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Coalescence in emulsions containing inviscid drops with high interfacial mobility

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Abstract

The drainage process of a thin liquid film between two droplets of low viscosity is analyzed in order to specify conditions for coalescence. The time available for drainage of the film is confined by the duration of a collision. A.K. Chesters (Int. J. Multiphase Flow, 2 (1975) 191) considered a similar problem and obtained an expression for the rate of drainage which neither contained the extent of flattening of the droplets nor the strength of the flow field. The same hydrodynamic analysis was used to evaluate the rate of drainage in the case of fully mobile interfaces at a vanishing viscosity ratio for the dispersed and continuous phase, from the balance of the driving and resistance forces of the film drainage. In the first stage of film drainage, the droplets remain perfect spheres. Once the pressure in the film exceeds the Laplace pressure, deformation sets in. The extent of flattening follows from an energy equation. The drainage process is described by two dimensionless groups: the Capillary number, which gives the strength of the flow field, and the Flow number, which is the ratio of the hydrodynamic and van der Waals forces. The time available for film drainage is obtained from the duration of a collision, which is determined by the rotation of the collision doublet. It is shown that flattening of the droplets retards drainage and reduces the coalescence probability considerably above a value of 0.02 for the Capillary number. Generally, drops with fully mobile interfaces are found to have a much higher coalescence probability than those having rigid interfaces.

Key words: Coalescence; Flattened drops; Low viscosity ratio; Mobile interfaces

Introduction

Coalescence is an important phenomenon in industrial processes such as emulsification and in separation technology, where droplet sizes are determined by the interplay of droplet break-up and coalescence. The actual number of coalescence events per unit time is termed the coalescence frequency, which is given by the product of the collision frequency and the probability that a collision results in coalescence:

coalescence frequency = collision frequency × coalescence probability

Groeneweg et al. [1] presented the collision frequency (CF) in a simple viscous shear flow as a function of the shear rate \( \dot{\gamma} \) and the volume fraction \( \phi \) of the dispersed phase:

\[
CF = \frac{8\phi \dot{\gamma}}{\pi}
\]  

The coalescence probability depends on the details on the drainage of the film between the droplets. The objective of the present work is to determine the coalescence probability in purified systems with very low viscosity ratios, \( \lambda = \eta_d/\eta_c \ll 1 \), where \( \eta_d \) is the viscosity of the dispersed phase and \( \eta_c \) is the viscosity of the continuous phase) e.g. for emulsions of water in paraffin oil for which \( \lambda = 0.02 \). To this end, the mutual approach of two droplets at small distances needs to be analyzed. During a collision in a viscous flow field, droplets move on different
streamlines which forces them to rotate around each other (Fig. 1). The distance between the droplets only decreases in the first half of the rotation. If coalescence has not yet taken place here, the droplets will separate again. The drainage of the thin film may be analyzed by means of a force balance comprising the force exerted on the droplets by the flow field and the resistance to drainage due to the viscous flow in the film.

A detailed solution for the motion of two equal-sized rigid spheres approaching each other along their line of centres at any distance under viscous flow conditions was obtained by Stimson and Jeffery [2] and Faxén [3] by solving the respective stream functions. Haber et al. [4] extended this to spheres of unequal size having a finite viscosity, thus providing an exact analysis of the mutual approach of two droplets along their line of centres in a viscous flow field. The force resisting the mutual approach of the droplets was given a constant relative velocity.

Approximate solutions using lubrication theory can be obtained in the limit of small separations where the resistance force is mainly dominated by the flow in the thinning film between the two spheres. The analysis of Haber et al. appears to be comparably inconvenient with respect to this limit as the flow around the entire droplets is taken into consideration.

The flow in the film is coupled to the flow inside the approaching particles via the mobility of the interfaces, which is especially relevant for pure fluids. In liquid−liquid systems containing surfactants in the continuous phase, the film drainage leads to interfacial tension gradients, which immobilize the film surfaces. These surfaces may then be considered to be rigid with respect to tangential stresses. The resistance against drainage of a film between rigid spherical interfaces was derived by Taylor, as cited in Ref. 5.

If the dispersed phase has a relatively low viscosity compared with the continuous phase (\( \lambda = \eta_d/\eta_c < 1 \)) and no surfactants are present, the motion of the interfaces is not impeded. Consequently, the film flow is not retarded near the fully mobile interfaces and a plug flow profile is established in the film. Davis et al. [6] derived the resistance force for this case and for the case in which the film flow is determined by the circulation within the particles. For the latter case, they assumed the pressure drop in the film to be determined by the tangential stress balance at the interfaces, but they did not account for the resistance originating from the continuous-phase viscosity. The same case was considered by other workers, who arrived at slightly different expressions for the resistance to drainage [7−9]. It was shown by Davis et al. [6] that the resistance against flow due to the viscosity of the film could be neglected down to a viscosity ratio of \( \lambda \approx 0.1 \). Below \( \lambda = 0.1 \), the film viscosity must be considered.

Up to now, no model for film drainage was retrieved from lubrication theory for spheres at a vanishing viscosity ratio. Beshkov et al. [8] derived an asymptotic solution from the exact theory for very low viscosity ratios (\( \lambda \to 0 \)) but as their solutions for higher viscosity ratios deviate from results that were shown to coincide with the exact solution [6], the reliability of their approach is not confirmed.

At moderate viscosity ratios (\( \lambda \geq 1 \)), the interfaces are considered to be partially mobile and the film flow is described by a superposition of the parabolic and the plug flow profiles [6]. The viscosity ratio appears as a parameter in order to define the rigidity of the interfaces. Rigid interfaces are regained in the limit of very high viscosity ratios (\( \lambda \to \infty \)).
Particles consisting of a fluid, e.g. drops or bubbles, may deform when they collide. A model developed by Mackay and Mason [10] was applied by Groeneweg et al. [11] to describe the coalescence of flattened drops having rigid interfaces. The thinning of a flattened film between partially mobile side walls was considered by Ivanov and Traykov [11]. The result was combined with relationships from Ref. 6 for spheres by Kumar et al. [12] in order to calculate the coalescence probabilities of deformable drops. The flow conditions in Ref. 12 remain somewhat unclear: the authors applied models that were derived under viscous flow conditions, but determined the collision duration and the driving force via inertia-driven collisions.

Chesters [7] introduced a model describing the situation of significantly flattened droplets at very low viscosity ratios (\( \lambda \to 0 \)). By this model, the drainage is controlled by the viscosity \( \eta_c \) of the film. Chesters derived the rate of drainage from boundary conditions for the pressure in the film and not from a force balance. The obtained expression is

\[
h(t) = h_0 \exp(-2\sigma t/3\eta_c R) \tag{2}
\]

where \( h_0 \) is the film thickness at which drainage starts, \( \sigma \) is the interfacial tension, \( t \) is time and \( R \) is the radius of the droplet. The equation includes neither the extent of deformation nor the driving force. However, during a coalescence process, the droplets will be flattened and as the resistance is in the film, the extent of flattening is expected to affect the drainage rate.

The aim of the present investigation is to obtain a simple two-dimensional model which is based on lubrication theory and describes the drainage of a viscous film between fully mobile interfaces at \( \lambda \to 0 \), allowing flattening of the droplets. Similar to the approach of Chesters, the starting point will be the pressure distribution in the draining film but the rate of drainage will be derived from the balance of forces, enabling both the treatment of spherical and flattened drops. The degree of deformation during the coalescence process will be analyzed and taken into account for the drainage rate. The version of the drainage model obtained will be linked to an expression describing the rotation of the collision doublet analogous to the procedure followed by Groeneweg et al. [1]. The speed of rotation governs the time available for drainage. Coalescence takes place if the draining film ruptures before the rotation is completed.

The drainage model and the time-scale enable the calculation of the coalescence probability as a function of the strength of the flow field. A dimensionless format will allow a more general evaluation of the results.

**Film-viscosity-controlled drainage between fully mobile interfaces**

If the viscosity of the droplets is much lower than that of the continuous phase, the flow in the film can be described as plug flow; this has been analyzed in detail by Chesters [13], where the consequence of the flattened geometry of the drops for the pressure in the film has been taken into account. Spheres are considered as a special case of flattened droplets with a vanishing flattening radius \( a = 0 \) (Fig. 2). The force of resistance against thinning of the film will be obtained by integrating the pressure over the whole film. Incorporating the result into a balance of forces will lead to an expression for the rate of drainage between spherical drops and for flattened drops at a vanishing viscosity ratio \( \lambda \to 0 \). In order to describe the entire

![Fig. 2. Geometric definitions for flattened spheres.](image)
drainage process, spherical and flattened drops need to be treated separately. During a collision, drops are only assumed to flatten if the pressure in the film exceeds the Laplace pressure. In that case, a second condition is required in addition to the balance of forces for evaluating the extent of flattening. For that purpose the energy conservation principle will be applied.

Force balance

In the coalescence process, the flow exerts a hydrodynamic force on the droplets, which are pushed towards each other if they are on different streamlines. If the droplets are close to each other, the drainage of the film in between them retards their relative motion. The interaction forces between the droplets at small distances can either increase the drainage rate (in case van der Waals forces are operational) or decrease it in the presence of repulsive forces. Here only the former case will be considered. The interplay of all these forces leads to the following force balance

\[ F_{\text{hydr}} + F_{\text{dr}} + F_{\text{vdw}} = 0 \]  

The terms are discussed separately below.

The hydrodynamic force \( F_{\text{hydr}} \) for a doublet of spheres with a viscosity ratio \( \lambda = \frac{\eta_d}{\eta_e} \) is treated analogously to that for rigid spheres, based on Jeffery’s theory [14] on the behaviour of rigid ellipsoids in a viscous shear flow. The hydrodynamic force experienced by a rigid prolate spheroid (\( F_{\text{hydr, rigid}} \)) along its principle axis was applied to a collision doublet with an axis ratio of 2 by Allan and Mason [15]. The results presented for drops in the same plane as the plane of shear depends on the angle of inclination \( \alpha \) (Fig. 1)

\[ F_{\text{hydr, rigid}} = 4.34 \pi \eta_e R^2 \gamma \sin(2\alpha) \]  

The \( \sin 2\alpha \) term arises from the proportionality of the force to the distance of the streamlines which carry the droplets (\( \cos \alpha \)) and the component of the force perpendicular to the film between the droplets (\( \sin \alpha \)). In Eq. (4), \( \gamma \) is the shear rate and \( R \) is the radius of the droplets. To account for the viscosity of the droplets, a correction term was introduced into the expression for the hydrodynamic force on spherical drops by Hadamard and Rybczinski [16]. The application of a similar correction for doublets results in

\[ F_{\text{hydr}} = 4.34 \left( \frac{2/3 + \lambda}{1 + \lambda} \right) \pi \eta_e R^2 \gamma \sin(2\alpha) \]  

In the limit \( \lambda \to 0 \), the resulting force is

\[ F_{\text{hydr}} = \frac{8.68}{3} \pi \eta_e R^2 \gamma \sin(2\alpha) \]  

The force resulting from the resistance to drainage \( (F_{\text{dr}}) \) depends on the degree of flattening of the droplets. Figure 2 represents the geometry and the relevant coordinates. The film is divided into two regions: a flattened one containing a film of thickness \( h_f \) and a non-flattened region, the film thickness of which is approximated by the Taylor expansion of a circle, \( h(r) = h_f + (r - a)^2 \bar{F} \) for \( a < R \), where \( r \) is the radial position in the film. The force \( F_{\text{dr}} \) is given by

\[ F_{\text{dr}} = \int_0^a 2\pi r (-\tau_{zz}(r)) \, dr \]  

where \( \tau_{zz}(r) \) is the normal component of the stress tensor in the film, which is defined as

\[ \tau_{ij}(r) = -p \delta_{ij} + d_{ij} \]  

where \( p \) is the pressure, \( \delta_{ij} \) is the kronecker delta (\( \delta_{ii} = 1 \) if \( i = j \), \( \delta_{ij} = 0 \) if \( i \neq j \)), and \( d_{ij} \) is the anisotropic part of the stress tensor, which depends on the fluid velocity gradients. For the analysis of Eq. (7), the pressure and velocity gradients in the film have to be evaluated. The pressure distribution is obtained from the Navier-Stokes equation neglecting gravitational terms

\[ \rho \frac{Du}{Dt} = -\nabla p + \eta_e \nabla^2 u \]  

where \( u \) is the velocity vector in the film, \( t \) is the time variable, \( p \) is the pressure and \( \rho \) is the density of the film phase. According to the plug flow
assumption and neglecting any radial flow, Eq. (9) simplifies to
\begin{equation}
\rho \left( \frac{du_r}{dr} + u_r \frac{\partial u_r}{\partial r} \right) = - \frac{\partial p}{\partial r} + \eta_c \frac{\partial}{\partial r} \left( \frac{\partial u_r}{\partial r} + \frac{u_r}{r} \right)
\end{equation}

(10)

where \( u_r \) indicates the radial component of the velocity in the film.

Introduction of the following dimensionless quantities (denoted by *):
\begin{itemize}
  \item \( t = \tilde{t}/\gamma \)
  \item \( u_r = \tilde{u} \gamma R \)
  \item \( r = \tilde{r} R \)
  \item \( h = \tilde{h} R \)
  \item \( p = \tilde{p} \gamma R^2 / \sigma \)
\end{itemize}
leads to a dimensionless form of Eq. (10). Defining the Capillary number as \( \Omega = \eta_c \gamma \tilde{R}/\sigma \) and the Weber number by \( We = \rho (\gamma R)^2 R/\sigma \), Eq. (10) becomes

\begin{equation}
We \left( \frac{\partial \tilde{u}_r}{\partial \tilde{t}} + \tilde{u}_r \frac{\partial \tilde{u}_r}{\partial \tilde{r}} \right) = - \frac{\partial \tilde{p}}{\partial \tilde{r}} + \tilde{\Omega} \frac{\partial}{\partial \tilde{r}} \left( \frac{\partial \tilde{u}_r}{\partial \tilde{r}} + \frac{\tilde{u}_r}{\tilde{r}} \right)
\end{equation}

(11)

The radial velocity \( \tilde{u}_r \) is related to the rate of drainage \( \frac{dh}{dt} \) by the condition of continuity, which, for the flattened region using cylinder coordinates [13], is given by

\begin{equation}
2\pi r h u_r = - \pi r^2 \frac{dh}{dt}
\end{equation}

(12)

The pressure is obtained by integrating the Navier-Stokes equation, Eq. (11). Defining
\[ \tilde{H} = 1/2 \ln \tilde{h} \]
the integral for the flattened region follows as [13]
\begin{equation}
\dot{p}_1 (\tilde{r}) = - We \int_0^{\tilde{r}} \left[ \left( \frac{d\tilde{H}}{d\tilde{t}} \right)^2 - \frac{d^2 \tilde{H}}{d\tilde{t}^2} \right] d\tilde{r} - 2\Omega \frac{d\tilde{H}}{d\tilde{t}} + c
\end{equation}

(13)

where \( c \) is an integration constant.

The resulting pressure, \( \dot{p}_1 (\tilde{r}) \) consists of an inertia term depending on the position in the film, and a viscous term invariant with respect to \( \tilde{r} \)
\begin{equation}
\dot{p}_1 (\tilde{r}) = \dot{p}_0 - \frac{We^2}{2} \left[ \left( \frac{d\tilde{H}}{d\tilde{t}} \right)^2 - \frac{d^2 \tilde{H}}{d\tilde{t}^2} \right]
\end{equation}

(14)

where \( \dot{p}_0 \) is the sum of the last two terms on the right-hand side of Eq. (13) and is determined from the balance between the Laplace pressure and the stress tensor \( \tilde{e}_{ij} \) at the centre of the film \((r=0)\) where the second term on the right-hand side of Eq. (8) vanishes. The axial velocity in the anisotropic part of the stress tensor \( u_z \), is related to the drainage rate by \( u_z (z) = \frac{2}{h} \frac{dh}{dt} \), where \( z \) indicates the axial position in the film (Fig. 2)

\begin{equation}
-2\sigma / R = - \rho_0 + 2\eta_c \frac{\partial u_z}{\partial z} \bigg|_{z=\eta_c/2} = - \rho_0 + 4\eta_c \frac{d\tilde{H}}{d\tilde{t}}
\end{equation}

(15)

which may be given a dimensionless form
\begin{equation}
\dot{p}_0 = 2 \left( 1 + 2\Omega \frac{d\tilde{H}}{d\tilde{t}} \right)
\end{equation}

(16)

Substituting \( \dot{p}_0 \) in Eq. (14), the pressure in the flattened region of the film becomes
\begin{equation}
\dot{p}_1 (\tilde{r}) = 2 \left( 1 + 2\Omega \frac{d\tilde{H}}{d\tilde{t}} \right) - \frac{We^2}{2} \left[ \left( \frac{d\tilde{H}}{d\tilde{t}} \right)^2 - \frac{d^2 \tilde{H}}{d\tilde{t}^2} \right]
\end{equation}

(17)

The resulting pressure in the flattened part of the film seems to contradict the assumption of really plane interfaces: the pressure inside the drops (and thus the Laplace pressure) is constant as a consequence of its low viscosity; whereas the pressure in the film depends on \( r \). A plane film can only be established if the \( r \)-dependent term may be neglected. If not, the film will tie in at the edges and form a dimple.

An estimate of the terms can be obtained by comparing the Capillary number to the Weber number for chosen system parameters. Typical values for a water–vegetable oil emulsion in a stirred vessel yield \( \Omega = 0.01 \) and \( We = 5.0 \times 10^{-5} \). Since \( We \) is much lower than \( \Omega \), \( \dot{p}_1 (\tilde{r}) \) will be constant in the film and dimple formation will be suppressed. For air bubbles in water, \( \Omega \) and \( We \) become of a comparable order of magnitude
because of the lower viscosity of the film phase, and dimple formation can be expected [17].

The pressure distribution in the non-flattened region \( \hat{p}_2(r) \) is obtained analogously to that in the flattened region. Here, the boundary condition is given by the reference pressure far from the film centre. Neglecting the inertia terms in this case yields [13]

\[
\hat{p}_2(r) = -\Omega \frac{d\hat{H}}{dt} \left[ 1 - a(r - \hat{a})/\hat{h} \right] \left[ 1 + (r - \hat{a})^2/\hat{h}^2 \right]^{-1}
\]

where \( b \) is the radius of curvature at the edge of the flat part of the film. For the evaluation of \( F_{\text{vdw}} \) in Eq. (7), the integration is the sum of two parts: in the first Eq. (17) has to be included in Eq. (8) and subsequently integrated in Eq. (7) from 0 to \( a \). For the second part, Eq. (18) has to be used. These standard algebraic manipulations (neglecting inertia terms, and assuming \( \Omega = 1 \)) lead to

\[
F_{\text{ar}} = \frac{2\hat{a}^2}{\Omega} + 3 \left[ \frac{\hat{a}^2}{\hat{h}} - \frac{1}{\hat{h} + (1 - \hat{a})^2} \right] \frac{d\hat{h}}{d\hat{t}}
\]

Van der Waals forces \( (F_{\text{vdw}}) \) enhance the drainage at small film thicknesses. In the calculation below, the non-retarded van der Waals force will be considered only. As at small distances the droplets will be flattened, the van der Waals force for flattened droplets has to be taken into account; this is much larger than the force for perfect spheres. The result of an analysis by Klahn et al. [18] is used here

\[
F_{\text{vdw}} = -\frac{A\hat{a}^2}{6\hat{h}^3}
\]

where \( A \) is the Hamaker constant.

The force balance equation results from Eqs. (6), (19) and (20)

\[
8.68 \sin 2\alpha + \frac{1}{F I \hat{h}^2} - \frac{2\hat{a}^2}{\Omega} - 3 \left[ \frac{\hat{a}^2}{\hat{h}} - \frac{1}{\hat{h} + (1 - \hat{a})^2} \right] \frac{d\hat{h}}{d\hat{t}} = 0
\]

where the Flow number as introduced by Chesters [7] is \( Fl = 6\pi \mu c R^3/\lambda \) (where \( \mu \) is the continuous-phase viscosity). The first term is the hydrodynamic force, the second is the van der Waals force, the third term is the flow resistance in the flat part of the film during drainage and the last is the resistance of the curved parts of the droplets. Equation (21) can only be solved if a relationship for \( \hat{a} \) is available. This can be obtained from an energy consideration.

**Energy equation**

The flattening of the droplets can be obtained from an energy consideration which states that the work performed for the movement of the drops equals the increase in interfacial energy due to flattening. Viscous dissipation in the film is neglected because plug flow is assumed and the film volume is small. Here the approach of Denkov et al. [19] is applied. The energy of movement is accounted for by the replacement of the mass centre of a droplet towards the flattened film assuming constant film thickness. The situation may be illustrated by a drop that is deformed while being squeezed against a flat surface. Denkov et al. [19] calculated the distance between the flattened film and the mass centre depending on the state of deformation (Fig. 2)

\[
z_m = \frac{3}{4R_3^3} \left[ \frac{1}{2} (R_s - \sqrt{R_s^2 - a^2}) (R_s + \sqrt{R_s^2 - a^2})^3 + \frac{2}{3} \sqrt{R_s^2 - a^2} (R_s + \sqrt{R_s^2 - a^2})^3 - \frac{1}{4} (R_s + \sqrt{R_s^2 - a^2})^4 \right]
\]

where \( R_s \) is the actual radius of the flattened drop and \( a \) is the radius of the flattened film. The work performed is given by the exerted force (hydrodynamic and van der Waals forces) multiplied by the difference between the original \( (R_o) \) and the actual \( (z_m) \) position of the mass centre. This work is
transformed into interfacial energy

\[ (F_{\text{hydr}} + F_{\text{vdW}})(R_0 - z_n) = \sigma \Delta S \]  

(23)

where \( \Delta S \) is the difference between the interfacial areas of the original spherical droplet and the actual flattened droplet (Fig. 2)

\[ \Delta S = 4\pi R_0^2 - \pi(R_0 + R - Q)^2 - 4\pi R_0^2 \]  

(24)

Equation (23) may also be presented in a dimensionless form by relating all length variables to the original drop radius

\[ \left( \frac{8.68}{3} \sin 2\alpha + \frac{1}{F_1 \bar{h}^3} \right) (1 - \bar{z}_m) \]  

\[ = \frac{4\bar{R}_0^2 - (\bar{R}_0 - \bar{Q})^2 - 4}{\Omega} \]  

(25)

The drop lengths \( R, Q \) and \( \alpha \) (see Fig. 2) are related to each other via the drop geometry

\[ R^2 = Q^2 + a^2 \]  

(26)

and the conservation of the volume of the deformed drop

\[ (Q + R_x)^2 \left( \frac{2}{3} R_x - \frac{1}{3} Q \right) = \frac{4}{3} \]  

(27)

**Time-scale of drainage**

During coalescence, not only does the translational motion of the droplets have to be considered but also the rotation. At large distances particle I approaches particle II along a straight line. When resistance to flow becomes noticeable, the collision sets in under a collision angle \( \alpha \) (Fig. 1). The two particles form a quasi-rigid dumb-bell that rotates around the centre of particle II, until the mirror situation occurs. At this point, particle I leaves the dumb-bell, again along a straight line. During the first half of the rotation, until the rotation angle reaches \( 0^\circ \), the hydrodynamic force facilitates film drainage. If coalescence has not occurred at \( \alpha = 0^\circ \), the hydrodynamic force will work against thinning in the second half of the rotation until the particles definitely separate. The model of Allan and Mason [15] related the angle of rotation to the time by

\[ \arctan \left( \frac{\tan \alpha}{2} \right) - \arctan \left( \frac{\tan \alpha}{2} \right) = 2t \]  

(28)

From Eq. (28) the angle of rotation is obtained at any instance; this is required to calculate the hydrodynamic force driving the drainage of the film (the first term in Eq. (21)). If the collision begins at small angles, the hydrodynamic force is too small to drain the film fast enough to a thickness where van der Waals forces are strong enough to prevent separation of the droplets at \( \alpha < 0^\circ \). Collisions at large \( \alpha \) are more favourable for coalescence, as will be shown below.

**The onset of drainage**

For the numerical integration of Eqs. (21) and (25), an initial thickness has to be calculated. This can be performed as follows. The resistance sets in when the resistance force for the drainage of spherical droplets (Eq. (19) for \( \alpha = 0 \)) equals the hydrodynamic force (dimensionless form of Eq. (5)). For \( \lambda \rightarrow 0 \) this leads to

\[ \frac{8.68}{3} \sin 2\alpha - 3 \left( \frac{1}{\bar{h} + 1} \right) \frac{d\bar{h}}{d\bar{t}} = 0 \]  

(29)

where the first term is the hydrodynamic force and the second term is the resistance to drainage for non-flattened spheres. As long as the resistance force does not exceed the hydrodynamic force, particle I will be carried along by the flow. This means that \( d\bar{h}/d\bar{t} \approx 1 \). Equating the two forces using \( d\bar{h}/d\bar{t} \approx 1 \) leads to \( h_0 = h/R = 0.0369 \). This is an order of magnitude smaller than that found by Groeneweg et al. [1] for rigid deformable spheres.

**Calculations on the film thickness and deformation**

At large separations where droplets are still assumed to be undeformed, the film thickness as a
function of time is calculated by Eqs. (29) and (28). At the moment that the pressure due to the model of spherical droplets reaches the Laplace pressure, deformation sets in and Eqs. (21), (25) and (28) need to be solved for the evaluation of the drainage and the extent of flattening. The equations were solved numerically using the Euler method.

In Figs. 3–6, the calculated film thickness and the radius of flattening are depicted for different collision angles and capillary numbers. Some important conclusions may be drawn from the resulting curves. Under the chosen conditions ($\Omega, F\ell$), a certain critical collision angle $\zeta_{\text{crit}}$ exists below which the film is not sufficiently thinned in order for van der Waals attractions to have influence and hold the drops together (Fig. 3).

Above the critical collision angle, drainage has advanced so far before $\zeta=0^\circ$ is reached that the film ruptures and the drops coalesce (Fig. 4). Just before coalescence occurs, flattening of the film sets in and the flattening radius $a$ diverges, followed by rupture of the film. Choosing a stronger flow field, the drops are pressed against each other more vigorously. They are then strongly deformed, which slows down the drainage process, and the droplets are prevented from coalescing (Fig. 5). If the collision angle is larger, there is more time available for drainage. In the situation shown in Fig. 6, the droplets are flattened shortly after the collision starts. Drainage is slowed down, but finally film drainage has advanced so far that van der Waals forces become predominant. The flattening radius diverges, followed by film rupture. Figure 6 also depicts the drainage according to Eq. (1) which predicts a slower drainage and thus a lower coalescence probability (smaller critical angle).

**Coalescence probability**

In the previous section, coalescence was found to take place at $F\ell=2.41 \times 10^9$ and $\Omega=0.01$, if the drops collide at an angle of $\zeta_0=10^\circ$ and larger, whereas collision at $9.8^\circ$ did not result in coalescence. Hence, if a collision occurs at an angle smaller
than $\varphi_{\text{crit}} = 10^\circ$, the time available for film thinning is not sufficient and coalescence of the colliding droplets will not take place. The fraction $Q'$ of collisions occurring at an angle $\alpha < \varphi_{\text{crit}}$ is given by

$$Q' = \frac{1}{2} (1 - \cos(2\varphi_{\text{crit}}))$$

The coalescence probability $CP$ is equal to the fraction of collision angles above the critical value

$$CP = 1 - Q'$$

For the example in which $\dot{\gamma} = 100 \text{ s}^{-1}$, $\eta = 0.05 \text{ kg m}^{-1} \text{s}^{-1}$, $R = 50 \mu\text{m}$ and $\sigma = 0.025 \text{ N m}^{-1}$, representing the conditions of Figs. 3 and 4, $\varphi_{\text{crit}} = 10^\circ$, resulting in a coalescence probability of 0.97. Consequently, almost every collision results in coalescence for this case where the droplets were supposed to have fully mobile interfaces. In Fig. 7 the coalescence probability is presented as a function of $\Omega$ at three $Fl$ numbers. The figures show that in a weak flow field, every collision leads to coalescence for dispersions at low viscosity ratios. Although in a stronger flow field the driving force for drainage is larger, at some point the pressure in the film exceeds the Laplace pressure during collision, and flattening sets in before van der Waals attractions are able to pull the drops together. The resistance against film drainage is thus considerably enhanced, resulting in a decrease of the coalescence probability. A greater flow number means that the van der Waals attraction is weaker with respect to the hydrodynamic forces, leading to a lower coalescence probability.

For a comparison with the coalescence probability of drops containing rigid interfaces, results obtained by Groeneweg et al. [1] have been transformed into a dimensionless form and are also depicted in Fig. 7. Significantly higher coalescence probabilities in the case of mobile interfaces were found, as expected.

Conclusions

During a collision, the mutual approach of two droplets is governed by the drainage of the thin film which separates them. Because of the small resistance offered by fully mobile interfaces, the distance at which this resistance becomes noticeable is considerably smaller in this case than for immobilized film surfaces, the difference being a factor of 10.

If the capillary number for the draining film is much larger than the Weber number, a perfectly flat film develops once the pressure in the film exceeds the Laplace pressure. The film does not tie
in at the edges and the formation of a dimple is suppressed.

The results show that the degree of drop deformation plays an important role during the course of film drainage and for the occurrence of coalescence. For this reason, flattening must be accounted for in the drainage model. In a weak flow field, the model predicts that colliding droplets basically remain undeformed, resulting in a fast-draining film and coalescence after every collision. Once the hydrodynamic force is strong enough to deform the droplets during a collision, the coalescence probability falls off because of the enhanced resistance to drainage of a flattened film.

In general, the film between drops of low viscosity and with fully mobile interfaces is found to drain much faster than the film between drops containing rigid interfaces. Consequently, the resulting coalescence probability is much higher in the former case.

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References