mobility of the interfaces during the drop motion (the surfaces remain mobile, e.g., with low molecular weight surfactants in relatively diluted solutions, below the critical micellar concentration).

## 2. Theoretical Background

We shall consider coalescence of a single drop against its homophase. Only the simplest relations, known from the literature, which allow a qualitative description of the trends in the lifetime will be presented here. A detailed hydrodynamic treatment falls out of the scope of the present article. So, in this section we wish to provide only some guidelines, required for understanding the experimental results reported in section 4.

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After having been released in the volume, the emulsion drop initially moves fast, according to the Stokes law, until it "arrives" at the liquid boundary, i.e., until it approaches the interface to a sufficiently small distance (of the order of or smaller than the drop diameter), so that the presence of the large surface be significant from the point of view of the hydrodynamics. Then, the drop markedly decelerates, which is of course due to the increased viscous friction in the gap. This sharp change in the law of drop motion can be observed directly (see below). We shall define the "lifetime",  $\tau$ , to be the time elapsed from the moment when the drop arrives at the interface and starts moving more slowly until it disappears (by coalescing with the large homophase). Let us say that the thinning begins at some initial gap width,  $h_{in}$ , and ends at the critical thickness,  $h_c$

$$\tau = \int_{h_c}^{h_{in}} \frac{dh}{V(h)} \quad (1)$$

Here  $V(h)$  is the velocity of thinning at the current gap width,  $h$ . In our further considerations we shall suppose that the interfaces are tangentially immobile. Such is really the case in the particular systems examined experimentally by us.

**2.1. Deformed Drop with a Film.** When the drop is deformed and a more or less plane-parallel intervening film exists, the lifetime is almost entirely determined by the drainage of that film (if a final equilibrium thickness cannot be reached). For a circular film with radius  $R_f$ , whose surfaces are stiff and flat, the known Reynolds equation connects the thinning velocity,  $V_{Re}$ , with the external driving force,  $F$  (see, e.g., ref 8):

$$V_{Re} = \frac{2Fh^3}{3\pi\eta R_f^4} \quad (2)$$

Here  $\eta$  denotes the dynamic viscosity of the liquid in the film. The radius  $R_f$  can be found from the stress balance on the film surface.<sup>9-11</sup> For a drop pressed by buoyancy against a large volume of the same phase, the corresponding relation reads<sup>9-11</sup>

$$R_f^2 = \frac{FR_c}{\pi\sigma} \quad (3)$$

where  $\sigma$  is the interfacial tension and  $R_c$  is the drop radius. Equations 2 and 3 may be inserted in (1), and the integration can be carried out easily if the force  $F$  does not depend on the thickness. The latter case holds when the disjoining pressure,  $\Pi$ , is much smaller than  $F/\pi R_f^2$  (relatively thick film and large  $F$ ). Thus, one obtains

$$\tau = \frac{3\eta FR_c^2}{4\pi\sigma^2} \left( \frac{1}{h_c^2} - \frac{1}{h_{in}^2} \right) \quad (4)$$

In most cases  $h_{in} \gg h_c$ , so that the second term in the parentheses may be discarded. Now we have to say something about the critical thickness of rupture,  $h_c$ , which is itself a function of the film radius and the applied force.<sup>11</sup> For the sake of estimates, the known Vrij formula can be utilized (see eq 20 in ref 11)

$$h_c = 0.268 \left\{ \frac{36\pi^3 A_H^2 R_f^4}{6.5F\sigma} \right\}^{1/7} \quad (5)$$

where  $A_H$  is the Hamaker constant of van der Waals interactions. (Equation 5 is valid for  $\Pi \ll F/\pi R_f^2$ .) The combination of eqs 4, 5, and 3, together with the expression for the buoyancy force,  $F = (4/3)\pi R_c^3 \Delta\rho g$ , yields

$$\tau = 4.088\eta\sigma^{-8/7} A_H^{-4/7} (\Delta\rho g)^{5/7} R_c^{25/7} \quad (6)$$

Here  $\Delta\rho$  is the density difference and  $g$  is the gravity acceleration.

Equation 6 predicts that the lifetime,  $\tau$ , should **increase** with the drop radius,  $R_c$ . Since  $F$  also rises, as  $F \sim R_c^3$ , we come to the conclusion that the higher the pushing force, the longer the drops live. This inference seems paradoxical at first sight, but the explanation is simple: larger force creates larger drop deformation (eq 3), and the thinning velocity depends strongly on the film radius (cf. eq 2,  $V \sim 1/R_f^4$ ). The effect of the increased viscous friction in a wider film outweighs the fact that bigger  $F$  favors faster drainage if all other parameters are fixed.

**2.2. Nondeformed Drop (Absence of Film).** It can be proven by rigorous hydrodynamic calculations<sup>12</sup> that only sufficiently large drops deform to a considerable extent. The intervening film which separates the drop and the outer volume phase can be observed directly (see section 4). On the other hand, micrometer-size droplets maintain their spherical shape up to the moment of coalescence.<sup>12</sup> In the latter case we can adopt a simplified approach, using the Taylor<sup>13</sup> formula for a hard sphere which approaches a solid plane wall:

$$V_{Ta} = \frac{Fh}{6\pi\eta R_c^2} \quad (7)$$

Equation 7 is a counterpart of eq 2 and has asymptotic validity, for  $h \ll R_c$ .  $V_{Ta}$  is the so-called Taylor velocity of thinning. After substituting  $V_{Ta}$  for  $V$  in eq 1 and performing the integration, we are left with

$$\tau = \frac{6\pi\eta R_c^2}{F} \log \left[ \frac{h_{in}^{(Ta)}}{h_c} \right] \quad (8)$$

where  $h_{in}^{(Ta)}$  denotes the gap thickness at which the drop motion switches from Stokes' to Taylor's regime. For gravity settling we write

$$\tau = \frac{9\eta}{2\Delta\rho g} \frac{1}{R_c} \log \left[ \frac{h_{in}^{(Ta)}}{h_c} \right] \quad (9)$$

In principle,  $h_{in}^{(Ta)}$  and  $h_c$  may depend on  $R_c$ . However, the dependence of the logarithm should be rather weak. Therefore, we may accept that  $\tau \sim 1/R_c$ . Equation 9 predicts that the lifetime,  $\tau$ , should **diminish** with the increase of the drop radius,  $R_c$  (and the driving force,  $F$ ). This trend is just the opposite to what was found in case 2.1 above (eq 6).

From a practical point of view, it may sometimes be difficult to study the pure Taylor regime experimentally. To observe the ascending drop by a microscope, one has to adjust the focus very close to the interface, at a distance equal to or smaller than  $h_{in}^{(Ta)}$ . In our experiments

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(described in the next section) we took special measures to start accounting the lifetime exactly from the moment when the drop decelerates at the surface (in other words, we adjusted the focus of the microscope at  $h_{in}^{(Ta)}$ ). Since  $h_{in}^{(Ta)} < R_c$  however, in some cases one starts observing the drop at larger separations from the flat boundary, where the contribution associated with the Stokes motion is significant. Later we shall discuss data of this kind as well; therefore, it is instructive to consider briefly the mixed Stokes–Taylor regime, when the drop is not very close to the interface.

The asymptotic law for the friction when sphere approaches a solid wall at large gap width,  $h \gg R_c$ , was formulated by Lorentz.<sup>14</sup> More recently Brenner<sup>15</sup> has derived a general equation for the drag force (and the particle velocity) at arbitrary distance from the plane wall. Brenner's result encompasses the limiting cases of Lorentz ( $h \gg R_c$ ) and Taylor ( $h \ll R_c$ ). On the other hand, Ivanov and Dimitrov<sup>16</sup> proposed a simple interpolation formula which approximates the equation of Brenner<sup>15</sup> with a very good accuracy (not worse than 7%) in the whole range of gap widths  $h$ . This expression reads<sup>16</sup>

$$\frac{1}{V} = \frac{1}{V_{St}} + \frac{1}{V_{Ta}} \quad (10)$$

where  $V_{Ta}$  is given by eq 7 and  $V_{St}$  refers to the Stokes law for motion of a sphere in an unbounded liquid:

$$V_{St} = \frac{F}{6\pi\eta R_c} = \frac{2\Delta\rho g}{9\eta} R_c^2 \quad (11)$$

After inserting eq 10 into eq 1, we derive an approximate equation for the lifetime in the mixed Stokes–Taylor regime:

$$\tau = \frac{9\eta}{2\Delta\rho g} \frac{1}{R_c} \left[ \log\left(\frac{h_{in}}{h_c}\right) + \frac{h_{in} - h_c}{R_c} \right] \quad (12)$$

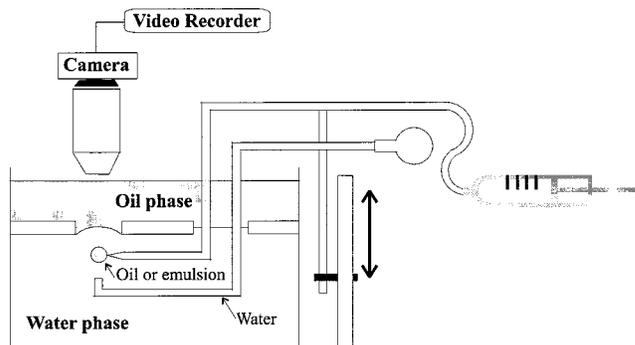
This simple result again predicts that the lifetime,  $\tau$ , should diminish with increasing  $R_c$  (similarly to eq 9).

In summary, we discover that the behavior of the lifetime as a function of the drop size can be qualitatively different, depending on whether the drop is deformed (with film) or remains spherical. Equations 6, 9, and 12 suggest that the function  $\tau(R_d)$  should have a minimum, because eqs 9 and 12 are anticipated to hold with smaller drops, whereas eq 6 is pertinent to larger ones. This surmise is verified by experiments described below.

We have to mention here that minimum in the  $\tau(R_d)$  dependence has been predicted also by rigorous hydrodynamic calculations.<sup>17,7</sup> The authors of refs 17, 18, and 7 considered a model drop shape-truncated sphere, and accounted for the contributions of the plane-parallel film and the adjacent curved meniscus region in the overall viscous resistance. A counterpart of eq 12 was derived for the drop lifetime (see eq 6 in ref 7); it gives results similar to those discussed in section 4 below.

### 3. Experimental Section

**3.1. Materials.** Lyophilized bovine serum albumin (BSA), p.a. grade, essentially fatty acid free (Sigma product) was used as received. All solutions were prepared with deionized water from



**Figure 1.** Sketch of the experimental setup for studying the stability of oil drops pressed by buoyancy under a large oil/water interface.

a Milli-Q system (Millipore). The bulk concentration of BSA was fixed to  $4 \times 10^{-4}$  wt %. With respect to this choice, we can say the following: Although somewhat low, such a concentration is still sufficient to ensure a significant coverage of the oil/water interfaces with protein. Graham and Phillips<sup>19</sup> measured the adsorption to be  $\sim 2$  mg/m<sup>2</sup> (at  $4 \times 10^{-4}$  wt % BSA, pH = 7, and ionic strength of 0.1 mol/L). The same authors in another paper<sup>20</sup> determined the surface viscosity—a value of about 10 g/s (10 sp) at  $6 \times 10^{-4}$  wt % BSA was reported (at petroleum ether/water boundary). Under the same conditions the elasticity of the interfacial layer was  $\sim 3$  dyn/cm.<sup>20</sup> The surface viscosity at  $6 \times 10^{-4}$  wt % BSA is lower than that at higher concentrations but is still substantially greater than the maximum values attainable with low molecular weight surfactants. In the latter case typical surface viscosities range between  $10^{-5}$  and  $10^{-2}$  g/s.<sup>21</sup> On the other hand, it is well-known that surfactants near the critical micellar concentration render the liquid interfaces of thinning films immobile.<sup>7,10</sup> We therefore believe it is plausible to assume that the adsorption layer of BSA at  $4 \times 10^{-4}$  wt % is essentially immobile too. Thus, compliance of the experimental system with the premises of the model considerations in section 2 is ensured.

It has to be pointed out that at higher concentrations of BSA (of the order of  $10^{-2}$  wt %) the drops are very stable, and coalescence is not observed in our experiments. This may be due to protein multilayers and/or surface aggregation, which suppresses the hydrodynamic fluctuations and, consequently, brings about increased stability with respect to rupture. It was mainly for this reason that we chose a substantially lower working concentration,  $4 \times 10^{-4}$  wt %, because for our purposes it was necessary that all droplets finally burst.

Soybean oil (supplied by Kraft Foods, Inc.) was chosen as an oil phase. It was purified by percolating through a column packed with alumina adsorbent (Florisil F101), as described by Gaonkar.<sup>22</sup> When BSA was dissolved in water (with the concentration of  $4 \times 10^{-4}$  wt %), pH was measured to be  $6.4 \pm 0.1$  and was not regulated by additives. The isoelectric point of BSA is at pH about 4.8, i.e., the molecules are negatively charged at pH  $\approx 6.4$ . The ionic strength was kept constant and equal to 0.15 M by addition of NaCl (Merck). This salinity effectively removes all electrostatic effects due to surface charges. Hence, one can safely assume absence of potential barriers associated with long-range repulsive disjoining pressure when a drop approaches the interface.

One experiment was carried out with styrene (Merck, stabilized against polymerization) and aqueous solution of  $7 \times 10^{-4}$  wt % sodium nonylphenol polyoxyethylene (25) sulfate (Rewopol), containing 0.15 M NaCl.

**3.2. Experimental Setup.** The apparatus used to observe coalescence of oil droplets at a planar oil/water interface is depicted schematically in Figure 1. It consists of a glass vessel,

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which is covered by a thin Teflon plate. This plate is positioned in such a way as to lie just at the liquid boundary. There are two holes in the plate: one of diameter 1.0 cm and another one of diameter 2.0 cm. A thin glass capillary passes through the wider hole; its tip is located about 0.5 cm below the oil/water interface. The capillary is used to release oil droplets. The droplets attach to the surface formed in the smaller hole. In this manner we avoid any disturbance from the meniscus due to the immersed capillary. The Teflon creates a slightly convex interface (Figure 1). The buoyancy pushes the droplets toward the hole center, where the level of the surface is the highest, and this prevents the droplets from drifting laterally during the course of measurements.

The experimental cell is placed on the table of a microscope Axioplan (Zeiss, Germany), and is thermostated at 25 °C. The microscope allows observation in transmitted as well as in reflected light and is supplied with long focal distance objectives (50 $\times$ , 10 $\times$ , and 2.5 $\times$ ). When an oil droplet approaches the interface closely, it begins to move upward more slowly (if film exists, it gradually thins), until coalescence with the bulk oil phase occurs. A CCD camera is mounted on the microscope for recording the process of thinning and the moment of droplet coalescence. The camera is connected to a video timer, video cassette recorder, TV monitor, and computer. The timer allows us to determine the droplet lifetime,  $\tau$ . The computer is capable of capturing and storing pictures from the video recorder. There is an image analysis program, which helps us to measure the droplet size with a high accuracy ( $\pm 0.5 \mu\text{m}$ ), from the stored pictures.

The empty cell is first rinsed with a small quantity of the aqueous solution and after that it is filled carefully with 30 cm<sup>3</sup> of the water phase, avoiding bubble formation. Next, 5.0 cm<sup>3</sup> of oil is gently poured above the aqueous phase. The formed interface is aged for a period of 10 min, and then droplets are injected through the glass capillary.

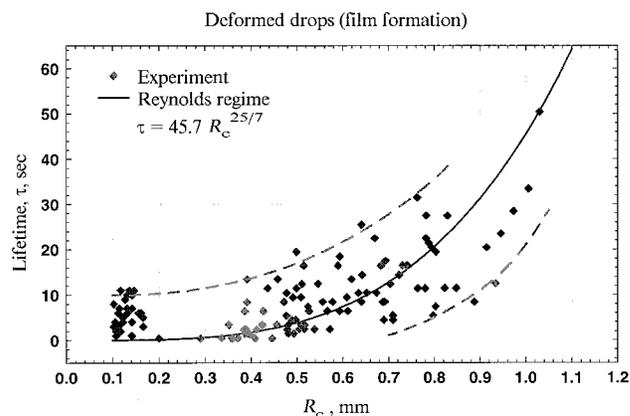
We have spent much effort in order to find experimental conditions allowing us to scan the whole curve  $\tau(R_c)$  in the three particular regimes of small, medium, and large drops, varying **the size only**. Three different procedures have been applied for coalescence measurements in the cases of small (micrometer size, up to  $R_c \approx 100 \mu\text{m}$ ), medium size ( $R_c$  between 100 and 500  $\mu\text{m}$ ), and large drops ( $R_c > 500 \mu\text{m}$ ).

The micrometer size droplets are produced by first preparing an emulsion. Twenty milliliters of water phase and 5 mL of oil phase are mixed together for about 15 s with a rotating blade homogenizer. After that, 0.2 mL of the obtained oil-in-water emulsion is introduced into the water phase in the experimental cell, by means of the glass capillary and the syringe (Figure 1).

The medium-size droplets are formed as follows: First, a small amount of oil is sucked into the capillary. Next, the capillary is immersed in the water phase, and oil is squeezed out by the syringe until a big drop of certain desired volume is formed on the tip. After that, this drop is sucked back into the capillary in a fast and sudden manner, using the syringe. Thus, some amount of aqueous phase also enters into the capillary, together with the oil. The turbulent flow in the narrow capillary leads to formation of emulsion droplets of medium size, which can subsequently be pushed out under the interface.

In the experiments with the large droplets (above 500  $\mu\text{m}$  radius) we used a method similar to that applied by Davis and Smith.<sup>23</sup> A single oil drop is formed at the tip of the glass capillary, and then it is blown out by some solution, with the help of a glass tube situated underneath (Figure 1). The experimental cell allows us to vary the radius of the released drops in the range 0.5–2.5 mm. In such a way individual drops are obtained. We do not wait for aging of the drops at the capillary tip—they are detached just after formation.

In the cases of small and medium sizes there are usually at least several droplets resting simultaneously at the interface. Two droplets which are almost in a lateral contact preferably coalesce with each other, rather than with the big oil phase. When the droplets are separated at a bigger distance, say one drop diameter, then they coalesce with the large homophase.



**Figure 2.** Measured lifetime,  $\tau$  (the points), plotted vs droplet radius,  $R_c$ , in the range of big drop sizes (above 100  $\mu\text{m}$ ). The system consists of soybean oil and aqueous solution of  $4 \times 10^{-4}$  wt % BSA + 0.15 M NaCl. Theoretical curve according to the Reynolds law for viscous friction (eq 6) is also drawn for comparison.

The interfacial tension,  $\sigma$ , of the boundary between soybean oil and the aqueous solution of BSA was measured at 25 °C by a Krüss K10T automatic tensiometer, using a du Nouy platinum ring. The value of  $\sigma$  turns out to be 15.0 dyn/cm.

#### 4. Results and Discussion

The aim of our work is to confirm experimentally the peculiar trends in the dependence of the lifetime upon the drop radius (section 2). The results with large drops are presented in Figure 2. We see that the scattering of the data is high. Perhaps, the reason for this is connected with the statistical nature of the coalescence process (due to appearance and growth of interfacial fluctuations<sup>24</sup>). The probabilistic aspect of the drop stability is now being studied in more detail by us and will be the subject of a separate publication.

What is important in Figure 2 is the marked tendency for increase of the lifetime with rising drop radius. The solid line in Figure 2 is drawn according to eq 6, with the coefficient in front of  $R_c^{25/7}$  treated as a free parameter. Obviously, the functional dependence  $\tau \sim R_c^{25/7}$  is in qualitative agreement with the experimental data. A similar trend in the lifetime was predicted also by other authors: Chen et al.<sup>25</sup> calculated the time required for a dimpled film to drain to zero thickness at the rim, and found  $\tau \sim R_c^{3.4}$ , which is very close to the power law in eq 6.

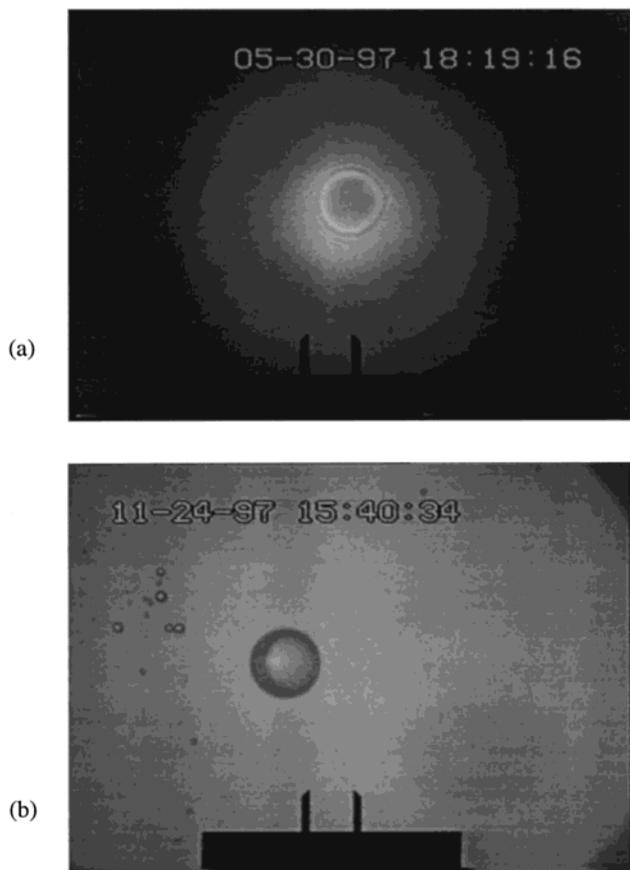
In our view, quantitative interpretation of the data from Figure 2 should not be sought, first, because of the large scattering, and, second, one should keep in mind that eq 6 is oversimplified to a great extent. Indeed, it does not account for the contribution of the meniscus region around the film to the overall viscous resistance. Moreover, the real film is slightly curved (because the large liquid interface is deformable). Even more important is perhaps the fact that protein-laden fluid interfaces often contain big lumps which may be accompanied by a considerable amount of entrapped liquid. Therefore, the film may not be exactly plane-parallel, and the aggregates can substantially influence the flow in the thin liquid layer. So, in such cases the applicability of the Reynolds equation (2) may be limited.

According to our observations, in the studied system films exist for droplets larger than about 100  $\mu\text{m}$  (radius).

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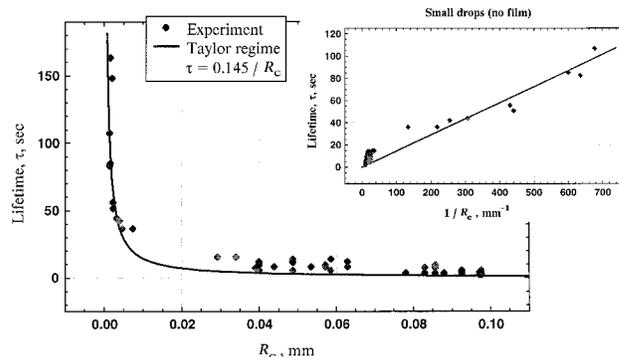


**Figure 3.** (a) Picture of a film with radius  $R_f \approx 13 \mu\text{m}$ , formed by a drop with radius  $R_c \approx 220 \mu\text{m}$ , observed in reflected monochromatic light. (b) Drop with radius  $R_c \approx 15.6 \mu\text{m}$ , shortly before coalescence. The reference distance between the two bars in both pictures is equal to  $20 \mu\text{m}$ . The system consists of soybean oil and an aqueous solution of  $4 \times 10^{-4}$  wt % BSA + 0.15 M NaCl.

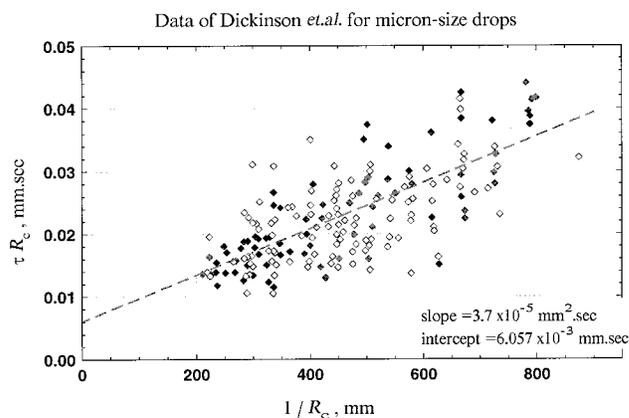
A picture of the intervening film between a drop with  $R_c \approx 220 \mu\text{m}$  and the large soybean oil/water surface is shown in Figure 3a. The picture was taken in reflected monochromatic light (so Newton fringes can be distinguished). The film radius,  $R_f \approx 13 \mu\text{m}$ , corresponds to the requirements of eq 3, where  $F$  refers to buoyancy (with  $\Delta\rho = 0.080 \text{ g/cm}^3$  (water/soybean oil),  $g = 981.55 \text{ cm/s}^2$ , and  $\sigma = 15.0 \text{ dyn/cm}$ ). Figure 3b presents a small non-deformed droplet, just before coalescence.

Our results for the lifetime of small (nondeformed) drops, for  $R_c < 100 \mu\text{m}$ , are shown in Figure 4. The hyperbolic dependence  $\tau \sim 1/R_c$  (eq 9) is confirmed: the droplet lifetime strongly decreases with increasing radius. The qualitative agreement between the experiment and the predicted functional dependence is very good. We have to point out that eq 9 is too oversimplified for a quantitative comparison to be sought. The Taylor formula (7) assumes that the large surface is perfectly flat. However, in reality the liquid boundary is deformed, which leads to a much more difficult hydrodynamic problem. In addition, at very small gap widths protein aggregates, protruding from the interfaces, may disturb the liquid flow in a rather complicated manner. This will eventually modify the viscous resistance and, hence, the thinning rate.

It is interesting to check if other experimental data with micrometer-size drops would also confirm the trend illustrated by Figure 4. We analyzed the results of Dickinson et al. (Figure 2 in ref 6), plotting the lifetime according to eq 12, Figure 5. We envisage the Stokes–Taylor regime, which is pertinent when the microscopic



**Figure 4.** Measured lifetime,  $\tau$  (the points), plotted vs droplet radius,  $R_c$ , in the range of small sizes. The system consists of soybean oil and aqueous solution of  $4 \times 10^{-4}$  wt % BSA + 0.15 M NaCl. A theoretical curve according to the Taylor law for viscous friction (eq 9) is also drawn for comparison. The inset shows the respective graph in the scale  $\tau(1/R_c)$ .



**Figure 5.** Data of Dickinson et al.<sup>6</sup> plotted according to our eq 12. The system consists of *n*-hexadecane and aqueous solution of  $10^{-4}$  wt % lysozyme, pH = 7, ionic strength 0.1 M.

observation of the drops starts at a distance from the interface larger than  $h_{in}^{(\tau a)}$  (cf. section 2.2). As one can see from Figure 5, there is a satisfactory straight line in the scale suggested by eq 12 ( $\tau R_c$  as a function of  $1/R_c$ ), which indicates an agreement with the Stokes–Taylor regime. From the slope and the intercept in Figure 5 we find  $h_c = 0.96 \mu\text{m}$  and  $h_{in} = 19.3 \mu\text{m}$ . While cautious about these numerical values (see above), we can mention that the critical thickness  $h_c$  is rather high. Some theoretical results in the literature seem to confirm such a behavior (i.e., large  $h_c$ ), in the case of small drops pressed by buoyancy against a homophase. Danov and Ivanov<sup>12</sup> have calculated  $h_c$  as a function of the drop radius and found a sharp increase in  $h_c$  (up to  $\approx 0.2 \mu\text{m}$ ) with diminishing  $R_c$  in the range from 10 to  $1 \mu\text{m}$  (see Figure 2 in ref 12).

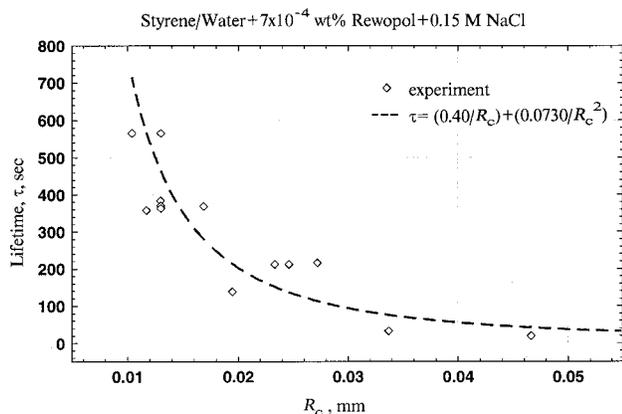
Experimental data of MacKay and Mason<sup>26</sup> can be very well interpolated by the equation

$$\frac{V_{St}}{V} = 1.774 + 1.223 \frac{R_c}{h} \quad (13)$$

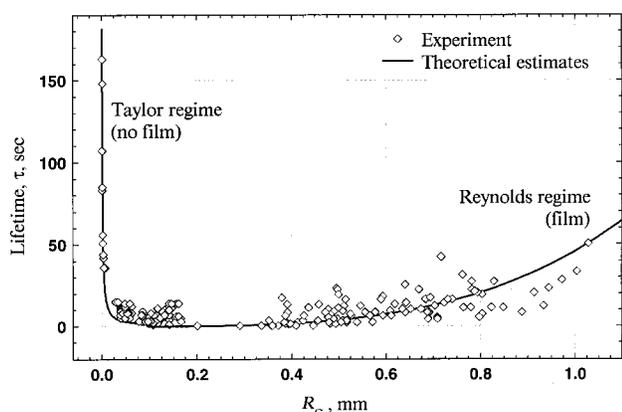
It is easy to verify that eq 12 can be obtained by inserting the relation

$$\frac{V_{St}}{V} = 1 + \frac{R_c}{h} \quad (14)$$

(26) MacKay, G. D. M.; Mason, S. G. *Can. J. Chem. Eng.* **1963**, *41*, 203.



**Figure 6.** Measured lifetime,  $\tau$  (the points), plotted vs droplet radius,  $R_c$ , in the range of small sizes. The system consists of styrene and aqueous solution of  $7 \times 10^{-4}$  wt % Rewopol + 0.15 M NaCl. A theoretical curve according to the Stokes–Taylor regime (eq 12) is also drawn for comparison.



**Figure 7.** Data from Figures 2 and 4 are plotted together (the theoretical curves are also included). Note the existence of shallow and broad minimum. Both Taylor and Reynolds regimes predict very unstable medium-size droplets.

into eq 1. Therefore, we may conclude that the results of MacKay and Mason<sup>26</sup> comply with the Stokes–Taylor regime (in the form of eq 12), up to slightly different numerical coefficients.

Another set of experimental data, measured by us in a system consisting of styrene and aqueous solution of  $7 \times 10^{-4}$  wt % Rewopol + 0.15 M NaCl are presented in Figure 6. The lifetime of micrometer-size droplets diminishes with increasing  $R_c$ , and the dependence is again in agreement with eq 12. From the numerical coefficients (given in Figure 6) we determine  $h_c \ll h_{in}$  and  $h_{in} = 1.45$  cm. The value of  $h_{in}$  is reasonable because in these experiments the lifetime is accounted from the moment when the drops are injected into the water phase through the capillary.

Let us now discuss the overall size dependence of the drop stability. Our data from Figures 2 and 4 are plotted together in Figure 7 (for the system with BSA). One sees that the coalescence behavior in the three regions (small, medium-size, and large drops) is following quite different trends. In the interval of  $R_c \sim 20$ – $500 \mu\text{m}$ , both regimes (Taylor and Reynolds) predict very unstable droplets, which is confirmed by the experimental measurements—Figure 7. In fact, the drops with  $R_c > \sim 100 \mu\text{m}$  form films, but this *does not* improve their stability appreciably (up to  $R_c \sim 500 \mu\text{m}$ ). Actually, in this interval the extent of droplet deformation is small, so the effect associated with increased viscous resistance will be insignificant. Ivanov and Dimitrov<sup>16</sup> have considered the real shape of ap-

proaching bubbles at small separation and have demonstrated that the viscous friction in the gap is equivalent to existence of a film which is exactly plane parallel. This justifies the notion of film formation even with drops which are relatively small and only slightly deformed.<sup>16</sup> On the other hand, eq 3 predicts that  $R_i/R_c = 2R_c(\Delta\rho g/(3\sigma))^{1/2}$ , which gives  $R_i/R_c \approx 0.05$  at  $R_c = 200 \mu\text{m}$ , for our system with BSA. Obviously, under these conditions the film diameter is indeed small.

As a complementary experiment, we decided to check the behavior of a system stabilized by a milk protein,  $\beta$ -casein. The lifetime of small (micrometer size,  $R_c = 1$ – $13 \mu\text{m}$ ) soybean oil droplets was measured at  $2 \times 10^{-5}$  wt %  $\beta$ -casein, ionic strength equal to 0.15 M NaCl, and pH = 6.4. The results show exactly the same trend as that illustrated by Figures 4 and 6.

Regarding the universality of the phenomena, we can say the following: The effects discussed above are due to the specific hydrodynamic regimes of thinning; they will manifest themselves whenever this hydrodynamics is a dominating factor of stability. We have cases with low molecular weight surfactant and globular and disordered protein (BSA,  $\beta$ -casein), which exhibit one and the same size dependence of droplet lifetime. This will be so when a stable film (or gap) with equilibrium thickness cannot be reached; i.e., the drop coalesces immediately once it arrives at a certain critical distance from the interface. Such a behavior is to be expected at relatively low concentration of surfactant (a case relevant to initial moments just after emulsion homogenization, when the interfacial adsorption layers are still incomplete).

At higher concentrations of surface-active substance, other factors of stability, more important than the hydrodynamics of gap thinning, come into play. The films will reach a quasi-equilibrium thickness, and the interfacial rheology will then determine to a large extent the stability against rupture, by the mechanism of damping the interfacial fluctuation waves or by reducing the probability for hole formation.

## 5. Conclusions

We demonstrate by direct measurements that the lifetime of drops pressed by buoyancy against a large interface depends on the size in a peculiar manner (with all other conditions being the same). Small (micrometer size) droplets are more unstable when their radius is larger. Just the opposite is the case of big drops (above  $\sim 300 \mu\text{m}$ ): the lifetime increases with the size. These effects are explained with different hydrodynamic regimes of thinning of the gap region. Small drops remain practically non-deformed up to coalescence (Taylor regime), whereas large drops form intervening thin liquid film (Reynolds regime). The experimental results are in good qualitative agreement with the predictions of simple theoretical considerations. In the range of medium-size drops the stability is always very low, irrespective of the presence or absence of film.

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