Experimental Characterization of the Post-Impact Behaviour of Non-Newtonian Droplets

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Abstract The present paper addresses the experimental and theoretical description of the dynamic behavior of non-Newtonian (shear-thinning) droplets impacting onto smooth and micro-patterned heated surfaces. The shear-thinning liquids are mixtures of water+xanthan gum prepared with different concentrations of the gum, namely 0.05%, 0.10%, 0.15% and 0.35%wt. For droplet impacts over the surfaces heated below the boiling temperature of the liquid, the shear-thinning effect is clearly governed by the concentration of the non-Newtonian component, which is associated to the consistency coefficient of the constitutive model describing the viscous behavior of the flow. In line with this, models predicting the spreading of Newtonian droplets are revisited and an alternative one is proposed, which integrates the non-Newtonian behavior. The results suggest that heating the surface (and consequently the liquid) alters the rheology of the non-Newtonian mixture and reverses the increase of the zero viscosity, which is observed for impacts onto non-heated surfaces, thus allowing a high spreading diameter and a significant recoiling phase for droplets with high concentrations of the non-Newtonian component.

Further heating the surface above the boiling temperature of the liquid, the droplets impact the surfaces within the nucleate boiling regime and thermal induced atomization occurs. In this case, image analysis is combined with Phase Doppler measurements to characterize the size and the velocity of the secondary droplets generated within this process. The results show that the thermal induced atomization is mainly triggered by the force balance between surface tension and vapor pressure forces, so the viscosity plays a secondary role. However, the size of the secondary droplets is affected by the non-Newtonian viscous behavior of the droplets. Based on these results, an empirical correlation is proposed predicting the size of the secondary droplets. Comparison with other data reported in the literature is difficult given that this kind of detailed characterization is still rare, despite being vital to understand, describe and control the thermal induced atomization.

1. Introduction

Unlike Newtonian fluids, for which the stress tensor is a linear function of the velocity gradient and therefore the viscosity remains constant, regardless of the shear rate, in non-Newtonian fluids, the stress tensor is a generic function of the velocity gradient and of its derivatives. Usually, non-Newtonian fluids are categorized in three main groups: i) Power-law (or Ostwald-De Waele) fluids, ii) Yield-stress fluids and iii) Viscoelastic fluids. Power law fluids are the simplest type of non-Newtonian Fluids, for which the viscosity \( \mu \) is simply related to the shear rate \( \gamma \) by the so-called Ostwald-De Waele:

\[
\mu = K \gamma^{n-1}
\]

(1)

Here \( K \) and \( n \) are constants of empirical nature. \( K \) is called as consistency coefficient and describes the fluid viscosity at low shear rates and matches with the Newtonian viscosity for \( n=0 \). The power-law index \( n \) determines the behaviour of the fluid. Hence, the fluids are shear-thinning when \( n<1 \) (i.e. the viscosity decreases with the shear rate) and shear thickening for \( n>1 \). From the physico-chemical point of view, the shear thinning behaviour can be explained by the breakdown of the structure formed by interacting particles within the fluid, while the shear-thickening is often related to flow-induced jamming (Frith et al. 2005, Bertola and Marengo, 2012).

Viscoplastic (or yield-stress) fluids only flow when the applied stresses overcome a critical value (the yield stress). For applied stresses lower than the yield stress, these fluids behave like elastic solids. The
simplest constitutive model describing the viscous behaviour of these fluids was proposed by Bingham (1916) and introduces the shear stress component as a linear function of the velocity gradient. This intercepts at a critical value $\tau_c$ corresponding to the threshold yield point. Further improvements to the Bingham model (1916) were later proposed by Herschel-Bulkley (1926) and by Papanastasiou (1987). The definition of yield-stress behaviour for a fluid instead of a solid is still a topic for discussion nowadays. More extensive reviews on this subject can be found for instance in Nguyen and Boger (1992), Barnes (1999) and Coussot (2007).

Finally, in viscoelastic fluids (e.g. several polymer melts or solutions), part of the deformation energy is stored and released later, being the delay between energy storage and release related to a relaxation time. The main characteristic of this group of non-Newtonian fluids is the occurrence of elastic stress effects, for sufficiently high shear rates. This characteristic leads to an anisotropic application of the normal forces (e.g. pressure) acting on liquid finite element, contrarily to what occurs in Newtonian fluids. Pioneering work introduced by Maxwell provides the basic constitutive model for linear viscoelastic fluids. A more elaborate model and probably the most popular is the Oldroyd-B model (Nguyen and Boger, 1992, Macosko and Naser, 1992, Joseph, 2002). More recent constitutive models have been proposed for instance by Zhu et al. (2009), to describe flow induced anisotropic behaviour of viscoelastic fluids.

Non-Newtonian fluid flows are present in a variety of situations. Droplet-wall interactions are a particularly interesting flow given its interest in numerous applications, such as coating, painting or printing (e.g. Koo et al., 2006, Lopez et al., 2007, Son and Kim, 2009). Also, droplet-wall interactions involving non-Newtonian fluids are an interesting problem, from the phenomenological point of view since they involve large special and temporal gradients, which will strongly alter the viscous behaviour. Consequently, the behaviour of non-Newtonian droplets can be significantly different form that of Newtonian ones. However, despite all the aforementioned arguments, non-Newtonian flows are studied for several decades (e.g. Mysels, 1949, Metzner, 1965) and droplet-wall interactions of Newtonian fluids are investigated for over a century (starting from the ground-breaking work of Lord Worthington, 1876), but the study of non-Newtonian droplets impacting onto rigid surfaces is still sparsely reported in the literature. The spreading of yield-stress (polymer) droplets over non-heated surfaces was investigated by several authors. From the various conclusions withdrawn in these studies, it is worth noting that the maximum spreading diameter decreases linearly with the yield stress magnitude (e.g. Nigen 2005, German and Bertola, 2009, Luu and Forsterre, 2009, Saidi et al., 2010). This contrasts with the power law dependence of the spreading diameter with the liquid viscosity that is usually reported for Newtonian droplets (e.g. Rioboo et al., 2002, Sikalo et al., 2002).

As aforementioned, most of these studies were performed for impacts onto cold and smooth surfaces. Exception is made to the work of Saidi et al. (2011) who attempted to quantify the effect of the surface topography and wettability on the dynamic behaviour of yield-stress droplets. The authors also tried to determine the effect of apparent wall slip, but the results obtained were inconclusive since, as well pointed by Bertola and Marengo (2012) it is impossible to distinguish between the two effects in the experiments performed by Saidi et al. (2011). Nevertheless the results suggest a weak dependence of the maximum spreading diameter on surface wettability. The research performed on the impact viscoelastic droplets also focus on the spreading over non-heated surfaces (e.g. Vignes-Adler, 2000). Some analysis of the disintegration of viscoelastic droplets was also performed in Rozhkov et al. (2002), but this is mainly the result of the impact onto a very small target. Most of the experimental results are also consistent in the fact that the addition of a viscoelastic component tend to preclude the occurrence of droplet rebound and/or disintegration (e.g. Bartolo et al., 2007), as a result of a strong dissipative effect occurring at the contact line.

An increasingly interest on droplet-wall interactions of non-Newtonian liquids and particularly of shear-thinning droplets is related to their relevance in various biological applications. For instance, droplet impacts of non-Newtonian preparations are the basic working principle of a method called cell printing. In this method various techniques similar to inkjet are being used to deploy living cells on a substrate to create tissue, neural cells and possibly organs (e.g. Xu et al., 2006, Tasoglu et al., 2010). In this case, great care is necessary as the cells are extremely sensitive to shear stresses and can be easily destroyed as the droplet impacts and spreads over the surface. Similar disruptive effects have been reported in the transport of DNA samples for several years (e.g. Robins, 1964). Blood is a shear-thinning fluid whose behaviour is well characterized by Eq. (1). Modifications of the values of the consistency coefficient $K$ and of the power-law index $n$ are suggested to be correlated with leukemia (Sharma and Bhat, 1992, Brust et al., 2013).

In this context, few studies have addressed the spreading behaviour of shear-thinning droplets over smooth and cold surfaces. German and Bertola (2009) and later An and Lee (2012a) report a significant
decrease in the viscosity during spreading, thus leading to a wider spreading diameter for the shear-thinning droplets. German and Bertola (2009) tried to relate this behaviour with the consistency coefficient \( K \) and with the power law exponent \( n \). Their conclusions are limited to the fact that it is very difficult to change \( K \) independently from \( n \). Nevertheless, their results suggest a dominant effect of \( K \) in the spreading, which was related to an increase of the concentration of the shear-thinning component. Based on their experimental data, An and Lee (2012b) adapted correlations existing in the literature to predict the spreading diameter of Newtonian droplets (devised from energy conservation principles) to their shear-thinning droplets. This adjustment was based on empirical fitting of the data combined with a re-scaling of the viscous dissipative term. Despite the modified relations reported by An and Lee (2012b) are well adjusted to their experimental data, they have a strong empirical nature. Also, almost any information is found in the literature concerning impacts over heated and/or over rough surfaces.

In line with this, the present paper focuses on the fluid dynamic and heat transfer processes occurring between non-Newtonian (shear-thinning) droplets and solid surfaces. In line with the aforementioned applications, major focus is put on the spreading (and receding) behaviour. The analysis will be divided in three main parts. The first concerns the experimental description of the spreading behaviour of shear-thinning droplets over cold and heated surfaces and will discuss on the influence of several parameters, including those relevant to the accurate devise of the viscosity constitutive model. Surface wettability and topography are also investigated for surfaces heated up to the boiling temperature (to avoid the occurrence of induced thermal atomization). Based on this analysis, an alternative relation is proposed here to predict the spreading of the shear-thinning droplets, which is compared with data reported in the literature and with our own experimental results. Finally, the surface temperature is further increased above the boiling temperature and secondary (thermal induced) atomization occurs, which will be characterized for impacts onto smooth surfaces, in terms of size and velocity of the ejected secondary droplets. Despite thermal induced atomization is an unwanted phenomenon for most of the applications referred in this Introduction, it must be characterized in order to be controlled. For instance, Bertola and Sefiane (2005) suggest that the thermal induced atomization can be controlled in viscoelastic droplets by adding a viscoelastic polymer, but their analysis is mostly qualitative and based on visualization, so either the size or the velocity of the droplets is investigated.

2. Experimental procedure

The experiments encompass the impact of droplets for a fixed initial diameter (\( D_0=3.2\text{mm} \)) impacting on solid and dry surfaces, with velocities \( U_0 \) ranging from 0.8 to 4m/s. The accuracy in the evaluation of the impact velocity \( U_0 \) is better than 3%, while for the droplet diameter \( D_0 \) is \( \pm 1.4\% \).

The surfaces are accommodated on a copper base in which a 264 W cartridge heater is inserted and are heated from room temperatures up to 140°C. Surface temperature of the targets is acquired using fast response type K thermocouples “Medtherm”. The thermocouples are 3mm apart, taking from the reference the thermocouple that is placed in the center of the droplet impact region (\( r=0\text{mm} \)). They are aligned with the top of the surface where the impact occurs. Another embedded thermocouple is used to control the cartridge heaters, using a PMA KS20-I controller. Care is taken to assure that the surface is dry and recovers the initial temperature before the impact of the droplet. The liquid is kept at the droplet generator at room temperature and atmospheric pressure. Ambient temperature and relative humidity were measured through the experiments to ensure that their variation did not produce relevant changes in the results.

The signal of the thermocouples is sampled with a National Instruments DAQ board associated with a BNC2120 and amplified with a gain of 300 before processing. Comprehensive description of the set-up can be found, for instance in Moita and Moreira (2012).

Droplet impacts are recorded using a high-speed camera (Phantom v4.2 from Vision Research Inc., with 512x512pixels@2100fps and a maximum frame rate of 90fps). To record the impact history of the millimetric droplets, the frame rate was set to 2200fps. For this set-up, the resolution is 25pixels/\( \mu \text{m} \). The spreading diameter is evaluated based on a home made post-processing routine developed in Matlab®. The spreading curves are averaged over 6 impact events, obtained at similar experimental conditions. Accuracy of the measurements is evaluated to be \( \pm 25\mu \text{m} \).

Besides water, which was used as the control fluid, the experiments were performed with shear-thinning mixtures of water with xanthan gum (wt%). The viscosity vs shear rate curves were fitted using the Cross
model (1965):

\[
\frac{\eta_{\text{eff}} - \eta_{\infty}}{\eta_0 - \eta_{\infty}} = \frac{l}{l + (C \dot{\gamma})^m}
\]

(2)

being \( \eta_{\text{eff}} \), \( \eta_0 \) and \( \eta_{\infty} \) the effective, zero-shear (upper limit) and infinite-shear (lower limit) viscosities, respectively. \( C \) is the Cross time constant and \( m = 1 - n \). Thus, as \( m \) increases, the mixture becomes more shear-thinning.

The fitting parameters are given in Table 1, which summarizes the main physico-chemical properties of the fluids, taken at ambient temperature and pressure. The rheological data was measured for controlled temperature conditions at ATS RheoSystems (a division of CANNON® Instruments, Co). The accuracy of the data is within ±5%. In the table, X stands for xanthan and the percentage following is the wt% of xanthan gum in the mixture with water. It is worth mentioning that except for the viscosity, all the other properties of the xanthan gum solutions are very close of those of water.

Table 1. Thermophysical properties of the working fluids taken at 20°C. Here X stands for Xanthan and the percentage following is the wt% of xanthan gum in the mixture with water.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>( \rho ) [kg/m(^3)]</th>
<th>( \sigma_0 ) [N/m(^3)] ( \times 10^3 )</th>
<th>( \eta_0 ) [Pa.s]</th>
<th>( \eta_{\infty} ) [Pa.s]</th>
<th>( C ) [s]</th>
<th>( m ) [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>996</td>
<td>72.75</td>
<td>8.9x10(^{-4})</td>
<td>8.9x10(^{-4})</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>X0.05%</td>
<td>997</td>
<td>73.00</td>
<td>0.08</td>
<td>1.9</td>
<td>0.8</td>
<td>0.678</td>
</tr>
<tr>
<td>X0.10%</td>
<td>997</td>
<td>72.00</td>
<td>0.22</td>
<td>2.6</td>
<td>1.3</td>
<td>0.696</td>
</tr>
<tr>
<td>X0.15%</td>
<td>997</td>
<td>71.50</td>
<td>0.58</td>
<td>3.6</td>
<td>1.65</td>
<td>0.707</td>
</tr>
<tr>
<td>X0.35%</td>
<td>997</td>
<td>72.95</td>
<td>13.29</td>
<td>5.1</td>
<td>13.97</td>
<td>0.804</td>
</tr>
</tbody>
</table>

2.1. Characterization of the surfaces

Apart from a smooth silicon wafer surface, which was used for the majority of the experiments, 3 surfaces micro-structured with regular patterns and 2 hydrophobic surfaces micro-structured with stochastic patterns were used. To prepare the surfaces with regular patterns, the wafer is coated with aluminum (to allow a deeper etching) and afterwards with photoresist. The regular patterns are transferred by high resolution printing (performed at INESC-MN) and photolithography and are then submitted to plasma etching for 5-7 hours. This procedure assures the anisotropic etching to create the required dimensions of the micro-patterns. Finally, wet etching is used to remove the aluminum coating. These patterns are composed by square pillars of size \( l \), height \( h_R \) and pitch \( \lambda \). Fig. 1 defines schematically these quantities.

The surfaces with stochastic profiles are prepared using a grafting technique. The roughness profiles of all the surfaces were measured using a Dektak 3 profile meter (Veeco) with a vertical resolution of 200 Angstroms. For the stochastic profiles, roughness amplitude must be quantified by average values. Following the procedures recommended by most of the previous studies on droplet/wall interactions (Rioboo et al. 2001, Moita and Moreira 2007, Moreira et al. 2010) the roughness amplitude of these surfaces was quantified by the mean roughness \( R_m \) (according to standard BS1134) and by the average peak-to-valley height \( R_p \) (according to standard DIN 4768).

Wettability was also characterized, being quantified by the static contact angle \( \theta \), using an optical tensiometer THETA from Attesion, with One-Attesion v1.8 software. Accuracy of the measures of the contact angle is ±1°, according to the manufacturer. An average value is considered for each pair liquid-surface which is determined from at least five measurements taken at different regions of the surface. The time evolution of the average contact angles is obtained by curve fitting and the final values are determined by extrapolation.
Fig 1. Schematic showing the definition of the dimensions $a$ and $\lambda_R$ characterizing the topography of the surfaces micro-structured with regular patterns.

Hysteresis was also taken for the surface with the highest contact angle, to verify that it was superhydrophobic. According for instance to Bhushan and Jung (2011), for a surface to be superhydrophobic the equilibrium angle must be higher than 150°, but the contact angle hysteresis must be lower than 10°. The hysteresis measured for the surface with the highest contact angle was 8°, so it can be considered superhydrophobic. None of the other surfaces satisfies the conditions for superhydrophobicity.

Table 2 summarizes the topographical and wetting properties of the working surfaces. Contact angles were measured with water at room temperature.

<table>
<thead>
<tr>
<th>Surfaces</th>
<th>$l$ [µm]</th>
<th>$h_k$ [µm]</th>
<th>$\lambda$ [µm]</th>
<th>$R_y$ [µm]</th>
<th>$R_z$ [µm]</th>
<th>$\theta$ [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smooth</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>76.1</td>
</tr>
<tr>
<td>Structured w/regular patterns</td>
<td>282</td>
<td>7.6</td>
<td>342</td>
<td>-</td>
<td>-</td>
<td>84.9</td>
</tr>
<tr>
<td>Structured w/stochastic profile</td>
<td>161.6</td>
<td>23.1</td>
<td>396.9</td>
<td>-</td>
<td>-</td>
<td>96.3</td>
</tr>
</tbody>
</table>

Table 2. Surface topography and wettability with water of the surfaces used in the present study. Here $l$ is the size of the side of the squares, $h_k$ is the height of the squared pillars and $\lambda$ is the pitch.

2.2. Characterization of the thermal induced atomization

Phase Doppler measurements were performed using a two-component system from Dantec. The optical configuration is summarized in Table 3. The measurement grid uses a radial system. As defined in Fig.2, where $r=0$mm corresponds to the center of the impact region. Here, U and V stand, as usual, for the axial and radial velocity components, respectively. Positive values of the axial velocity $U$ are taken downwards, in the direction of gravity, the same as for the impact velocity of the primary droplet $U_0$.

Measurements are reported at $z=5$mm, above the surface and at radial coordinates $r=0$mm, $r=3$mm and $r=6$mm. These coordinates were selected based on previous work (e.g. Moreira et al., 2007).

Temperature variation of the refractive index $n$ of water, was estimated for the range up to the boiling temperature of the liquids, as in Dreisbach (1948) or Pitcher et al. (1990), by making use of the Eykman formula $(n^2-1)/(n+0.4)=A\theta$, where $A$ is a fitting constant (Moita and Moreira, 2009). Despite the scattering angle used here is not the one reducing to the minimum the influence of the refractive index in the measures, inaccuracy of the size measurements is still better than 7%. Regarding the refractive indexes of the water+xanthan mixtures, the values were taken by interpolation, following the study of Basavaraju et al. (2007).

To obtain statistically representative measurements, ten thousand valid samples were considered for each impact condition. This number results from a discrete probability distribution assessment as performed by Panão and Moreira (2008) and by Panão (2012).
Table 3. Outline of the phase Doppler optical configuration.

<table>
<thead>
<tr>
<th></th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transmitting optics</td>
<td></td>
</tr>
<tr>
<td>Laser power [mW]</td>
<td>300-400</td>
</tr>
<tr>
<td>Laser wavelengths [nm]</td>
<td>514 and 488</td>
</tr>
<tr>
<td>Beam spacing [mm]</td>
<td>60</td>
</tr>
<tr>
<td>Frequency shift [MHz]</td>
<td>40</td>
</tr>
<tr>
<td>Transmitter focal length [mm]</td>
<td>510</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Receiving optics</td>
<td></td>
</tr>
<tr>
<td>Scattering angle [°]</td>
<td>30</td>
</tr>
<tr>
<td>Receiver focal length [mm]</td>
<td>500</td>
</tr>
</tbody>
</table>

Fig 2. Radial system of coordinates used in the measurements with the phase Doppler instrument.

Whenever relevant, the so-called extended PDF analysis (Moreira et al., 2007, Moita and Moreira 2009) will be presented. In this approach, Phase Doppler measurements are combined with those obtained from image analysis to cover a wider size range of the secondary droplets. Hence, the diameter of large secondary droplets (from 40 µm up to a few millimeters) is evaluated from image post-processing. For this purpose, fifteen images are evaluated for each time step \( t = t/(D_0/U_0) \), to obtain statistically representative results. Then, PDF’s of drop diameters are then built at dimensionless time bins \( \Delta t^* = 0.5 \), for \( 0 \leq \Delta t 100 \), which covers the most relevant period of droplet impact.

While droplet count in an image at a given time \( t_1 \) and location corresponds to all droplets generated up to that time, the phase Doppler instrument gives instantaneous measurements, so they are statistically different. This issue was solved by integrating the size distributions obtained with the phase Doppler instrument in time from the instant of impact up to \( t_1 \). A uniform spatial distribution of the droplets is considered, which is based on the distributions obtained by image analysis. Finally, the size distributions obtained by each technique are scaled by equating the count values within the overlapped size range, between 40mm and 250µm, by means of a least square method, for each time step.

3. Results and discussion

3.1. Spreading of shear-thinning droplets

Compared to Newtonian droplets (e.g. water) the morphology of shear-thinning droplets spreading onto smooth and cold surfaces is quite similar. Quantitative differences are however evidenced, which are associated with the non-linear viscous dissipation occurring at acceleration and deceleration of the fluid during spreading and receding. A direct comparison, as shown in Fig. 3 emphasizes the main differences between Newtonian and non-Newtonian fluids. Here, the temporal evolution of the spreading ratio, i.e. the
spreading diameter made non-dimensional with the droplet’s initial diameter \( \beta(t) = d(t)/D_0 \) is plotted for droplets impacting onto a non-heated smooth silicon wafer surface. The results can be interpreted by associating the concentration of the shear-thinning component to the fitting parameters of the constitutive models.

\[
\eta_0 = \mu_0/\rho
\]

Fig. 3. Temporal evolution of the spreading rate of droplets of Newtonian (water, \( D_0 = 3.2\)mm) and non-Newtonian (water+xanthan gum, \( D_0 = 3.2\)mm) liquids, impacting on a non-heated and smooth silicon wafer surface, at: \( a) U_0 = 0.8\)m/s and \( b) U_0 = 2.0\)m/s.

The \( \eta_0 = \mu_0/\rho \) value of the viscosity increases with growing mass fraction of the xanthan gum, as observed in Table 1. The higher concentrations slightly increase the power law index \( m \), but mainly increase the consistency parameter \( K \). Hence, a slightly faster expansion of the lamella is observed for the mixture with the largest concentration of the xanthan gum, due to the lower value of the infinite viscosity, but when the shear rate quickly decreases, as the lamella approaches its maximum diameter and the liquid decelerates, the zero viscosity becomes quite large. Consequently, a strong damping effect is observed during the receding stage of the droplets with highest xanthan concentration. So, overall the maximum diameter is lower for increasing xanthan concentrations, but the equilibrium diameter overpasses that of the mixtures with lower xanthan concentrations (X0.05%) and gets closer to the equilibrium diameter of the water, for the latest stages of spreading (Fig. 3a). The limited recoiling phase is more evident for higher impact velocities, since although the shear rates at the beginning of the expansion of the lamella are higher, thus decreasing the viscosity (so the difference between the maximum diameters is not so accentuated), the dissipation associated to these large velocity gradients is actually larger (Fig. 3b), so the increase of the zero viscosity during the recoiling phase will be more noticeable. The acceleration during lamella expansion, due to shear-thinning effects is mild and therefore difficult to detect during the spreading period. However, one can notice it as the time period required for the lamella to attain its maximum diameter is slightly smaller for larger concentrations. A more detailed investigation for data obtained with a higher temporal resolution is nevertheless required to deepen the description of this effect.

The spreading curve of water stands out from the shear-thinning mixtures, even for those with the lowest concentration. In the absence of shear-thinning effects, the spreading diameter of the water droplets is larger and its maximum value is consequently attained latter, when compared to the non-Newtonian droplets.

These results are consistent with those reported by German and Bertola (2009) and by An and Lee (2012a,b). The effect of the Xanthan gum concentration (i.e. higher \( K \) and slightly higher \( m \) coefficients) is actually dominant when compared to other factors such as the surface wettability, as shown in Fig. 4.

In fact, the influence of surface topography seems quite less evident when compared to the previous results presented for Newtonian-droplets (e.g. Moita and Moreira, 2012): a significant influence of the surface micro-patterning is only observed in the receding phase, for the cases in which the micro-patterning leads to a noteworthy modification of the wettability, quantified by the contact angle. This behaviour can be due to the aforementioned increase of the liquid viscosity, which in turn results in a thicker lamella. Therefore, the ratio thickness of the lamella/amplitude of the rough pillars becomes smaller and the surface is “smoother” in relation to the new effective thickness of the lamella. This maybe so since for the mixture with higher xanthan concentration, the main difference is only for the spreading curve over the smooth
surface, for which the spreading diameter is significantly larger when compared to the other surfaces. The maximum spreading is followed by a very limited recoiling phase, as discussed at the beginning of this section. Only when the contact angle differs from 76° to 90° and the surface is already hydrophobic, the dissipation at the contact line is lessened and allows a mild recoiling phase. Nevertheless, between hydrophobic surfaces, there is not a remarkable difference between the curves, as these surfaces are made hydrophobic at the expense of the modification of their topography, for which the thick lamella obtained for the mixture X0.35% is clearly insensitive.

![Effect of surface wettability on the spreading behaviour of a 3.2mm droplet impacting onto various non-heated surfaces at U_d=2.0m: a) X0.05%, b) X0.35.](image)

**3.1.1. Influence of surface temperature (T_w<T_{boiling})**

The effect of surface temperature is not dominant, while the surface temperature is kept bellow the liquid saturation temperature and the lamella does not boil. However, the results presented in Fig. 5 suggest that the heat transferred to the lamella alters the rheology of the mixtures and reverses the shear thinning effect. This is particularly evident in the droplets of the mixtures with higher xanthan concentration, impacting the surface with larger velocity (i.e. when the shear-thinning is more evident), as shown in Fig. 5d): a lower spreading diameter is observed for droplet impacts at room temperature, which is followed by a very limited receding phase (as discussed in the previous paragraphs). This behavior contrasts to the relatively high value of β_{max}, obtained as the droplet hits the surface at T_w=100°C, which is followed by an evident receding phase. This effect cannot be related to evaporation of the water since when the water evaporates, the xanthan concentration would be higher, so the equilibrium diameter should be also larger as discussed above. Hence, these results should be indeed attributed to rheological modifications of the mixtures. At this stage of the research it was not possible to perform a detailed characterization of the viscosity of the various mixtures at different temperatures, to confirm this hypothesis. Such analysis will be presented in a future work. However, one may argue that as aforementioned in the Introduction, physically, the shear thinning is explained by the breakdown of the structure formed by interacting particles. Hence the heat transfer from the surface to the liquid during the spreading of the lamella may contribute to the breakdown of this, which given the time scale associated to the heat transfer, that is smaller than that related to the spreading process, may be particularly evident at later stages of spreading and at the recoiling phase.
Fig. 5. Temporal evolution of the spreading rate of droplets ($D_0=3.2\text{mm}$) of water+Xanthan gum solutions, impacting on a smooth silicon surface heated at various temperatures, $T_W<$ $T_{\text{boiling}}$. The droplet is and impacts on the surface at $U_0=3.2\text{m/s}$. a) X0.05%, b) X0.10%, c) X0.15%, d) X0.35%.

3.2. Theoretical prediction of the spreading diameter

Most contemporary semi-empirical models for the description of the spreading derive analytical expressions to predict the spreading diameter based on a simple energy conservation equation (neglecting variations of the potential energy):

$$E_{ki}+E_{si} = E_{kf} + E_{sf} + E_{\text{diss}}$$  \hspace{1cm} (3)

being $E_k$ and $E_s$ the kinetic and surface energy, respectively and $E_{\text{diss}}$ the energy dissipated by viscous effects. The subscripts $i$ and $f$ stand for the initial and final states, respectively. The final state ($f$) is usually taken at the position where the diameter of the lamella is maximum, where $E_{\text{diss}}$ and $E_{sf}$ can be easily determined (Moita and Moreira, 2011). Exception is made to a few authors such as Scheller and Bousfield (1997) who considered an entirely empirical approach, without using energy conservation. Nevertheless, a force balance between inertial, viscous and surface tension forces is considered.

Major differences between the various existing models lay in the assumptions regarding the shape of the lamella, the estimation of the viscous dissipation and the way to account for wettability effects. The energy dissipation term, can be determined by:

$$E_{\text{diss}} = \int \int_0^{t_f} \frac{\partial \phi}{\partial V} V dt \approx \phi V t_f$$  \hspace{1cm} (4)
where \( \phi = \mu \left( \frac{\partial U_j}{\partial x_i} + \frac{\partial U_i}{\partial x_j} \right) \), \( \partial t \) is the dissipation function and the known time period after impact, for which the effect of viscous dissipation is expected to be relevant. The viscous dissipation function is subsequently scaled based on different assumptions. For instance, Chandra and Avesdian (1991) scale the viscous function with the impact velocity \( U_0 \) and with the thickness of the lamella \( h \), which was determined by mass conservation, approximating the lamella to a flattened disk. Others, such as Pasandideh-Fard et al. (1996) proposed to use the boundary layer thickness \( \delta \) as a scaling length, claiming that an overestimation of the maximum spreading diameter is obtained when \( h \) is used in the scaling. Wettability effects can be explicitly accounted in the spreading diameter by introducing the contact angle in the term of the surface energy of the spreading droplet, being the discussion focused on weather is more appropriate to use the equilibrium angle \( \theta \), or the dynamic contact angle \( \theta_d \). From the phenomenological point of view, it is recognized that the dynamic angles are more representative although good results can be obtained using the static angle, given the low velocity of the contact line at maximum extent conditions. The equilibrium contact angle is also often preferred given the difficulty in obtaining accurate measures of the dynamic contact angle. In the present paper, the dynamic contact angle is considered, which was evaluated during the post-processing procedures, while determining the spreading diameter from the recorded images. Concerning the shape of the lamella, most models take the lamella as a flattened disk with diameter \( d(t) \) and height \( h(t) \), so that relations between \( d(t) \), \( h(t) \) and \( D_0 \) can be easily determined by mass conservation. In this context, Roisman et al. (2009) report the incapability of energy conservation-based models to describe the flow inside the droplet, due to this simplification of the shape of the lamella. These authors compared experimental data with numerical results for the shape of the lamella and found that its thickness for sufficiently high Reynolds and Weber numbers does not depend on liquid viscosity and surface tension. Hence, an approximation for the maximum spreading could be derived out of the kinematics. In line with this, 3 different modes where considered to cover a wide range of possible cases in droplet impact, based on the Weber numbers \( We = \frac{\rho D_0 U_0^2}{\sigma_w} \) and on the Reynolds number \( Re = \frac{\rho D_0 U_0}{\mu} \), reminding that \( \rho \), \( \sigma_w \) and \( \mu \) are the density, surface tension and dynamic viscosity of a Newtonian fluid. In this context, Attané et al. (2007) also discuss the limitations of considering the lamella approximated to a flattened disk, but at the end describe the wetting effects with the static contact angle and address the spreading lamella as a flattened disk based on the argument that it is a good approximation because the viscous dissipation at the moment of impact is less relevant when compared to an adequate description of the spread factors larger than 1.

Given the various morphological similarities observed between the spreading of Newtonian and non-Newtonian droplets, a logical approach is to adapt the existing models to the non-Newtonian case, namely by integrating in the model the accurate constitutive models describing the viscous dissipation and making the adequate scaling. Following this approach one made an exhaustive review of the models and correlations reported in the literature predicting the spreading diameter of Newtonian droplets and compared them with our own experimental results. Hence Fig. 6 confronts the models of Pasandideh-Fard et al. (1996), Scheller and Bousfield (1997), Attané et al. (2007), German and Bertola (2009) and Roisman (2009) with our data obtained from impacts of a 3.2mm droplet of distilled water over a smooth silicon wafer surface. These models were selected as they are illustrative of the various approaches and simplifications summarized in the previous paragraphs. It should be noticed that regarding the model of Attané et al. (2007), only the equation associated to the so called free-spreading model was considered.

Deviations between the experimental data (dots) and the theoretical predictions (lines) can be explained by several differences in the experimental conditions and particularly in the wettability and topography of the impacting surfaces, which can significantly affect the spreading diameter. However, the disagreement between experiments and theory is also due to the empirical nature of the correlations. Most of the models deviate from our experimental data between 20-40%, exception made to the model of Roisman (2009) which deviates only 10%. One of the reasons for this better agreement may be the scaling, which considers different shapes of the lamella, resulting in different equations, depending on the relative importance of the inertia vs capillary and viscous terms. Such approach allows the model to follow well the trend of the maximum spreading diameter at both regions of low and high Weber numbers.
Fig. 6. Comparative analysis between various semi-empirical models for the prediction of the spreading diameter of Newtonian droplets impacting onto cold and rigid surfaces.

It is worth mentioning that despite the aforementioned limitations, these models already provide very satisfactory quantitative description of the spreading diameter of Newtonian droplets. Hence, the approach which resulted in the best correlation agreeing with the experimental spreading diameter, i.e. the model of Roisman (2009) was modified to include the proper constitutive models describing the non-Newtonian behaviour of the spreading droplets. The resulting relation is evaluated by comparison with the experimental data presented in section 3.1. Hence, the relation of Roisman (2009) can generally be represented as:

$$\beta_{\text{max, predicted}} = C_1 (Re_{\text{eff}}^2 Oh)^n$$

(5)

scaling the viscous dissipation term with the boundary layer thickness $\delta$, as suggested by An and Lee (2012b), an effective Reynolds number $Re_{\text{eff}} = U_0 D_0 / \eta_{\text{eff}}$ can be defined with:

$$\eta_{\text{eff}} = \frac{\eta_0 - \eta_\infty}{\frac{\rho U_0 D_0}{\eta_{\text{eff}}}} \cdot \sqrt{\frac{C \cdot C_3}{2D_0}} \cdot \eta_{\text{eff}}$$

(6)

In a different approach, one may also directly introduce the scaling of the lamella thickness $h$ in the model, considering an effective viscosity, also based on the Cross model. The resulting modified formula is given by:

$$\beta_{\text{max, predicted}} = C_1 \left[ \frac{\rho U_0 D_0}{\eta_0 - \eta_\infty} \cdot \eta_{\text{eff}} \cdot \left( 1 + C \cdot C_3 \cdot \frac{3 \beta_{\text{max}}^2 \cdot U_0}{2D_0} \right)^m \cdot \eta_{\text{eff}} \right]^n$$

(7)

Comparing the theoretical predictions with the experimental data, as depicted in Fig. 7 one may notice a slightly better agreement between the modified Roisman relation (eqs. 6-7) for the spreading of the mixtures
with lower concentration of the shear-thinning component (Fig. 7b). Regarding the largest spreading of the mixture with the largest concentration, shown in Fig. 7b, slightly better agreement is obtained for the experimental data when using the scaling based on the thickness of the lamella (eq. 7) for the impacts at the lower velocities (lower Reynolds number), but a larger disagreement is obtained for the impacts at higher velocities. These trends are probably related to the assumptions that are made. Hence, for lower impact velocities and higher xanthan concentrations, the effect of viscous and surface tension forces is more relevant and the non-Newtonian behavior is more evident and strongly affects the thickness of the lamella, which is too high to be well represented by $\delta$. Thus, for these conditions, the most adequate scaling is obtained directly using the thickness of the lamella $h$. Hence, the best solution is to use a different scaling, depending on the relative importance of the viscous dissipation effect (i.e. weather one is considering low or high Reynolds numbers, associated to the variation of the impact velocities and of the xanthan concentration. In line with these results one proposes a combined solution with a different scaling, depending on the $Re_{eff}$. Hence, for lower values of $Re_{eff}$<580 (Region I) the formulation used is given by eqs. (7), while for $Re_{eff}$ >3200, (Region II) one recommends the use of eqs. (5-6) instead.

![Fig. 7. Theoretical prediction of the maximum spreading diameter vs. experimental data for: a) X0.05% solution, b) X0.35% solution.](image)

This combined solution is plotted in Fig. 8, together with the experimental results of An and Lee (2012a). The agreement with the experimental data is rather good, within ±10% variation. The discrepancies observed for the results reported in the literature are also not evident, thus confirming the secondary role of the surface wettability for these experimental conditions. Largest variations are observed for impacts at lower velocity for which capillary effects are more important (e.g. An and Lee, 2012b). Between these regions there is a transition zone, which is not well described yet.

The relation proposed here is not yet independent from empirical fitting and therefore still has room to be improved, particularly to predict more accurately the spreading behavior of the droplets with larger concentration of the shear-thinning component, impacting the surface at higher velocities. Also, the effect of the surface temperature is not accounted yetm as further investigation is required to explain in detail the phenomena described in section 3.1.
3.3. Droplet morphology for surface temperatures $T_w \approx T_{\text{boiling}}$: thermal induced atomization

Up to now, the surface temperature was kept low enough to prevent thermal induced atomization. Further heating the surface, up to $T_w=140^\circ\text{C}$, the heat transfer regime falls fully within the nucleate boiling region and thermal induced atomization occurs. Visualization of droplet impacts, supported by combined image analysis and Phase Doppler measurements suggest that the secondary atomization is triggered mainly at the same time instant, regardless of the impact conditions and xanthan concentrations, but much fewer droplets seem to be generated for higher concentrations of the xanthan gum. As the concentration increases and consequently $K$ and $m$ parameters of the constitutive model are higher, large vapour bubbles are produced over the lamella and secondary atomization is mainly generated as they burst. The secondary droplets produced are clearly in a smaller number, which associated to the difficulty in keeping the surface clean for these higher xanthan concentrations, makes the phase Doppler measurements very time consuming. For these reasons, measurements obtained for X0.35% are not presented here, as, up to now, they did not render reliable results.

Hence, the results suggest that the triggering of the thermal induced atomization is not significantly dependent on the viscous dissipation, but instead is governed by the competition between surface tension and vapour forces, similarly to what occurs for the Newtonian droplets (Moita and Moreira, 2009). Nevertheless, the size of the secondary droplets is related to the thickness of the lamella and therefore, depends on the concentration of the shear-thinning component.

Fig. 9 depicts the size distribution of the thermally induced secondary droplets, resulting from droplet impacts at different velocities, for three xanthan concentrations. The droplets generated for the highest concentrations are slightly larger. Few smaller droplets are visualized, but form very close to the lamella, below 5mm, so they are not detected in the control volume.

Following the study of Moita and Moreira (2009) for Newtonian fluids, the thermal induced atomization is dominated by the competitive effect between surface tension forces and vapour pressure forces, occurring during phase change. Hence, the empirical correlation suggested by Moita and Moreira (2009):

\[
\frac{SMD}{D_0} = C W e^a R e^b J a^c
\]

was considered here, to evaluate how well it could predict the Sauter Mean Diameter (SMD) of the secondary droplets generated during the thermal induced atomization of the non-Newtonian droplets. The Reynolds number was replaced by the $Re_{\text{eff.}}$, $Ja = C_p(T_w - T_{\text{sat}})/h_{\text{fg}}$ is the Jakob number, being $C_p$ the heat capacity, $T_{\text{sat}}$ the saturation temperature and $h_{\text{fg}}$ the latent heat of vaporization. Since the $h_{\text{fg}}$ of the mixtures is always the same, the Jakob number remains constant so that eq (8) is simplified into:
\[ SMD / D_0 = B We^a Re^b \]  

(9)

The fitting of the experimental data to such correlation is shown in Fig. 10.

![Graph showing size distribution for secondary droplets](image)

**Fig. 9.** Size distribution for the secondary droplets (measured by Phase Doppler Anemometry) resulting from the impact of 3mm non-Newtonian droplets onto a smooth and heated silicon wafer surface \((T_W=140^\circ C)\) for various Xanthan gum concentrations. a) \(U_0=1.4m/s\), b) \(U_0=3.2m/s\).

Qualitatively, there is a good correlation, thus suggesting that the main governing parameters for the triggering of the thermal induced atomization are already taken into account in the present correlation. However, a proper fitting entails a change in the exponent values, in comparison to the original correlation proposed by Moita and Moreira (2009). The lower exponents of \(Re_{\text{eff}}\) and \(We\) numbers can be associated to the fact that the thermal induced atomization is mainly a phenomenon controlled by vapour pressure and surface tension forces. However, the higher exponent associated to the \(Re_{\text{eff}}\) in comparison to the exponent of the Weber number can be explained by a non-negligible dependency of the size of the secondary droplets with the thickness of the lamella, which varies significantly with the concentration of the shear-thinning component. This effect is partially captured by the \(Re_{\text{eff}}\). However, a more detailed analysis is now required, over a wider range of experimental data, to effectively validate the empirical relation proposed here.

![Graph showing correlation for SMD](image)

**Fig. 10.** Correlation for the SMD determined from the secondary droplets generated during the thermal induced atomization on non-Newtonian droplets.

4. Final Remarks

The study presented here focus on the experimental and theoretical description of the dynamic behavior of non-Newtonian (shear-thinning) droplets impacting onto smooth and micro-patterned and heated surfaces.
The shear-thinning liquids are mixtures of water+xanthan gum prepared with different concentrations of the gum, namely 0.05%, 0.10%, 0.15% and 0.35%wt.

The analysis emphasizes the spreading over the surfaces, while the surface is heated bellow the boiling temperature of the liquid. Further increasing the surface temperature, thermal induced atomization occurs, for which image analysis is combined with Phase Doppler measurements to characterize the size and the velocity of the secondary droplets.

For droplet impacts over the surfaces heated bellow the boiling temperature of the liquid, the shear-thinning nature of the liquid is clearly affecting the spreading and receding motion. Hence the initial acceleration of the flow associated to an increased dissipation (higher values of zero viscosity) at the end of the spreading phase lead to a smaller diameter which occurs earlier for the mixtures with higher concentrations of the shear-thinning component. The strong increase of the zero viscosity also precludes the occurrence of the receding phase for the largest xanthan concentrations. This behavior, which is governed by the concentration of the non-Newtonian component, is well related to the consistency coefficient of the constitutive model, which describes the viscous behavior of the flow. The results further suggest that heating the surface (and consequently the liquid) alters the rheology of the non-Newtonian mixture and reverses the increase of the zero viscosity, which is observed for impacts onto non-heated surfaces, thus allowing a high spreading diameter and a significant recoiling phase for droplets with high concentrations of the non-Newtonian component.

In line with this, models predicting the spreading of Newtonian droplets are revisited and an alternative relation is proposed, which includes the non-Newtonian behavior of the spreading lamellas.

Concerning the thermal induced atomization, the results show that this mechanism is mainly triggered by the force balance between surface tension and vapor pressure forces, so the viscosity plays a secondary role.

Nonetheless, the size of the secondary droplets is affected by the non-Newtonian viscous behavior of the droplets. Based on these results, an empirical correlation is proposed predicting the size of the secondary droplets, which includes the non-Newtonian dependence based on an effective Reynolds number.

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