Drainage and rupture of a Newtonian film between two power-law liquid drops interacting under a constant force

I.B. Bazhlekov*, F.N. van de Vosse, A.K. Chesters

Section Materials Technology, Faculty of Mechanical Engineering, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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Abstract

The deformation, drainage and rupture of the film of a Newtonian fluid between colliding drops of a power-law liquid is studied numerically for gentle constant-force collisions at small Reynolds numbers. The whole shear-thinning range of the power-law parameter, \(n\), is investigated, together with a range of transformed dispersed to continuous-phase viscosity ratios, \(\lambda^*\), covering the transition from partially mobile to immobile interfaces. The problem is solved numerically by means of a finite-difference method for the equations in the continuous phase and a finite-element method for the non-Newtonian flow in the drops.

The final stage of drainage is well described by a power-law empirical dependence of the minimum film thickness on time for the whole range of \((\lambda^*; n)\) values investigated. The boundaries of the partially mobile, transitional and immobile drainage region in \((\lambda^*; n)\) plane as well as the coefficients of the empirical dependence are obtained. The application of the results for power-law drops to practically more relevant general viscous dispersed phases is discussed.

The rupture of the film due to van der Waals forces is studied for a wide range of the transformed Hamaker constant, \(A^*\), including both 'rim' and 'nose' rupture modes. The results indicate that the transformed critical rupture thickness, \(h_c^*\), is only weakly dependent on the non-Newtonian flow in the drops, being primarily determined by \(A^*\), as predicted by the approximate relation given in [A.K. Chesters, Trans. Inst. Chem. Engrs. Part A 69 (1991) 259–270]. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

In many of the practically interesting blends and dispersions one or more of the phases show non-Newtonian behavior under processing conditions. This can strongly effect sub-processes such as breakup
and coalescence and thereby the properties of the final products. To date, theoretical studies on coalescence have been limited to Newtonian phases (e.g. [1–5]). The present study offers an extension of these investigations to a non-Newtonian dispersed phase, beginning with one of the simplest cases: the shear-thinning power-law liquid. This case is chosen both because it is instructive to examine the influence of non-Newtonian rheology without the complications of elasticity and because power-law behavior is often exhibited to a fair approximation in practice (by many suspensions and weak solutions of synthetic and biopolymers, see for example [6]). The viscoelastic case will be the subject of a later paper. In the present study we adopt the same framework approach as in the above-mentioned papers in which coalescence is split into three elements (see, for example, [1]):

1. the external flow, governing the frequency, strength and duration of collisions;
2. the process of film formation and drainage and
3. the destabilization of the film by van der Waals and other intermolecular forces, leading to rupture.

Element (1) furnishes the initial and boundary conditions for (2), which in turn provides those for (3). The elements (2) and (3) are considered here. In a previous paper [7], the influence of the dispersed to continuous-phase viscosity ratio, $\lambda$, on the film-drainage was investigated. The present paper extends this investigation to include the influence of power-law behavior of the dispersed phase, confining considerations to the constant-force case.

In Section 2 the mathematical model and the numerical method of solution are described briefly, the greater part being essentially the same as in [7,8]. Section 3 presents the numerical results and discusses their practical application. Section 3.1 explores the asymptotic drainage behavior, identifies the limiting regimes of immobile and partially mobile interfaces and provides simple empirical relations for final drainage rates. Section 3.2 examines the applicability of these results to practical systems in which the power-law region may be bounded by Newtonian plateaus. In Section 3.3 van der Waals forces are included and empirical relations derived for the critical rupture thickness. Finally, the conclusions of this study are presented in Section 4.

2. Mathematical formulation and numerical methodology

Two drops of the same power-law liquid interacting along the line of their centers under a constant force in an immiscible Newtonian fluid are considered in the presence of van der Waals intermolecular forces (see Fig. 1). The drops are constrained to approach each other at a specified velocity $V$, which is adjusted during the drainage process to maintain a constant interaction force. The same procedure, can however, be used for approach velocities or interaction forces that are more representative of actual drop collisions. The interfacial tension, $\sigma$, is supposed constant.

2.1. Governing equations

The model is simplified by a number of approximations, which are valid in the limit of gentle collisions (film radius much smaller than drop radii) and which have been discussed in [7]. The extension of these simplifications to the shear-thinning case is discussed briefly at the close of this section. The governing

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1 Although the present approach is in principle applicable to shear-thickening liquids (power-law index, $n>1$), this behavior is much less common in practice (see [6]) and will not be considered here.
The equations are then the same for unequal and equal sized drops when formulated in terms of the equivalent radius

\[ R_{eq}^{-1} = \frac{1}{2}(R_1^{-1} + R_2^{-1}). \]  

(1)

The effect of van der Waals forces is represented by an attractive force between the interfaces of \(-\Pi\) per unit area, where \(\Pi\) is the disjoining pressure. For the small film thickness concerned, \(\Pi\) is given by the non-retarded Hamaker expression

\[ \Pi = -\frac{A}{6\pi h^3}, \]  

(2)

where \(A\) is the Hamaker constant. The resulting governing equations are set out below.

The lubrication approximation of the Stokes equations applies in the film in integral form

\[ \frac{\partial h}{\partial t} = \frac{1}{r} \frac{\partial (rh u)}{\partial r}, \]  

(3)

\[ \tau = -\frac{h}{2} \frac{\partial p}{\partial r}, \]  

(4)

where \(h\) is the gap thickness, \(\tau\) the tangential stress exerted on the interface by the film, \(p\) the pressure in the film and \(u\) is the mean velocity in the film, consisting of the sum of uniform and parabolic parts, \(u_u\) and \(u_p\), respectively

\[ u = u_u + u_p = u_u - \frac{\lambda}{12\mu} h^2 \frac{\partial p}{\partial r}. \]  

(5)

Note that \(u_u\) is also the tangential interface velocity. The choice of the characteristic drop viscosity on which \(\lambda\) is based is discussed below. In the large \(\lambda\) limit the second term on the right hand side of Eq. (5) dominates and the interface may be approximated as immobile, while in the small \(\lambda\) limit, the first term
dominates and the interface is termed partially mobile. In the former case the drainage rate is determined by the continuous-phase viscosity and in the latter by the dispersed-phase viscosity.

Creeping flow equations apply in the drops

\[
\nabla \cdot v = 0, \tag{6}
\]

\[
\nabla \cdot (-p_d I + \tau_d) = 0, \tag{7}
\]

where \( p_d \) is the pressure and \( v \) the velocity in the drops. The viscous (deviatoric) stress tensor, \( \tau_d \), is given by the power-law constitutive relation

\[
\tau_d = \eta |\Pi_{2d}|^{\frac{2}{n-1}} 2D, \tag{8}
\]

where \( 2D \) is the rate of deformation tensor given by \( 2D = (\nabla v + (\nabla v)^T) \) and \( \Pi_{2d} \) is its second invariant; \( \eta \) and \( n \) are the parameters of the power-law model (material parameters).

The boundary conditions at the interfaces consist of continuity of tangential velocity and stress, together with a jump in normal stress associated with the interfacial tension

\[
\begin{align*}
  u_u &= v_r, \\
  \tau &= (\tau_d)_{nt}, \\
  p &= \frac{2\sigma}{R_{eq}} - \frac{\sigma}{2} \left( \frac{\partial^2 h}{\partial r^2} + \frac{1}{r} \frac{\partial h}{\partial r} \right) + \frac{A}{6\pi h^4}. 
\end{align*} \tag{10}
\]

The outer boundary conditions at sufficiently large \( r, r_1 \), are

\[
\begin{align*}
  p(r_1) &= 0, \\
  \left( \frac{\partial h}{\partial t} \right)_{r_1} &= -V(t). 
\end{align*} \tag{13}
\]

where \( t \) denotes time and \( V(t) \) is adjusted such that

\[
2\pi \int_0^{r_1} \left( p - \frac{A}{6\pi h^3} \right) r \, dr = F = \frac{2\pi a^2 \sigma}{R_{eq}}. \tag{14}
\]

\( F \) is a given interaction force (the balance between the repulsive force due to the excess film pressure and the attractive van der Waals force) which is here chosen as constant and \( a \) is a measure of the film radius (\( a=\text{constant} \)), determined by relation (14).

The initial condition, at \( t=0 \), is

\[
h = h_0 + \frac{r^2}{R_{eq}}. \tag{15}
\]
A transformation of the variables in the Eqs. (3)–(15) is possible, which renders them dimensionless and reduces the number of parameters to three: the power-law parameter, \( n \), and the dimensionless groups \( \lambda^* \) and \( A^* \) containing, respectively, the viscosity ratio \( \lambda \) and the Hamaker constant. The transformation is

\[
\begin{align*}
  r^* &= \frac{r}{R_{eq} a'}, \\
  h^* &= \frac{h}{R_{eq} a'^2}, \\
  \tau^* &= \frac{\tau}{R_{eq}}, \\
  \tau_d^* &= \frac{\tau_d}{\sigma a'}, \\
  z^* &= \frac{z}{R_{eq} a'}, \\
  p^* &= \frac{p}{\sigma}, \\
  p_d^* &= \frac{p_d}{R_{eq}}, \\
  u^* &= \frac{u \mu}{\sigma a'^2}, \\
  v^* &= \frac{v \mu}{\sigma a'^2}, \\
  A^* &= \frac{A}{4 \pi \sigma R_{eq}^2 a'^6}, \\
  \lambda^* &= \lambda a'.
\end{align*}
\]

where \( a' \) is the dimensionless radius of the film: \( a'=a/R_{eq} \) and \( \mu \) is a characteristic drop viscosity. The viscosity of the power-law liquid in the drops is not constant in general but depends on time as well as on spatial variables. Thus, different possibilities for the choice of the characteristic viscosity exist. That which is consistent with the other characteristic quantities is used here. The characteristic velocity and length used in the above transformation are \( \sigma a'^2/\mu \) and \( a'R_{eq} \), which define the characteristic rate of deformation

\[
\gamma' = \frac{\sigma a'}{\mu R_{eq}}.
\]  

(16)

Thus, from Eqs. (8) and (16) it follows that

\[
\mu = \eta^{1/n} \left( \frac{\sigma a'}{R_{eq}} \right)^{(n-1)/n}.
\]  

(17)

This choice of the characteristic viscosity proves to be an optimal one with respect to the number of parameters in the final equations, which reduce to three: \( \lambda^*, A^*, n \). For any other choice of \( \mu \) an extra parameter will appear. Thus, the above transformation with \( \mu \) given by Eq. (17) seems to be most suitable for numerical investigations of film drainage and rupture.

The equations for the transformed variables now become

**Film equations:**

\[
\begin{align*}
  \frac{\partial h^*}{\partial t^*} &= -\frac{1}{r^*} \frac{\partial (r^* h^* u^*)}{\partial r^*} + \frac{1}{r^*} \frac{\partial}{\partial r^*} \left( h^* r^* \frac{\partial p^*}{\partial r^*} \right), \\
  \tau^* &= -\frac{h^*}{2} \frac{\partial p^*}{\partial r^*}.
\end{align*}
\]  

(18)

(19)

**Drop equations:**

\[
\begin{align*}
  \nabla^* \cdot v^* &= 0, \\
  \nabla^* \cdot (-p_d^* I + \tau_d^*) &= 0, \\
  \tau_d^* &= ||H_2D^*||^{(n-1)/2} 2D^*, \\
  2D^* &= (\nabla^* v^* + (\nabla^* v^*)^T).
\end{align*}
\]  

(20)

(21)

(22)

\footnote{For example, \( \mu = \eta^{1/n}(\sigma R_{eq})^{(n-1)/n} \).}
Boundary conditions at the interfaces:

\[ u^*_u = u^*_r, \quad (23) \]

\[ \tau^* = (\tau^*_d)_{zz}, \quad (24) \]

\[ p^* = 2 - \frac{1}{2} \left( \frac{\partial^2 h^*}{\partial r^* z^2} + \frac{1}{r^*} \frac{\partial h^*}{\partial r^*} \right) + \frac{2A^*}{3h^*}. \quad (25) \]

Initial condition:

\[ h^*(r^*, t^* = 0) = h^*_0 + r^* z^2. \quad (26) \]

Outer boundary conditions:

\[ p^*(r^*_l) = 0, \quad (27) \]

\[ - \left( \frac{\partial h^*}{\partial t^*} \right)_{r^*_l} = V^*(t^*), \quad (28) \]

\[ \int_0^{r^*_l} \left( p^* - \frac{2A^*}{3h^*} \right) r^* \, dr^* = 1. \quad (29) \]

Before closing we note that the extension of the various approximations underlying the governing equations to the shear-thinning case involves no qualitatively new considerations. Eq. (25), for example, assumes a negligible viscous contribution to the normal stress exerted on the interface by the dispersed phase. The relative importance of this contribution is given by

\[ \frac{(\tau^*_d)_{zz}}{2\sigma/Re_{eq}} = a^* \frac{\tau^*_e}{2}. \]

Accordingly, in the limit of gentle collisions (\( a^* \to 0 \)), this contribution becomes negligible.

2.2. Numerical scheme

The solution scheme for Eqs. (18)–(29) is as follows. Starting from a given \( h^*(r^*) \), provided in our case by Eq. (26), \( p^* \) is calculated from Eq. (25) and \( \tau^* \) from Eq. (19), providing (via Eq. (24)) the boundary condition for Eqs. (20)–(22). The solution of these equations in the drops then furnishes \( u^*_u \) via Eq. (23).

Now having \( u^*_u \) and \( p^* \) the film thickness at the next time instant can be obtained from Eq. (18) with boundary conditions (27)–(28) and the whole process repeated. The right-hand side of Eq. (28) is held constant at some value, \( V_{ap}^* \), until Eq. (29) is satisfied (the right-hand side of Eq. (29) being zero initially) and is then decreased, finally becoming almost 0, in such a way as to continuously satisfy Eq. (29).

Eq. (18) is integrated by means of first order Euler explicit scheme in combination with second order finite-difference discretization for the spatial derivatives. The Eqs. (20)–(22) are solved by means of a finite-element method, approximating the interface as flat. The computational domain, finite-element mesh and boundary conditions are shown in Fig. 2. The finite elements used provide a second-order approximation for the velocity and a discontinuous linear one for the pressure. For spatial discretization non-uniform meshes of triangular elements are used (see Fig. 2). In the area adjacent to the film (\( r^* < 1.3 \)
and small $z^*$ the spatial step is of order 0.02 and constantly increases becoming two orders of magnitude larger far from the film (at large $r^*$ or $z^*$). The mesh for the finite-difference discretization of Eq. (18) consists of the nodes of the finite-element mesh at $z^*=0$. Note that being of second order the finite element sides are represented by three nodes and thus the spatial step in the film-equation discretization increases continuously from 0.01 in the film region, $r^*<1.3$, to 0.5 far from it ($r^*_l$). In order to linearize the drop equations (21)-(22) the method of successive iterations is used: typically two to four iterations were sufficient for convergence within 0.01% relative error with respect to the interfacial velocity $u^*_0$.

The time integration was based on a multiple time step approach with automatic choice of the time steps. Compared to integration using a single time step this approach significantly reduces the CPU time without influencing the accuracy (see [9]).

The values of the parameters $h^*_0$, $r^*_l$, $V^*_a$ and of the spatial steps are chosen large/small enough for the results to be independent of their exact values. Appropriate choices proved to be $r^*_l=10$, $h^*_0=8$, $V^*_a=\max\{20\lambda^*;10\}$. For Newtonian drops the meshes described above supply satisfactory accuracy [7]. To check this in the case of power-law drops calculations have been performed using a mesh which is twice as fine. The results show (see Fig. 4a for $n=0.4$) that the finite-element meshes used in the present study are fine enough.

3. Results and discussion

3.1. Film formation and drainage

The numerical results are obtained for a wide range of the transformed viscosity ratios, $10^{-2} \leq \lambda^* \leq 10^4$, and power-law indices, $0.1 \leq n \leq 1$. In the discussion attention is paid to the small $\lambda^*$ values, for which the influence of viscous forces exerted by the dispersed phase on the film is stronger.

In Fig. 3 the evolution of the film-thickness profiles is shown for $\lambda^*=0.1$ and three different values of $n$: 1 (the Newtonian case), 0.6 and 0.2. In all cases a dimple is formed in the film-thickness range $h^*_{\min} \approx 0.1–0.3$. The main difference between the film shape in the three is the depth of the dimple ($h^*(r^*=0)–h^*_{\min}$), which increases with decreasing $n$. However, this effect seems to be more related to the increasing contribution of the parabolic part of the film flow (see [7]) than to the shear-thinning behavior of the drops. Thus,

![Finite-element mesh used for discretization of the equations in the drops in the dimple stage of drainage.](image)
decreasing $n$ the ‘effective drop viscosity’ (and thus the ‘effective viscosity ratio’) increases, which in fact leads to transition from partially mobile interfaces for $n=1$, to immobile ones for $n=0.2$.

The most important characteristic in regard to the occurrence of coalescence is the evolution of the minimal film thickness, $h_{\text{min}}$, which together with the critical film thickness determines the time of rupture (coalescence). Fig. 4 shows the evolution of the minimal film thickness for different $n$ values and three values of $\lambda^*$ (0.1, 10 and 100). As in the case of Newtonian drops (see [7]; Eq. (30)), once the dimple becomes pronounced ($h_{\text{min}} < 0.1$) the drainage rate is well approximated by a simple power-law

$$h_{\text{min}}^* = K(\lambda^*, n)(t^*)^m(\lambda^*, n).$$

It is also seen from Fig. 4b and c that at given $\lambda^*$ the final drainage rate is independent of $n$ below some value (for $\lambda^* = 10$, $n \leq 0.4$; for $\lambda^* = 100$, $n \leq 0.6$). This results from a transition to the immobile regime of drainage, where $K$ and $m$ depend only on $\lambda^*$ (corresponding, in original variables, to a drainage rate which depends only on the continuous-phase viscosity). Comparing the values of $K$ and $m$ at given $n$ and decreasing $\lambda^*$ reveals another boundary in the parametric plane ($\lambda^*, n$) — the transition to partially
Fig. 4. Variation of the minimal film thickness as a function of time for different $n$ values and (a) $\lambda^*=0.1$, the crosses (×) correspond to results for $n=0.4$ obtained with a mesh which is twice as fine, (b) $\lambda^*=10$, (c) and (d) $\lambda^*=100$. Solid lines correspond to the numerical results and dashed lines to the asymptotic ones given by Eq. (30).

mobile drainage. Thus, for $n=1$ and $\lambda^* \leq 10$ or for $n=0.8$ and $\lambda^* \leq 3$ $K$ and $m$ depend on $n$ but not on $\lambda^*$ (corresponding, in original variables, to a drainage rate which depends only on the dispersed-phase viscosity). Additional calculations have, therefore, been performed: first to find the boundaries of the three drainage regimes — partially mobile, transitional and immobile; secondly to give information about the corresponding $K$ and $m$ values.

In Fig. 5 the boundaries between the three regimes are shown. These boundaries have been obtained based on values of $K$ and $m$ in a mesh in the ($\lambda^*$; $n$) plane having steps of 0.5 in log $\lambda^*$ and 0.1 in $n$.\footnote{The accuracy in the position of the boundaries shown in Fig. 5 is about 0.25 log $\lambda^*$ in the $\lambda^*$ direction and 0.05 in the $n$ direction.} With the boundaries of the three different film drainage regimes the values of $K$ and $m$ can be summarized as follows:
Fig. 5. The boundaries between the three regimes of film drainage.

Table 1
The values of $K$ and $m$ for different $n$ values in the partially mobile regime of drainage

<table>
<thead>
<tr>
<th>$n$</th>
<th>0.3</th>
<th>0.4</th>
<th>0.5</th>
<th>0.6</th>
<th>0.7</th>
<th>0.8</th>
<th>0.9</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K$</td>
<td>1.0</td>
<td>0.56</td>
<td>0.40</td>
<td>0.33</td>
<td>0.28</td>
<td>0.24</td>
<td>0.21</td>
<td>0.18</td>
</tr>
<tr>
<td>$m$</td>
<td>−0.4</td>
<td>−0.44</td>
<td>−0.48</td>
<td>−0.53</td>
<td>−0.57</td>
<td>−0.61</td>
<td>−0.64</td>
<td>−2/3</td>
</tr>
</tbody>
</table>

- immobile regime (see also [7])
  \[ K = 0.6(\lambda^*)^{-1/2}; \quad m = -\frac{1}{7}, \quad \text{for all values of } n. \] (31)
- partially mobile regime in which $K$ and $m$ depend only on $n$ as given in Table 1.
- transitional regime, where $K$ and $m$ depend on both $n$ and $\lambda^*$ as given in Table 2.

**Remark 1.** The asymptote given by Eq. (30) is much more sensitive to $m$ than to $K$ values (small changes in $m$ lead to considerable changes in $K$).

Table 2
The values of $K$ and $m$ in the transitional regime of the film drainage

<table>
<thead>
<tr>
<th>$n$</th>
<th>0.3</th>
<th>0.4</th>
<th>0.5</th>
<th>0.6</th>
<th>0.7</th>
<th>0.8</th>
<th>0.9</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda^*$</td>
<td>0.03</td>
<td>0.3</td>
<td>1.0</td>
<td>3.0</td>
<td>10</td>
<td>10</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>$K$</td>
<td>1.7</td>
<td>0.553</td>
<td>0.385</td>
<td>0.2</td>
<td>0.18</td>
<td>0.18</td>
<td>0.165</td>
<td>0.15</td>
</tr>
<tr>
<td>$m$</td>
<td>−0.46</td>
<td>−0.47</td>
<td>−0.5</td>
<td>−0.5</td>
<td>−0.54</td>
<td>−0.59</td>
<td>−0.64</td>
<td>−0.65</td>
</tr>
<tr>
<td>$\lambda^*$</td>
<td>1.0</td>
<td>3.0</td>
<td>10</td>
<td>30</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>$K$</td>
<td>1.0</td>
<td>0.52</td>
<td>0.28</td>
<td>0.18</td>
<td>0.114</td>
<td>0.09</td>
<td>0.06</td>
<td>0.059</td>
</tr>
<tr>
<td>$m$</td>
<td>−0.5</td>
<td>−0.5</td>
<td>−0.525</td>
<td>−0.532</td>
<td>−0.53</td>
<td>−0.55</td>
<td>−0.56</td>
<td></td>
</tr>
<tr>
<td>$\lambda^*$</td>
<td>100</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td></td>
</tr>
<tr>
<td>$K$</td>
<td>1.0</td>
<td>0.054</td>
<td>0.04</td>
<td>0.034</td>
<td>0.054</td>
<td>0.053</td>
<td>0.054</td>
<td></td>
</tr>
<tr>
<td>$m$</td>
<td>−0.515</td>
<td>−0.53</td>
<td>−0.54</td>
<td>0.054</td>
<td>0.053</td>
<td>0.054</td>
<td>0.054</td>
<td>0.054</td>
</tr>
</tbody>
</table>
3.2. Application of the present results

The first question, which can be answered based on the results presented in Section 3.1, is the mobility of shear-thinning drops significant during a given collision? Based on the parameters of the system (σ, λ, η, n, R₁, R₂, F) together with Fig. 5 the regime of film drainage can be predicted and the above question answered. If the drainage regime is immobile, Eq. (30) is applicable with m and K given by Eq. (31). If not the mobility of the drops can be taken into account by making use of either Table 1 or 2.

As discussed by Macosko [6] one of the disadvantages of the power-law model is that it often fails to describe the low deformation rate region. At low deformation rates the viscosity predicted by the power-law model (n<1) tends to infinity, rather than to a constant value, as is usually observed experimentally (see Fig. 2.4.1 of [6]). More realistic models, such as those of Ellis, Cross or Carreau–Yashuda, include both power-law and Newtonian regions. The disadvantage of such models with respect to a parametric investigation is the large number of parameters involved, which makes the generation of empirical formulas like Eq. (30) extremely difficult. An approximate solution in such cases should be provided by taking the viscosity to be constant below some deformation rate and given by a power-law above it.

To evaluate this approach, consider the example depicted in Fig. 6, in which μ* denotes the actual viscosity divided by the characteristic viscosity, μ (Eq. (17)). In this example the viscosity obeys a variant of the Cross model

\[ μ^* = \frac{100}{(1 + 100(\Pi_2 D^r)^{0.33})}. \]  

A first approximation to this shear rate dependence is seen to be obtained by treating μ* as constant (μ*=85) at small deformation rates and given by a power-law (n=0.4) at high ones. A small λ* value,

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6 Cross and Carreau–Yashuda models give also second Newtonian region at high shear rate, but in real drop collisions the shear rate is thought to be small and because of that this region is not discussed here. However, the approach presented in the present section can also be applied to this region.
Fig. 7. The dependence of the minimal viscosity on the minimal film thickness during film drainage between power-law drops for different values of the power-law index $n$.

$\lambda^*=0.1$, is considered, for which the drainage is partially mobile (see Fig. 5) in both Newtonian ($n=1, \mu^*=85$) and power-law ($n=0.4, \mu^*=1$) regimes.

The natural question then is at which deformation rates film drainage takes place. At any given phase of drainage the deformation rate in the drop depends strongly on the location, varying from a maximum near the location of minimum film thickness ($r^*\approx 1$, small $z^*$ in Fig. 2) to almost zero for $r^*\gg 1$ or $z^*\gg 1$. At the location of maximal deformation rate $\mu^*$ is minimal. The dependence of $\mu^*_\min$ on $h^*_\min$ is shown in Fig. 7 for different values of $n$. For the case of particular interest here ($n=0.4$) the later stages of drainage are seen to be characterized by large values of $\mu^*_\min$, indicating that for a drop phase obeying Eq. (32) a Newtonian approximation is much better than a power-law one. The film thickness at which the Newtonian approximation becomes realistic is that at which the drainage rate in the Newtonian case becomes equal to that for $n=0.4$. For $\lambda^*=0.1$ the film drainage in both cases is partially mobile (see Fig. 5). Thus, the respective drainage rates in the two cases are obtained from Eq. (30) with $K$ and $m$ given by Table 1

$$\frac{dh^*_\min}{dt^*} = mK(t^*)^{m-1} = mK\left(\frac{h^*_\min}{K}\right)^{(m-1)/m},$$

$$(\frac{dh^*_\min}{dt^*})_{n=1} = -0.12 \left(\frac{h^*_\min}{0.18}\right)^{5/2}, \quad (33)$$

$$(\frac{dh^*_\min}{dt^*})_{n=0.4} = -0.2564 \left(\frac{h^*_\min}{0.56}\right)^{3.27} \quad (34)$$

$^7$ Taking as viscosity 85 times the characteristic viscosity for $n=0.4$, as given by Eq. (17).
Fig. 8. The rate of drainage as a function of the minimal film thickness for power-law drops at \(n=0.4\) (solid line) and Newtonian drops for which \(\mu^*=85\) based on the characteristic viscosity for \(n=0.4\) (dashed line).

From the definitions of \(h^*\) and \(t^*\),

\[
(h^*)_{n=1} = (h^*)_{n=0.4}, \quad (t^*)_{n=1} = (t^*)_{n=0.4}, \quad \mu_{n=0.4} = \mu_{n=1} = \frac{1}{85}.
\]

If Eq. (33) is expressed in terms of \((h^*)_{n=0.4}\) and \((t^*)_{n=0.4}\), it becomes

\[
\frac{dh^*_{\min}}{dt^*} = \frac{0.12}{85} \left( \frac{h^*_{\min}}{0.18} \right)^{5/2} .
\] (35)

Fig. 8 shows that the drainage rates given by Eqs. (34) and (35) become equal when \(h^*_{\min} \approx 0.025\). A reasonable approximation to the drainage behavior of the Cross liquid (Eq. (32)) should thus be obtained by applying Eq. (34) when \(h^*_{\min} > 0.025\) and Eq. (35) when \(h^*_{\min} < 0.025\). In Fig. 9 these approximations (in integrated form \(8\): Eq. (30)) are compared with the numerical solution, making use of the Cross equation (32) throughout. The agreement is seen to be sufficiently close for practical purposes, the largest discrepancy occurring around the transition point, \(h^*_{\min} = 0.025\). In the Appendix A the above procedure, combined with results for film rupture (see the following Section 3.3), is illustrated by its application to the separation of sedimenting drops of Xanthan gum in a vegetable oil.

3.3. The combined effect of power-law flow in the drops and van der Waal forces on film rupture

The influence of the shear-thinning character of the drop fluid on film rupture due to van der Waals forces is discussed here. As in the previous section attention is concentrated on small \(\lambda^*\) values (\(\lambda^*=0.1\) is considered here), for which the influence of the drop flow on the film drainage is strongest. The numerical results presented cover the range of the transformed Hamaker constant, \(A^*\), from \(10^{-6}\) to \(10^2\),

\(\text{To avoid a discontinuity in } t^* \text{ at the transition point } h^*_{\min} = 0.025, \text{ a modest shift in the } t^*\text{-origin has been applied to the Newtonian relation.}\)
Fig. 9. Predictions for the minimal film thickness as a function of time. Solid lines represent the numerical results obtained using a Cross model (32) and a power-law model (22). Dashed lines represent approximations based on Eq. (30) and matched at $h_{\text{min}}=0.025$.

Fig. 10. Variation of the minimal film thickness, $h_{\text{min}}^*$, as a function of time, $t^*$, for $n=0.6$, $\lambda^*=0.1$ and different values of the transformed Hamaker constant $A^*$ (solid lines). Dashed lines represent the rupture time, $t_c^*$, and critical film thickness, $h_c^*$, for $A^*=10^{-3}$.

which includes both the ‘nose’ and ‘rim’ rupture modes (rupture at $r^*=0$ or at $r^*\approx1$, respectively). The most important quality in regard to the occurrence of coalescence is the rupture time, $t_c^*$. An equivalent parameter is the critical film thickness, $h_c^*$, which has the advantage that is primarily dependent on $A^*$.

In Fig. 10 the evolution of the minimal film thickness, $h_c^*$, is presented for $n=0.6$ and different $A^*$ values. The definitions of the rupture time and the critical film thickness are illustrated graphically by

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9 The critical film thickness is defined as the values of $h_{\text{min}}^*$ in the absence of van der Waals forces at $t=t_c^*$. 


the dashed line at $A^* = 10^{-3}$. It is seen that when van der Waals forces become comparable with the other forces they become dominant very fast leading to film rupture.

In Fig. 11 $h^*_c$ is shown for different values of $A^*$ ($10^{-6} \leq A^* \leq 1$) and $n$ (0.2; 0.4; 0.6; 0.8 and 1). The transition from 'nose' and 'rim' rupture occurs around $A^* = 0.1$ and depends only weakly on $n$. Thus, for all $n$ values the rupture is 'nose' for $A^* \geq 1$ and 'rim' for $A^* \leq 10^{-2}$. Fig. 11 indicates that the critical film thickness, $h^*_c$, is only weakly dependent on the power-law parameter. A similar dependence of $h^*_c$ on the transformed viscosity ratio, $\lambda^*$, was obtained by Bazhlekov and Chesters [8], where it was found that the dependence is not direct, but through the film-thickness profile. This is also true for the dependence $h^*_c(n)$. Based on the above and the discussions in Section 3.2 (see also [8]) it can be concluded that the approximate relation put forward earlier by Chesters [1]

$$h^*_c = \left(\frac{A^*}{2}\right)^{1/3},$$

(represented by the dashed line in Fig. 11) provides a good first approximation for the rupture of Newtonian films between drops of a generalized Newtonian liquid. It is demonstrated in the Appendix A of the present study how the above formulae, combined with information of the film drainage can be used in practical situations to predict the time of rupture. As in the case of Newtonian drops at arbitrary viscosity ratio, $\lambda^*$, (see [8]) the empirical relation

$$h^*_c = \frac{2}{3}(A^*)^{0.3},$$

gives a better fit than Eq. (36) for small $A^*$ values ($A^* < 10^{-5}$); however it is less successful in the regime of 'nose rupture', $A^* > 1$.  

4. Conclusions

The numerical results presented in Section 3.1 indicate that for shear-thinning drops the (transformed) drop separation at which the dimple is formed as well as the film profile are weakly dependent on
the power-law index $n$. The rate of drainage of the film, however, in general depends strongly on $n$ and is well described by a power-law dependence (Eq. (30)) of the minimal film thickness, $h_{\text{min}}^*$, on time, $t^*$. Three regimes of drainage are distinguished — partially mobile, transitional and immobile — and the corresponding coefficients in Eq. (30) obtained. Comparison between matched solutions based on appropriate power-law rheology with the numerical result obtained (Section 3.2) for a liquid obeying the Cross model shows that the empirical formula Eq. (30) can be successfully used for predicting the rate of drainage of a Newtonian film between drops of a generalized Newtonian liquid.

The influence of the shear-thinning flow in the drops on the rupture of the film due to van der Waals forces for the practically interesting range of the transformed Hamaker constant, $A^*$, covering the transition from ‘nose’ to ‘rim’ rupture has been explored. The numerical results show that the critical rupture thickness, $h_c^*$, is only weakly dependent on the details of the non-Newtonian flow in the drops. This suggests that the given earlier dependence of $h_c^*$ on $A^*$ for Newtonian drops can be successfully used in the case of drops of generalized Newtonian liquid.

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**Appendix A. Separation of sedimenting drops of Xanthan-gum solution in a vegetable oil**

As illustration we consider the separation of sedimenting drops of a shear-thinning solution of Xanthan gum (35 wt.% Xanthan, density $\rho_d=1000 \text{ kg/m}^3$) in a vegetable oil (density $\rho_c=900 \text{ kg/m}^3$, viscosity $\mu_c=0.1 \text{ Pa s}$), see Fig. 12. The interfacial tension Xanthan–vegetable oil is supposed to be 0.025 N/m. The volume fraction, $\alpha$, of sedimenting drops is supposed to be low and the question of interest is whether the area fraction, $\alpha_s$, of drops residing at the Xanthan–oil interface is also low.

![Fig. 12. Schematic picture of sedimentation of Xanthan drops in vegetable oil.](image-url)
We assume that the confluence time $^{10}$ is much smaller than the time, $t_c$, required for drainage of the film between a drop and the interface. The number concentration, $N$, of drops in the bulk must satisfy the following relation:

$$N = \frac{3\alpha}{4\pi R^3}, \quad (A.1)$$

and the flux, $f$, of drops to the interface (or any other horizontal plane) per unit area and time is thus given by

$$f = NU = \frac{3\alpha U}{4\pi R^3}, \quad (A.2)$$

where $U$ denotes the sedimentation velocity. At equilibrium this must equal the number of drops coalescing at interface per unit area and time

$$f = \frac{N_s}{t_c}, \quad (A.3)$$

where $N_s$ denotes the number concentration of drops at the interface, related to $\alpha_s$ as

$$N_s = \frac{\alpha_s}{\pi R^2}. \quad (A.4)$$

Combination of Eqs. (A.2)–(A.4) now yields the relation between $\alpha_s$ and $\alpha$

$$\frac{\alpha_s}{\alpha} = \frac{3U/t_c}{4R}. \quad (A.5)$$

$\alpha_s$ will, thus, become much greater than $\alpha$ if the time required for film drainage greatly exceeds the time required for a sedimenting drop to move one diameter. (The fact that Eq. (A.5) predicts that $\alpha_s/\alpha \to 0$ as $t_c \to 0$ is due to our negligence of the confluence time, implying that a drop which coalesces with the interface is thus immediately pulled into the Xanthan layer by interfacial–tension forces.) Assuming the viscosity of the sedimenting drops to be considerably greater than that of the surrounding oil,$^{11}$ $U$ is well approximated by the Stokes formula

$$U = \frac{2R^2 g}{9\mu_c} (\rho_d - \rho_c) \quad (A.6)$$

and Eq. (A.5) becomes

$$\frac{\alpha_s}{\alpha} = \frac{Rgt_c}{6\mu_c} (\rho_d - \rho_c). \quad (A.7)$$

To obtain a prediction for $t_c$, an analysis similar to that in Section 3.2 is combined with the results for the critical film thickness (see Section 3.3). According to Macosko [6] (Fig. 2.1.2 and Table 2.4.1) Xanthan

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$^{10}$ The time required for a drop to merge with Xanthan layer once film rupture has occurred.

$^{11}$ Eq. (A.6) can be used a posteriori to check the order of magnitude of the drop viscosity, the shear rate within the drop being at most of order $U/R$. For drop radii of a few mm or less the drop viscosity proves indeed to be at least an order of magnitude greater than that of the oil.
Fig. 13. Xanthan viscosity, $\mu_X$, as a function of shear rate, together with approximations in the shear-thinning and Newtonian regions.

has shear-thinning behavior with two Newtonian regions at high and low shear rates, respectively, and its viscosity is given by (Cross model)

$$\mu_X = 0.005 + \frac{15 - 0.005}{1 + 6.3 |\Pi_{2D}|^{0.4}} \text{ (Pa.s)}, \quad (A.8)$$

which can be approximated (see Fig. 13) by a shear-thinning relation and a Newtonian region for low shear rate

$$\mu_S = 1.8 |\Pi_{2D}|^{(0.3-1)/2} \quad (n = 0.3; \quad \eta = 1.8) \quad \text{for} \quad |\Pi_{2D}| > 5 \times 10^{-3} \text{ (s}^{-2}),$$

$$\mu_N = 12 \quad (n = 1; \quad \eta = 12) \quad \text{for} \quad |\Pi_{2D}| > 5 \times 10^{-3} \text{ (s}^{-2}). \quad (A.9)$$

The equivalent radius given by Eq. (1) is

$$R_{eq} = 2R \quad \text{(the radius, } R, \text{ of the interface } S \text{ is infinity)} \quad \text{and the interaction force drop-interface is } F = (4/3)\pi R^2 (\rho_d - \rho_c) g. \quad \text{From Eq. (14) the dimensionless film radius } a' \text{ is}$$

$$a' = \frac{a}{R_{eq}} = \sqrt{\frac{R^2 (\rho_d - \rho_c) g}{3\sigma}} \approx 0.0114 \times R \text{ (mm)}. \quad (A.10)$$

Knowing the dimensionless film radius, the characteristic viscosities and transformed viscosity ratios in the shear-thinning and Newtonian regions are found to be (see Eq. (17))

$$\mu = \eta^{1/n} \left(\frac{\sigma a'}{R_{eq}}\right)^{(n-1)/n} = 3.08 \text{ (Pa.s)}, \quad \lambda_S^* = \frac{\mu}{\mu_c} a' = 7.17 R \text{ (mm)} \text{ in the shear-thinning region},$$

$$\mu_N = 12 \text{ (Pa.s)}, \quad \lambda_N^* = \frac{\mu_N}{\mu_c} a' = 13.7 R \text{ (mm)} \text{ in the Newtonian region}. \quad (A.11)$$

From Fig. 5 the film drainage regimes in both regions can be determined and the coefficients $K$ and $m$ in Eq. (30) can be found. In the shear-thinning region, for $R > 0.04 \text{ mm} \quad (\lambda_S^* > 0.3)$ the drainage will be

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12 The high shear rate region is not considered because it is not relevant as far as coalescence is concerned.
immobile, i.e. $K_S=0.6 (\lambda_S^d)^{-0.5}$ and $m_S=-0.5$ (for drop radii smaller than 0.04 mm values for $K$ and $m$ from Table 2 have to be used). In the Newtonian region, for $R<0.8$ mm ($\lambda_N^*<10$) the drainage will be partially-mobile, i.e. $K_N=0.18$ and $m_N=-2/3$ (see Table 1). For simplicity, in order to use the above values of $K$ and $m$, drops of radii in the interval 0.04 $< R < 0.8$ mm are considered.

The first question regarding the coalescence time, $t_c$, is in which region rupture is expected. For a given drop radius the point of transition between the shear-thinning and Newtonian drainage regimes is the solution of

$$\left( \frac{\partial h_{\text{min}}}{\partial t} \right)_S = \left( \frac{\partial h_{\text{min}}}{\partial t} \right)_N,$$

(A.12a)

or

$$\frac{1}{\mu} \left( \frac{\partial h_{\text{min}}}{\partial t^*} \right)_S = \frac{1}{\mu_N} \left( \frac{\partial h_{\text{min}}}{\partial t^*} \right)_N.$$

(A.12b)

The coefficients in the dimensionless form Eq. (A.12b) appear because of different characteristic viscosities in the two regions, which affects the transformation of $t$, whereas the transformation of $h$ does not depend on the characteristic viscosity. To solve Eq. (A.12) for the minimal film thickness an expression for $h_{\text{min}}/h_{\text{min}}$ (see the equation preceding Eq. (33)) is used with coefficients $K_S, m_S$ in the left-hand side and $K_N, m_N$ in the right-hand side. This results in the following $R$-dependence of the minimal film thickness in the transition point from shear-thinning to Newtonian film drainage

$$h_{tr} = 2Ra^2 \left( \frac{\mu K_N m_N}{\mu_N K_S m_S} (K_S)^{(m_S-1)/m_S} (K_N)^{-(m_N-1)/m_N} \right)^{((m_S-1)/m_S)-((m_N-1)/m_N)^{-1}}.$$  \( \text{(A.13)} \)

The dimensional critical film thickness, $h_c$, given by Eq. (36) is

$$h_c = 2Ra^2 \left( \frac{A}{16\pi R^2 a^2} \right)^{1/3} = \left( \frac{AR}{2\pi \sigma} \right)^{1/3},$$

(A.14)

where $A$ is the Hamaker constant ($A=5 \times 10^{-20}$ J is used here). Now comparing $h_{tr}$ with $h_c$ the region of rupture can be determined

- If $h_{tr}<h_c$ the film is predicted to rupture in the shear-thinning region and $t_c$ can be estimated using $K_S$ and $m_S$ in Eq. (30)

$$t_c = \frac{2R\mu}{\sigma a^2} \left( \frac{h_c}{2Ra^2 K_S} \right)^{1/m_S}.$$  \( \text{(A.15)} \)

- If $h_{tr}>h_c$ the film is expected to rupture in the Newtonian region and $t_c$ can be estimated using $K_N$ and $m_N$ in Eq. (30)

$$t_c = \frac{2R\mu_N}{\sigma a^2} \left( \frac{h_c}{2Ra^2 K_N} \right)^{1/m_N} + \frac{2R\mu_N}{\sigma a^2} \left( \frac{\mu}{\mu_N} \left( \frac{h_{tr}}{2Ra^2 K_S} \right)^{1/m_S} - \left( \frac{h_{tr}}{2Ra^2 K_N} \right)^{1/m_N} \right).$$  \( \text{(A.16)} \)

where the last term accounts for an initial phase of drainage in shear-thinning region (at smaller drop viscosity). This initial phase is significant only when $h_c$ is of order of $h_{tr}$, when most of the drainage is in shear-thinning region; for $h_c \ll h_{tr}$ its influence on $t_c$ is negligible.
Finally, by substitution of Eq. (A.15) or (A.16) in Eq. (A.7) the ratio $\alpha_S/\alpha$ as a function of $R$ can be obtained. The result is shown in Fig. 14. For very small drops $\alpha_S/\alpha$ is underestimated (see Remark 2).

**Remark 2.** The applicability of the results of the present study to the case considered above has to be checked. First, the approximation of gentle collisions, $a \ll R_i$ ($a' \ll 1$), is well satisfied in the range of $R$ considered here (for $R=0.4$ mm $a' \approx 0.05 \ll 1$ see Eq. (A.10)). Secondly, the applicability of the asymptotic relation (30) must be considered. From Fig. 4a it can be estimated that for $n=0.3$ Eq. (30) provides an acceptable approximation for $h_{\text{min}}^* < 0.13$. Thus, if the transformed rupture film thickness, $h_c^*$, is smaller than 0.13 Eq. (30) would be valid. In Fig. 14 the solid line corresponds to $100 h_c^*$ and it is seen that for $R > 0.2$ mm Eq. (30) can be used, but for smaller drops $R < 0.2$ mm Eq. (30) does not provide a satisfactory approximation. For slightly smaller drops ($R < 0.15$ mm $h_c^* > 0.3$) rupture is expected before film formation (see Fig. 3) and results of the much simpler case of coalescence of spherical drops (in the present situation a spherical drop and a plane interface) can be used.

**References**


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For the range of $R$ shown in Fig. 14 $h_c < h_{\text{tr}}$ (rupture in the Newtonian region) and $t_c$ is obtained using Eq. (A.16).

