Droplet dynamics during flight, impact and evaporation

Erik-Jan Staat

DROPLET DYNAMICS DURING FLIGHT, IMPACT AND EVAPORATION

Erik-Jan Staat

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1

Introduction

1.1 Droplet dynamics

When you look outside on a rainy day, you have the ultimate opportunity to observe droplets during flight and impact. Scientists have done this on many occasions, so raindrops have been studied from their size and shape during flight [1] to the sound they produce upon impacting a puddle [2]. Apart from their natural occurrence, droplets are also found in applications such as inkjet printing [3], spray coating [4], spray cooling [5], fuel injection [6], fire suppression [7], agriculture [8], and medicine [9]. The flight, impact and evaporation of droplets are separate stages of processes involved in these examples and a better understanding of the dynamics of droplets and their interaction with the underlying substrate aids directly in the optimization of these processes, which in part drives scientific research on this topic.

Droplets have been studied for centuries, but many of the physical mechanisms underlying the observations remained elusive until recently with the advent of high-speed imaging technology having the spatial and temporal resolutions that are required to resolve the dynamics on the micro- and nanoscale [10, 11]. The resolutions that are required are determined by the relevant length and time scales of the process that is studied. The characteristic time scales of droplet dynamics depend on parameters such as the droplet

Figure 1.1 – The stages of a droplet during its lifetime that are studied in this thesis. (a) The droplet is in flight at some time after droplet generation, but before interaction with a substrate. (b) The moment of impact on a solid surface. (c) The shape of the droplet changes due to the interaction with the substrate. In this case, the droplet has just reached its maximum spreading diameter. (d) When the droplet’s kinetic energy reaches zero, it sits on the substrate until it is completely evaporated.

size and velocity, the properties of the liquid, the ambient conditions, and the substrate material properties (in the case of substrate interaction), but it is not always known beforehand which time scales are relevant.

Let us consider the isolated droplet in Fig. 1.1, that undergoes all three stages that are studied in this thesis: Flight, impact and evaporation. After the droplet is generated it is in flight and its only interaction is with the surrounding gas (Fig. 1.1a) until it impacts the substrate in Fig. 1.1b. The impact time of a droplet is usually defined as the droplet diameter over the droplet velocity, which is approximately the time in between Figs. 1.1b and 1.1c, in which the droplet is depicted at its maximum spreading diameter. Once the kinetic energy of the droplet is dissipated, the droplet sits on the substrate and evaporates (Fig. 1.1d), the process that in most situations takes the longest time. Notable exceptions are observed for heated substrates or for droplets that are so tiny, that they evaporate while in flight. Throughout this thesis we will evaluate these time scales and compare them to various other time scales, e.g. the capillary time scale or the time scale of thermal conduction, in order to identify the relevant parameters.

1.2 Droplets in flight

Although free falling drops through air have been studied for decades [1, 12], there still is a common misconception about their shape. Many people think

Figure 1.2 – Schematic of the mechanism of the dynamic surface tension of a surfactant solution. (a) A liquid-air interface is freshly formed and no surfactant molecules are adsorbed at this interface. The surface tension is equal to that of the pure solvent. (b) With increasing surface age, more surfactant molecules diffuse from the bulk to the surface and adsorb, resulting in a decrease of the surface tension. (c) The surfactant concentration at the liquid-air interface reaches an equilibrium a finite amount of time after the fresh interface was formed.

that a falling drop has a pointy tear shape, while in reality this shape can only be observed for drops that slide over a solid surface. The shape of a free falling drop is ultimately determined by a competition between the surface tension and the drag of air. The effect of air drag on the shape is negligible in the case of small droplets, resulting in a shape with the minimal surface area, i.e. a sphere. The drag of air will flatten a large drop to a pancake shape, but when the drop is very large, this shape is unstable and the drop will break up into smaller droplets. The cutoff radius for which a drop is considered small depends on the liquid, for water this radius is typically 1 mm. The inverse problem of determination of the surface tension from the shape of a falling droplet can be investigated when the shape of a small droplet deviates from its spherical equilibrium, for example due to pinch-off, break-up, or the kick of an acoustic field. The surface tension and viscosity can then be measured by monitoring how the droplet recovers its equilibrium shape.

In many practical situations, surface active agents (surfactants) are added to droplets to lower their surface tension. For example, they are added to inks used in inkjet printing to promote droplet spreading and to prevent flooding of the nozzle plate [13]. How do these surfactants affect the droplet behavior in flight? First of all, the surface tension will not be a constant anymore, but a quantity that depends on the age of the surface. The mechanism that causes this time-dependency is that after a fresh surface is formed (see Fig. 1.2a),

the surfactant molecules need time to diffuse from the bulk to the liquid-air interface and reduce the surface energy by adsorbing [14, 15]. Therefore, the surface tension of a surfactant solution is highest when a fresh interface is formed and decreases over time as more surfactant molecules adsorb (Fig. 1.2b) until an equilibrium surfactant concentration at the liquid-air interface is reached (Fig. 1.2c). In this thesis we will investigate the influence of surface active agents on the surface tension and viscosity at the time scale of drop formation in inkjet printing ($\approx 100 \mu\text{s}$) by ultra high-speed imaging of the shape oscillation of picoliter droplets.

1.3 Droplet impact

Probably the most well-known result of drop impact on a solid surface is the splash, but it is by far not the only one. What happens to a drop upon impact depends on many parameters and ranges from gentle deposition to full rebound without leaving any residue on the substrate [18–20]. Parameters such as the drop size and velocity, the liquid density, surface tension and viscosity, and roughness of the substrate and its wetting properties all influence the drop impact behavior. A very remarkable effect can be observed when the drop impacts a heated surface, like for example in spray cooling or fuel injection. When the substrate temperature is considerably higher than the

Figure 1.3 – The Leidenfrost effect. (a) The lifetime of a gently deposited water drop decreases with the plate temperature T until it significantly increases at a distinct temperature: the Leidenfrost temperature (data taken from Ref. [16]). (b) Side view of a droplet in the Leidenfrost state revealing the vapor layer that prevents contact between the droplet and the substrate (picture reprinted from Ref. [17]).

boiling point of the liquid, the drop makes a dry rebound, in the absence of boiling [21]. In order to investigate what causes this surprising behavior, let us first consider a drop that is gently deposited on a plate with a controlled constant temperature. As is seen in Fig. 1.3a, the lifetime of the drop decreases with increasing substrate temperature, until the lifetime suddenly increases significantly at a distinct plate temperature. What happens here is that the evaporation rate is so high, that a layer of vapor is formed under the droplet, which prevents direct contact between the liquid and the solid (see Fig. 1.3b). The heat transfer from the plate to the drop is now limited by the thermal conductivity of the vapor, which is very low, resulting in a longer drop lifetime. This phenomenon is called the Leidenfrost effect and the temperature that marks the transition into this regime the Leidenfrost temperature. This effect is well-studied in the static situation and has been observed for the dynamic case [21], but there are many open questions. What is the influence of the impact parameters on the Leidenfrost temperature? What is the influence of the substrate temperature on the spreading and splashing behavior of droplets? Can we tune the transition temperature by changing the parameters of the substrate? In this thesis we will address these questions by a systematic study of droplet impact on heated surfaces.

1.4 Droplet evaporation

Everyone that has ever spilled coffee on a table knows that coffee droplets eventually dry up when in contact with air at room temperature, as is evidenced by the residual coffee stain [22]. Of course a higher ambient temperature increases the evaporation rate, just as a higher plate temperature results in a shorter droplet lifetime in the experiment in Fig. 1.3a for plate temperatures below the Leidenfrost transition temperature. In experiment we however see that the drying time of a droplet is shorter on a dry, cold day than it is on a near-tropical day, why is this? It was discovered almost a century ago that the diffusion of vapor through the surrounding gas is the rate-limiting mechanism of evaporation [23], and because the rate of diffusion strongly depends on the humidity in the air, this explains our observations.

The process of droplets that evaporate on a solid substrate receives a lot of attention because of its relevance to many industrial applications, such as spray coating, dish washing machines and inkjet printing. The time it takes for a droplet to evaporate is an important quantity in these applications. For an isolated droplet of a pure liquid on an isothermal substrate this lifetime

can be calculated analytically [24–26], but then how can it be that a ceramic plate is completely dry when the dish washer is finished, while the plastic plate next to it still has drops on it? Clearly there is an influence of the material properties of the substrate on the evaporation rate, that is not captured by the analytical solution.

The phase transition from liquid to vapor requires energy and when this energy is not supplied by the direct surrounding of the droplet, it will cool down. When the temperature of the droplet drops, the evaporation rate also goes down, so this is where the thermal properties of the substrate affect the evaporation rate. The influence of the thermal properties of the substrate on the evaporation rate has been studied for microliter drops [27, 28], but not for smaller droplets. The evaporation of such smaller droplets on substrates with poor thermal conductivity are, for example, encountered in inkjet printing, where picoliter droplets evaporate on paper or vinyl. In this thesis we investigate the evaporation of picoliter droplets on a substrate with poor thermal conductivity.

1.5 Guide through the thesis

The chapters in this thesis are in the order of Fig. 1.1. First we study droplets in flight, then impacting drops and finally droplet evaporation. In chapter 2 we present an ultrafast imaging technique to measure the surface tension and viscosity of picoliter droplets in flight. Using this technique, we study the influence of surfactants on the surface tension and viscosity at a very short time after droplet generation. Chapters 3 through 6 contain a systematic study of droplet impact on heated substrates. We investigate the dynamic Leidenfrost effect on smooth surfaces, micro-structured surfaces and substrates with a carbon-nanofiber coating. In chapter 7 we study the evaporation of picoliter droplets. Finally, chapter 8 contains our conclusions and gives an overview of possible future research.

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2

Ultrafast imaging method to measure surface tension and viscosity of inkjet printed droplets in flight*

In modern drop-on-demand inkjet printing, the jetted droplets contain a mixture of solvents, pigments and surfactants. In order to accurately control the droplet formation process, its in-flight dynamics, and deposition characteristics upon impact at the underlying substrate, it is key to quantify the instantaneous liquid properties of the droplets during the entire inkjet printing process. An analysis of shape oscillation dynamics is known to give direct information of the local liquid properties of millimeter-sized droplets and bubbles. Here, we apply this technique to measure the surface tension and viscosity of micrometer-sized inkjet droplets in flight by recording the droplet shape oscillations microseconds after pinch-off from the nozzle. From the damped oscillation amplitude and frequency we deduce the viscosity and surface tension, respectively. With this ultrafast imaging method we study the time-dependent role of surfactants in freshly made inkjet droplets in flight and compare to complementary techniques for dynamic surface tension measurements.

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2.1 Introduction

Inks used in inkjet printers are a complex mixture of solvents, co-solvents, pigments and one or more surfactants [1]. The solvents carry the pigment particles to the medium and evaporate, solidify or crystallize, while the surfactants prevent wetting of the nozzle plate and promote spreading of the droplet after it impacts the underlying medium. In order to accurately control the droplet formation process, its in-flight dynamics, and subsequent interaction with the substrate, it is key to quantify the liquid properties of the droplet during the entire inkjet printing process.

The surface tension of a surfactant solution is determined by the concentration of adsorbed surfactant molecules at the liquid-air interface. When a fresh interface is formed, the surface tension equals that of the solvent [2] and it decreases while surfactants adsorb at the interface, until reaching an equilibrium surfactant concentration. The associated timescales of the adsorption process are governed by the diffusion time of the surfactant molecules to diffuse from the so-called adsorption depth h to the interface [3]. This depth depends on the bulk surfactant concentration, the critical micelle concentration, and the surface concentration of surfactants at equilibrium surface tension [3]. The typical diffusion time then scales with the surfactant diffusion coefficient D as $\tau_D \sim h^2/D$ and ranges from milliseconds to days, depending on the surfactant type and surfactant concentration [4, 5]. As the surfactants in inkjet printing must act before the ink dries, it is required that they adsorb as fast as possible. Droplet formation, however, is an extremely fast process that takes in the order of 10 μs , which is shorter than the approximately 100 μs that a droplet is typically in flight and much shorter than the time a droplet needs to evaporate, which is several seconds (see chapter 7). A surfactant with a typical adsorption time scale of the order of milliseconds is considered a fast adsorbing surfactant [4, 5], therefore it is clear that the surface tension of an ink is higher during droplet formation and flight than during the later spreading and evaporation phases. Methods exist to measure the time-dependent dynamic surface tension, however, these measurement techniques require separate, off-line setups or are not fast enough to operate at the microseconds timescale of the inkjet process [6].

It was shown before that the surface tension and viscosity can be extracted directly from an analysis of the eigenfrequencies of shape modes of oscillating droplets [7–15]. Over the past decades this method has also been proven to be very robust for various other systems, including jets [16, 17], bubbles [18, 19],

Figure 2.1 – **A** Schematic of a droplet that is symmetrical around the vertical axis showing the definitions of the distance from the center of mass to the liquid-air interface R , the polar angle θ , and the equilibrium radius R_0 (dotted line). **B** The amplitude-time curve of the shape oscillation for a mode $n = 2$ of a droplet of equilibrium radius $R_0 = 15 \mu\text{m}$. The damping rate $\beta_2 = 22 \times 10^3 \text{ s}^{-1}$ is determined from the amplitude decay. **C** The corresponding Fourier transform of the amplitude-time curve, indicating the eigenfrequency of the shape mode $\omega_2 = 57 \text{ kHz}$.

liquid samples of blood and biological tissues [20, 21], and soap bubbles [22, 23]. The very early work of Rayleigh [24] and Lamb [25] showed that a liquid that is deformed from its equilibrium state can be treated as an oscillator system, where surface tension provides the restoring force. The generalized system of a *damped* oscillator of an immiscible viscous fluid within another fluid was first described by Lamb [26] and revisited by others [27–30]. However, the analysis up to now has focused on mm-sized droplets or has only measured the evolution of the aspect ratio of μm -sized droplets.

Here, we present an ultrafast imaging method to measure the surface tension and viscosity for μm -sized inkjet droplets (corresponding to picoliters) in flight. We extend the well-known method to measure surface tension and viscosity from the eigenfrequencies of shape modes of oscillating droplets to the μm -regime by employing ultrafast imaging. Ultrafast imaging is necessary as the microscopic length scale of picoliter droplets poses a few challenges. First, the eigenfrequencies of shape mode oscillations scale with the droplet radius as $R_0^{-3/2}$ and thus, high-speed imaging is not only required to capture droplets in flight moving at a speed near 10 m/s ($\sim 10 \mu\text{m}/\mu\text{s}$), but also to resolve the details of the surface mode oscillations. Secondly, the viscous effects become increasingly important, as can be evaluated from balancing the viscous forces and the capillary forces through the Ohnesorge number $\text{Oh} = \mu/\sqrt{\sigma\rho R_0}$, with μ being the dynamic viscosity, σ the surface tension, and ρ the density,

especially for higher mode numbers n , since the Ohnesorge number scales with the mode number as $\text{Oh}_n = \sqrt{2n} \text{Oh}$ [31]. Thus, a decreasing droplet size leads to a faster decay of the oscillation amplitude due to damping.

The chapter is organized as follows. In the next section we revisit the background theory to extract the surface tension and viscosity from oscillating droplets. Then we present high-speed imaging experiments at two different timescales (μs and ms) to vary the age of the freshly made droplet surface in section 2.3 and describe the image analysis and requirements for obtaining sub-pixel accuracy in section 2.4. The results are presented in section 2.5 and compared to a complementary, off-line technique to measure the dynamic surface tension.

2.2 Shape mode oscillations

Here we briefly summarize Rayleigh's original treatment [24], to express the shape of an axisymmetrically deformed drop at any moment in time t as a sum of Legendre polynomials P_n

$$R(\theta, t) = \sum_{n=0}^{\infty} a_n(t) P_n(\cos \theta), \quad (2.1)$$

with θ the polar angle and $a_n(t)$ the time-dependent surface mode amplitude coefficients and n the mode number (see Fig. 2.1A for the definitions of R and θ). Assuming incompressibility of the liquid and no evaporation, we find that $a_0(t) = R_0$, where R_0 is the radius of a sphere with the volume of the drop, or the equilibrium radius. Since we place the origin of the coordinate system at the center of mass of the drop, it follows that $a_1(t) = 0$, and Eq. (2.1) simplifies to

$$R(\theta, t) = R_0 + \sum_{n=2}^{\infty} a_n(t) P_n(\cos \theta). \quad (2.2)$$

For a freely oscillating drop with small amplitude of oscillation the mode coefficients can be expressed as [25, 26]

$$a_n(t) \sim e^{-\beta_n t} \cos\left(\sqrt{\omega_n^2 - \beta_n^2} t\right), \quad (2.3)$$

with eigenfrequency ω_n

$$\omega_n^2 = n(n-1)(n+1) \frac{\sigma}{\rho R_0^3} \quad (2.4)$$

and

$$\beta_n = (n - 1)(2n + 1) \frac{\mu}{\rho R_0^2} \quad (2.5)$$

the damping rate of each mode n . Each depends on the liquid density ρ , surface tension σ and dynamic viscosity μ .

Figure 2.1B shows the amplitude-time curve of the shape oscillation for an $R_0 = 15 \mu\text{m}$ droplet for a mode $n = 2$. Figure 2.1C shows the corresponding Fourier transform $\tilde{a}_n$, indicating the eigenfrequency of the shape mode. Thus, measuring $\tilde{a}_n(t)$ while knowing n , ρ and R_0 gives $\sigma(t)$. Measuring $\beta_n(t)$ from the decay rate, knowing n , ρ and R_0 , gives $\mu(t)$. In the example of Fig. 2.1, we used pure water; the surface tension was chosen to be $\sigma = 72 \text{ mN/m}$, the viscosity was $\mu = 1 \text{ mPas}$, and the density was $\rho = 1000 \text{ kg/m}^3$, therefore the eigenfrequency of the mode $n = 2$ was $\omega_2 = 57 \text{ kHz}$ with a damping rate of $\beta_2 = 22 \times 10^3 \text{ s}^{-1}$. When we want to record ten instances of every oscillation cycle, this requires ultrafast imaging at interframe times of 1-5 microseconds or up to 1 Mfps [32].

2.3 Droplet formation

To test the dynamic effect of the surface tension and viscosity at two different timescales, droplets of different sizes were produced. In the first set of experiments droplets were detached from the tip of a needle, where it was pendant for about five to ten seconds, i.e. the concentration of surfactants at the interface has had enough time to reach equilibrium. The liquid was pushed out of a syringe (Hamilton Co.) by a syringe pump (PHD 2000, Harvard Apparatus) through a tube to a needle (19 gauge, flat tip, stainless steel, Hamilton Co.). The flow-rate of the pump was kept low ($\approx 0.05 \text{ mL/min}$) to ensure that the detachment was solely due to gravity and that we were in the regime where the surfactant adsorption at the liquid-air interface has reached an equilibrium. We used two different surfactants: 0.25 % (w/w) sodium dodecyl sulfate (SDS, Fluka) in pure water and 0.1 % (w/w) 1,2-hexanediol (HD, 98%, Aldrich) in pure water. To test the accuracy of the technique we also performed experiments with pure water alone (18,2 M Ω ·cm, Milli-Q). The falling droplet was recorded with a high-speed camera (Fastcam SA-X2, Photron) running at a frame rate of 20 kHz in back-illumination. A macro lens at a magnification of 1:1 was used to ensure sufficient spatial resolution. Figure 2.2 shows a representative recording of an oscillating water drop of $R_0 = 1.5 \text{ mm}$ analyzed with this setup.

Figure 2.2 – Representative high-speed recording of the shape oscillation of a purified water drop shortly after detachment from the tip of a needle. In the enlargement one can see the center of mass (black dot), the distance from the center of mass to the boundary R , and the polar angle θ .

To investigate the surface tension and viscosity of the same liquid at a shorter timescale, we used a drop-on-demand printhead (MD-K-130, microdrop Technologies GmbH) that is actuated with an arbitrary waveform generator (33220A, Agilent) and a wideband amplifier (model 7602M, Krohn-Hite) to generate a jet that breaks up into droplets about one hundred microseconds after actuation. The typical droplet size of a few tens of micrometers in radius, the velocity of a few meters per second and the corresponding eigenfrequency of shape oscillations of several tens of kHz dictate a requirement for spatial and temporal resolution that can not easily be met with conventional high-speed imaging [32]. The inkjet printing process, however, is highly repeatable, and we can record the shape oscillations of the droplets using stroboscopic imaging. The droplet is back-illuminated and its image is captured with a CCD camera (Sensicam QE, PCO AG) at a predetermined delay time after printhead actuation. By accurate control of the timing of the light source, camera and waveform generator with a pulse/delay generator (model 575-XC, BNC) the images obtained from many different droplets can be made into a sequence of the whole process. Motion blur is reducing by using a pulsed laser (EverGreen, Quantel) for illumination. To also eliminate speckle and fringes due to interference and diffraction of the coherent laser light, the laser was projected on a fluorescence plate (LaVision) to produce broadband incoherent illumination while keeping the short exposure time [33]. Figure 2.3 shows a representative sequence of a jet that breaks up into droplets, generated and recorded with this setup.

Figure 2.3 – Stroboscopic sequence of a drop-on-demand printed jet that breaks up into droplets recorded using the iLIF method [33]. The head droplet of $R_0 = 31 \mu\text{m}$ makes a shape oscillation as it travels through the field of view of the camera. The scale bar indicates a size of $50 \mu\text{m}$ and the interframe time is $5 \mu\text{s}$.

2.4 Image analysis

In each frame of every recording we detected the position of the liquid-air interface by determining the inflection-point of the intensity in the direction normal to the interface. In this way, we obtained a description for the drop boundary with sub-pixel accuracy. For a complete description of the technique on which this analysis is based, please see Van der Bos et al. [34].

The origin of the coordinate system was placed at the center of mass of the droplet and the interface was divided in two parts along the axis of symmetry. The resulting halves were compared to check for axisymmetry and if this was not the case, the recording was not analyzed further. In the case of axisymmetry, the right halve was used for the remainder of the analysis. Then the interface was converted to polar coordinates and the distance from the center of mass to the droplet boundary R as function of the polar angle θ was obtained. Figure 2.4 shows the detected drop boundary $R(\theta)$ (orange markers) of the frame shown in the enlargement of Fig. 2.2. Please note that the smoothness of the curve is only due to the used inflection-point method, there has been no smoothing or averaging of the data. Equation (2.2) was then fitted to the data to find the equilibrium radius R_0 and the mode coefficients $a_2 \dots a_n$, up to $n = 20$. The black solid line in Fig. 2.4A is the best fit to Eq. (2.2) and is within 0.1 pixels of the detected boundary (see the residue in

Figure 2.4 – A Graph showing the detected boundary (orange markers) and the determination of the oscillation mode coefficients via the best fit of Eq. (2.2) up to $n = 20$ (black solid line) for one single frame of the recording in the sequence of Fig. 2.2 at $t = 12.5$ ms, see the enlargement in Fig. 2.2. The dotted line indicates the equilibrium radius R_0 . **B** The residual of the droplet boundary and its best fit to Eq. (2.2).

Fig. 2.4B). By repeating this process for the subsequent frames of the recording, the time-dependent values of the mode coefficients $a_n(t)$ were found. We can now determine the viscosity from the decay of the amplitude of the mode coefficients. Also the surface tension can be extracted directly, either from the Fourier transforms of $a_n(t)$, or by fitting Eq. (2.3) to the experimental $a_n(t)$. Both methods yield the same result and as we already perform the fitting procedure to obtain the damping, we opt to use the latter method to determine the surface tension. For pure water we obtain the mode coefficients shown in Fig. 2.5. The surface tension and viscosity that we find for a microliter drop ($\sigma = 72 \pm 1$ mN/m and $\mu = 1.1 \pm 0.2$ mPas) and a picoliter droplet ($\sigma = 73 \pm 2$ mN/m and $\mu = 1.0 \pm 0.5$ mPas) are both in good agreement with the expected values, which are $\sigma = 72.8$ mN/m and $\mu = 1.0$ mPas.

Figure 2.5 – Graphs showing the oscillation modes $n = 2$ (blue markers), $n = 3$ (green markers) and $n = 4$ (red markers) for pure water drops of two different sizes. The gaps in the data are discarded frames due to reflections at the drop boundary, resulting in unreliable edge detection. The surface tension σ and viscosity μ are calculated from the best fits of Eq. 2.3 (dashed lines in A and B). **A** The water drop ($R_0 = 1.5$ mm) depicted in Fig. 2.2, $\sigma = 72 \pm 1$ mN/m and $\mu = 1.1 \pm 0.2$ mPas. **B** An inkjet printed water droplet ($R_0 = 32$ μ m), $\sigma = 73 \pm 2$ mN/m and $\mu = 1.0 \pm 0.5$ mPas. **C** The residues of the oscillation modes in A and their best fit of Eq. (2.3). **D** The residues of the oscillation modes in B and their best fit of Eq. (2.3).

2.5 Results

By adding the SDS as a surfactant solution, it is expected that there will be an influence of surface age on the surface tension and indeed Figs. 2.6A and 2.6B confirm this hypothesis. The surface tension of the microliter droplet ($\sigma = 35 \pm 1$ mN/m) is much lower than that of the inkjet printed picoliter droplet ($\sigma = 63 \pm 1$ mN/m). Another interesting observation is that the measured viscosity of the large drop ($\mu = 1.8 \pm 0.4$ mPas) is higher than that of the inkjet printed drop ($\mu = 1.0 \pm 0.2$ mPas), while the liquid is identical. We attribute this to the presence of adsorbed surfactant molecules at the interface. When the droplet is oscillating, the local surfactant concentration changes due to expansion and compression of the droplet surface. The resulting

Figure 2.6 – Graphs showing the oscillation modes $n = 2$ (blue markers), $n = 3$ (green markers) and $n = 4$ (red markers) for drops of the SDS solution of two different sizes. The surface tension σ and viscosity μ are calculated from the best fits of Eq. 2.3 (dashed lines in A and B). **A** A drop of the SDS solution ($R_0 = 1.2$ mm), $\sigma = 35 \pm 1$ mN/m and $\mu = 1.8 \pm 0.4$ mPas. **B** An inkjet printed SDS solution droplet ($R_0 = 34$ μ m), $\sigma = 63 \pm 1$ mN/m and $\mu = 1.0 \pm 0.2$ mPas. **C** The residues of the oscillation modes in A and their best fit of Eq. 2.3. **D** The residues of the oscillation modes in B and their best fit of Eq. 2.3.

surface tension gradient gives rise to a redistribution of surfactant molecules over the droplet interface, which counteracts the droplet deformation. This additional resistance to deformation of the droplet increases the decay rate of the oscillation amplitude [35, 36]. This effect of surfactants is usually called the Gibbs elasticity and its influence on the oscillation frequency and damping rate has been reported before for oscillating mm-sized droplets of surfactant solutions [10]. In the case of μ m-sized droplets we do not observe the effect of the Gibbs elasticity, because in this case only a few surfactant molecules are adsorbed at the liquid-air interface, so the surface tension gradient due to droplet deformation is small.

For the HD solution the influence of the surface age on the fluid properties is not known a priori. Although 1,2-hexanediol has surfactant-like properties due to its structure [37], the dynamic surface tension of a dilute HD solution

Figure 2.7 – Dynamic surface tension of the HD solution. The red circles give the values found from droplet oscillations, the blue crosses are the MBPM measurements and the black dotted line is the best fit of Eq. (2.6) to the MBPM data with $\sigma_0 = 72.8$ mN/m.

has not been reported to our knowledge. Our experiments show that there is a significant effect of surface age on both the surface tension and the viscosity: The surface tension decreases from 64 ± 1 mN/m for the μm -sized droplet (surface age between ≈ 200 μs and 10 ms) to 58 ± 1 mN/m for the mm-sized droplet (surface age of ≈ 5 s) and the viscosity increases from 1.1 ± 0.2 mPas (μm -sized droplet) to 1.5 ± 0.2 mPas (mm-sized droplet). The surface age of the μm -sized droplet is not known exactly because the liquid-air interface in the nozzle (i.e. the meniscus) is not a fresh interface at the moment a jet is ejected from the printhead. The surfactant concentration on the surface before droplet generation is determined by the jetting frequency, which in this experiment was 100 Hz, setting the upper bound of the surface age of the droplet. The lower bound of the surface age is set by the droplet formation time, which in this case was approximately 200 μs .

We have performed dynamic surface tension measurements of the very same HD solution using the maximum bubble pressure method (SITA online t60, SITA Messtechnik GmbH) and, as is seen in Fig. 2.7, both the surface tension measured from droplet oscillations at the longer timescale and the trend that a fresher surface has a higher surface tension are in agreement with the MBPM

measurements (blue crosses).

We compare the values of the surface tension that we found from droplet oscillations to the empirical formula which was successfully used to describe the dynamic surface tension of various types of surfactant solutions [38, 39]

$$\frac{\sigma_0 - \sigma(t)}{\sigma(t) - \sigma_{eq}} = \left(\frac{t}{\tau}\right)^k, \quad (2.6)$$

in which τ and k are fitting parameters, σ_0 is the surface tension of a freshly formed interface at $t = 0$, and σ_{eq} is the equilibrium surface tension. The surface tension of a freshly formed interface is equal to that of the solvent, so with $\sigma_0 = 72.8$ mN/m we fit Eq. (2.6) to the MBPM data to find $\sigma_{eq} = 57.6$ mN/m, $\tau = 2.1$ ms, and $k = 0.77$, see the black dotted line in Fig. 2.7. As is seen in Fig. 2.7, the values of the surface tension that were measured from the shape oscillations of both the mm- and μ m-sized droplets agree with this model, within the experimental uncertainty. A printhead with a higher jetting frequency is needed to reduce the uncertainty in the surface age and this remains a topic for future research.

2.6 Conclusions

In conclusion, we have developed a technique based on the stroboscopic imaging of the shape oscillation of inkjet printed droplets to measure in-line the surface tension and viscosity of a liquid during the process of inkjet printing. With this technique we show that the surface tension of an ink containing surfactants right after droplet formation is significantly higher compared to the equilibrium value. We attribute this to the surfactant adsorption process, which needs more time to reach an equilibrium than the droplet is in flight. On the other hand, the viscosity of the same surfactant solution is lower during droplet formation than it is when the surface is fully covered with surfactant molecules. We attribute this to the high surface coverage of surfactant molecules, which is accompanied by an increased resistance to interfacial deformation of the droplet due to the Gibbs elasticity.

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3

Drop impact on superheated surfaces*

At the impact of a liquid droplet on a smooth surface heated above the liquid's boiling point, the droplet either immediately boils when it contacts the surface ("contact boiling"), or without any surface contact forms a Leidenfrost vapor layer towards the hot surface and bounces back ("gentle film boiling"), or both forms the Leidenfrost layer and ejects tiny droplets upward ("spraying film boiling"). We experimentally determine the conditions under which impact behavior in each regime can be realized. We show that the dimensionless maximum spreading Γ of impacting droplets on the heated surfaces in both the gentle and spraying film boiling regimes shows a universal scaling with the Weber number We ($\Gamma \sim We^{2/5}$), which is much steeper than for the impact on non-heated (hydrophilic or hydrophobic) surfaces ($\Gamma \sim We^{1/4}$). We also interferometrically measure the vapor thickness under the droplet.

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3.1 Introduction

When a drop impinges gently on a surface heated well above the liquid's boiling temperature, the liquid may evaporate so fast that the drop floats on its own vapor. The vapor layer then acts as a thermally insulating film causing the drop to evaporate much more slowly than if it remained in contact with the surface. This phenomenon is known as the Leidenfrost effect [1]; the temperature at which the evaporation time of the drop reaches its maximum is called the Leidenfrost temperature. Since it was first reported in 1756, various aspects of the Leidenfrost effect have been studied, most importantly the determination of the Leidenfrost temperature for different liquids and surfaces [2, 3]. In general, measurements of the Leidenfrost temperature were performed with zero or at most small incident velocity because the characteristic time scale of the impact, of order of several milliseconds, is negligible compared to the drop's total evaporation time. In other words, the Leidenfrost temperature is assumed not to be affected by the impact dynamics (hence to be referred to herein as the static Leidenfrost temperature), and is commonly considered as the lowest boundary of the film boiling regime [4–7]. However, in most realistic situations where the impact velocity is not negligible, the Leidenfrost temperature should be regarded as a dynamic quantity [3] (see review articles [8, 9]). One can define the dynamic Leidenfrost temperature T_L as the minimum temperature of the surface at which the developing vapor layer causes an impinging droplet to bounce. As compared to the static case, there have been very few studies that focus on the dependence of T_L on impact conditions. The goal of this chapter is to experimentally determine this dependence and to study the droplet impact dynamics on heated surfaces.

3.2 Experimental details

In order to study droplet impact dynamics on heated surfaces, we generate droplets by pushing liquid from a syringe at a small rate (≈ 0.05 mL/min) through a pipe and into a capillary needle (inner diameter 100 μm). The droplet that is formed at the tip of the needle detaches as soon as the gravitational force overcomes the surface tension. We use two different liquids: milli-Q water (density $\rho_w = 998$ kg/m³, surface tension $\sigma_w = 72$ mN/m and viscosity $\nu_w = 1.0$ mm²/s) and a Fluorinert liquid FC-72 ($\rho_{fc} = 1680$ kg/m³, $\sigma_{fc} = 11.9$ mN/m, $\nu_{fc} = 0.38$ mm²/s, and boiling temperature 56 °C). By varying the height of the needle, we control the velocity V_0 of the droplet before impacting

Figure 3.1 – Schematics of the experimental setup used to study droplet impact on heated surfaces. A liquid droplet of initial diameter $D_0 \approx 2$ mm falls on a heated plate P and spreads to its maximum diameter D_m . The plate is placed on a holder H which can be heated by six cartridge heaters embedded symmetrically inside. The holder has a 2 cm-diameter hole in the center allowing bottom-view observation. The side view of the impact is recorded by camera S and the bottom view is recorded by camera B connected to a long working distance microscope C via mirror M.

the surface. We simultaneously capture side-view and bottom-view images of the droplet as it spreads using two synchronous high-speed cameras (Fastcam SA1 & SA2, Photron). From the series of recorded images in each experiment, we obtain the impact velocity V_0 , the drop diameter D_0 (typically 1.7 mm and 2.2 mm for water and 1.1 mm for FC-72), and the maximum spreading diameter D_m (Fig. 3.1). As a result, we can estimate the drop’s kinetic energy compared to its surface energy by computing the Weber number $We = \rho D_0 V_0^2 / \sigma$. In our experiments, We is varied from 0.5 to 500 for water and from 6 to 600 for FC-72.

The test surfaces in most of our experiments are polished silicon plates (silicon wafers of 0.5 mm thickness with an average surface roughness ≈ 5 nm). The plate is placed on top of a polished stainless-steel holder (Fig. 3.1). At the center of the holder, a 2 cm-diameter hole allows for bottom-view observations if a sapphire plate (thickness 5 mm) is used instead of the silicon one. We embed in the holder a temperature probe and six cartridge heaters (Omega, Inc.) symmetrically around the hole to control its temperature and consequently the temperature of the test surface. Since sapphire and silicon both have

high thermal conductivity, the temperature difference between the holder and the test surface is only a few degrees and can be neglected in the explored temperature range (from 200°C to 600°C). As a result, the surface temperature T is approximated as the holder's temperature.

3.3 Results

3.3.1 Impact phase diagram

We repeat the droplet impact experiment numerous times using water as the working fluid for different Weber numbers ($0.5 \leq \text{We} \leq 500$) and surface temperatures ($250^{\circ}\text{C} \leq T \leq 560^{\circ}\text{C}$), and observe the drop's behavior during impact. Figure 3.2 shows three distinct impact regimes, each one of which is exemplified by a series of images taken from a high-speed recording of a representative experiment.

Figure 3.2a shows images of an experiment in the contact boiling regime. The bottom views in these images evidently show that, shortly after impact, the liquid makes partial contact with the surface. The contact leads to a high rate of heat transfer from the heated surface and, consequently, formation and growth of vapor bubbles. The vapor pressure increases abruptly causing disruption of the liquid's bottom surface, as well as violent, sometimes explosive, ejection of tiny droplets due to the venting of the vapor bubbles (clearly seen from the side views). In the phase diagram (Fig. 3.3), this regime corresponds to the region with red diamonds.

The gentle film boiling regime is shown in Fig. 3.2b. The name refers to situations in which the vapor layer is sufficiently thick to prevent the liquid from touching the surface and there is no droplet ejection due to expansion of vapor bubbles (disintegration of the impacting droplet may happen, but due to other mechanisms, e.g. instability at the rim of the spreading lamella at high Weber number). This regime corresponds to the region with blue circles in Fig. 3.3.

The spraying film boiling regime (Fig. 3.2c) is similar to the gentle film boiling regime in that the liquid is not in contact with the surface (bottom views in Fig. 3.2c). However, the side-view images reveal spraying-like ejection of small droplets from the top of the liquid, although the ejection is not as vigorous as in the case of contact boiling. This regime corresponds to the region with green squares in Fig. 3.3.

Figure 3.2 – Series of images of representative water droplet impacts in three regimes. The Weber number in all three experiments is 32. Each image has both a bottom and a side view of the impact. Images in the same column are taken at the same time after impact. (a) The surface temperature $T = 380^\circ\text{C}$; contact boiling. The first sign of droplet ejection is seen at 0.6 ms after impact. (b) $T = 500^\circ\text{C}$; gentle film boiling. (c) $T = 580^\circ\text{C}$; spraying film boiling. The contrast of the side-view images was enhanced to show tiny droplets ejected upward at 1.9 ms. The inset bar (shown in upper left image) indicates a length scale of 2.5 mm.

Figure 3.3 – Phase diagram for water droplet impact on a heated surface showing three separate regions: contact boiling regime (red diamonds), gentle film boiling regime (blue circles), and spraying film boiling regime (green squares). Each region has an inset illustrating typical droplet impact behavior in that regime. The dashed lines between different regimes are drawn to guide the eye.

Let us discuss the transition between the contact boiling and the gentle film boiling regimes in Fig. 3.3. This transition marks the dependence of the dynamic Leidenfrost temperature T_L on the Weber number We . While there have been disparate conclusions regarding whether T_L increases [10, 11], or decreases [12, 13] with We , our data show unambiguously that T_L increases along with We . We account for this change in T_L by comparing the pressure in the vapor layer and the drop’s dynamic pressure: an impinging droplet bounces back from the heated surface (hence in the gentle film boiling regime) if the vapor pressure overcomes the drop’s dynamic pressure. Note that increasing the surface temperature raises the vapor pressure, while the drop’s dynamic pressure is essentially determined by We . Therefore, a higher surface temperature is necessary to keep droplet impact at higher Weber number in the gentle film boiling regime. As a result, we conclude that the dynamic

Leidenfrost temperature increases with increasing Weber number, consistent with our experimental results.

The second transition in Fig. 3.3 is between the gentle and spraying film boiling regimes. From $We = 11$ and $T = 560^\circ\text{C}$, the transition temperature decreases with increasing Weber number. To understand this result, we argue that droplet ejection in the spraying film boiling regime is caused by the bursting of vapor bubbles in the liquid film. As We is increased, the liquid film gets thinner and it is easier for the boiling bubbles to burst through the liquid's upper surface. As a result, the transition temperature decreases as the Weber number increases, in accordance with our experimental results. We stress that the bursting of vapor bubbles in the liquid film is a crucial condition for the transition from gentle to spraying film boiling regime. We confirm this by noting that for a fixed Weber number ($We = 30$), adding $50\text{ }\mu\text{m}$ particles to the liquid (the estimated liquid film thickness is about $300\text{ }\mu\text{m}$) effectively reduces the transition temperature.[†] This observation implies that the transition from gentle to spraying film boiling is related to the vapor bubble formation inside the liquid film, which is enhanced due to an increase of nucleation sites provided by the particles.

3.3.2 Maximum spreading

To obtain a quantitative understanding of the spreading dynamics of drop impact on the Leidenfrost vapor layer, we measure the maximum spreading diameter D_m of the drop in the gentle and spraying film boiling regimes and compare it with scaling arguments and experimental data available in literature [14–16]. In Fig. 3.4, we show a log-log plot of the dimensionless maximum spreading $\Gamma = D_m/D_0$ versus the Weber number. The plot consists of five sets of data: one set was taken using water on superhydrophobic surfaces at room temperature and atmospheric pressure (data by Tsai et al. [16]), two sets were taken using water and FC-72 in the gentle film boiling regime, one using water in the spraying boiling regime, and one using ethanol in the gentle film boiling regime (data by Chaves et al. [14]). Despite a wide variation in surface temperature ($250^\circ\text{C} \leq T \leq 560^\circ\text{C}$), and differences in liquid (viscosity, surface tension, density) and thermal properties (heat capacity and latent heat of evaporation) between water, FC-72, and ethanol, all the data in the gentle and spraying film boiling regimes fall on a unique, single curve, signalling universality of the spreading dynamics in the film boiling regime.

[†]A systematic study of the effect of particles on the transition temperature is beyond the scope of this thesis.

Figure 3.4 – Log-log plot of the maximum spreading diameter normalized by the drop’s diameter ($\Gamma = D_m/D_0$) versus the Weber number (We) for impact in both the gentle and spraying film boiling regimes. Experimental data for water drops spreading on superhydrophobic surfaces at room temperature by Tsai et al. [16] (open downward triangles), ethanol in the gentle film boiling regime by Chaves et al. [14] (solid right triangles), FC-72 in the gentle film boiling regime (solid left triangles), water in the gentle film boiling regime (solid circles), and water in the spraying boiling regime (solid squares). The solid line represents the best fit for the experimental data for $We > 10$ in the present study with the slope 0.39. The dashed line represents the scaling $\Gamma \sim We^{1/2}$ resulting from the balance between the drop’s initial kinetic energy and its surface energy at maximum deformation. The dash-dotted line represents the scaling $\Gamma \sim We^{1/4}$ resulting from a momentum argument [15].

For $We > 10$, our data is best fitted by the scaling $\Gamma \sim We^{0.39} \approx We^{2/5}$. This is much steeper than the well established scaling law $\Gamma \sim We^{1/4}$ [15] found for the impact of various different liquid droplets on both hydrophilic [15], hydrophobic, and even superhydrophobic surfaces (see [16] and the data of that paper which we have included in Fig. 3.4). In this last situation, the liquid spreading is lubricated by an air layer between the drop and the solid surface. Given the universality of the 1/4-scaling law and the slip due to the air lubrication layer, dissipation clearly does not play a role for the 1/4-

scaling law. The steeper and also universal 0.39-scaling is therefore the more remarkable. This effect may be due to an extra driving mechanism caused by the evaporating vapor radially shooting outwards and taking the liquid along. This interpretation is consistent with the experimentally found ambient pressure dependence of Γ [16]. Note that balancing the surface energy σD_m^2 and the initial kinetic energy $\rho D_0^3 V_0^2$ would lead to an even steeper scaling $\Gamma \sim We^{1/2}$, which is not observed.

3.3.3 Vapor film thickness

While the existence of the vapor layer is crucial in understanding the spreading dynamics and heat transfer of droplets impacting heated surfaces, there has been hardly any experimental measurement of the thickness of the vapor layer

Figure 3.5 – (a) Interference pattern showing the thickness variation of the vapor layer during impact of a droplet (the image was taken 0.3 ms after the camera detected the droplet). The image was taken from the bottom view of droplet impact using a high-speed color camera connected to a long working distance microscope at 10 000 frames per second. The Weber number is 3.5 and the surface temperature is 350 °C. The inset bar indicates 0.2 mm. (b) Profile of the vapor thickness extracted from the color image.

to date. Here, we provide direct measurements of the vapor thickness of drop impact in the gentle film boiling regime using interferometry. In Fig. 3.5a, we show the interference pattern from a bottom view of an impinging drop at $We = 3.5$ and $T = 350^\circ\text{C}$. The novelty here is that by using a color high-speed camera (Photron Fastcam SA2), we are able to simultaneously obtain interference patterns formed by light of different wavelengths (Fig. 3.5a). The fringe spacings for different lights are then used to extract the absolute thickness of the vapor [17]. In Fig. 3.5b, we show the measured vapor layer profile. Even for the drop at this low Weber number, the vapor thickness is one order of magnitude smaller than that in the case of a static Leidenfrost drop at a similar surface temperature (as predicted by Gottfried et al. [3] and verified experimentally by Biance et al. [18], the vapor thickness is roughly $20\text{ }\mu\text{m}$ in the static case), consistent with our finding that higher velocities require a higher surface temperature for the gentle film boiling regime to occur. Surprisingly, the measured vapor thickness is close to the air thickness measured indirectly for drop impacts on unheated surfaces [19].

3.4 Conclusions

In conclusion, we have experimentally explored the (We, T) phase space of impact of liquid droplets on heated smooth surfaces. The impact behavior can be separated into three regimes: Contact boiling, gentle film boiling, and spraying film boiling. We show that the transition temperature from the contact boiling regime to the gentle film boiling regime (the dynamic Leidenfrost temperature T_L) increases monotonically with increasing Weber number. We also find that the transition temperature from the gentle film boiling to spraying film boiling regime is related to boiling bubbles inside the liquid film and decreases with increasing We . For impacting droplets in both the gentle and the spraying film boiling regimes (both occurring when the surface temperature is higher than T_L), the maximum deformation displays universality regardless of the variation in surface temperature and liquid properties.

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4

Droplet impact on superheated micro-structured surfaces*

When a droplet impacts a surface heated above the liquid's boiling point, the droplet either contacts the surface and boils immediately (contact boiling), or is supported by a developing vapor layer and bounces back (film boiling, or Leidenfrost state). We study the transition between these characteristic behavior and how it is affected by parameters such as impact velocity, surface temperature, and controlled roughness (i.e. micro-structures fabricated on silicon surfaces). In the film boiling regime, we show that the residence time of impacting droplets strongly depends on the drop size. We also show that the maximum spreading factor Γ of droplets in this regime displays a universal scaling behavior $\Gamma \sim We^{3/10}$, which can be explained by taking into account the drag force of the vapor flow under the drop. This argument also leads to predictions for the scalings of the thickness and the velocity of the vapor shooting out of the gap between the drop and the surface. In the contact boiling regime, we show that the structured surfaces induce the formation of vertical liquid jets during the spreading stage of impacting droplets.

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4.1 Introduction

Central to many technological processes such as spray cooling and fuel injection in combustion engines is the phenomenology of individual droplets impacting superheated surfaces [1, 2]. The goal of these processes is to enhance the heat transfer rate between the liquid and the solid surface [2]. Effective heat transfer requires that the liquid contacts the solid surface upon impact (the contact boiling regime). However, contact is only possible as long as the temperature of the hot surface is lower than a critical value, the Leidenfrost temperature [3, 4]. Beyond this temperature, the liquid remains separated from the hot solid surface by a developing vapor layer. In this so-called film boiling regime, the vapor layer, due to its poor thermal conductivity, drastically reduces the heat transfer from the solid to the liquid and potentially risks surface overheating and equipment burnout. As a result, studies of heat transfer enhancement cannot be separated from those of the Leidenfrost temperature, especially in the context of droplet impact on superheated surfaces.

An alternative way of improving the heat transfer performance is by enhancing the surface area, which is typically achieved by roughening the surface, or by fabricating micro-structures on top of it [5–8]. It was shown that surfaces with micro-structures of different sizes and shapes enhanced the heat flux during spray cooling [9], although it is not clear whether the geometrical shape or the structure size has the dominant effect on the heat transfer [5, 7, 9]. This lack of understanding [7], together with the lack of systematic studies of the Leidenfrost temperature for these surfaces, have made it difficult to utilize surface enhancement efficiently.

Beside surface temperature, surface roughness, droplet size, and droplet velocity are also crucial contributing factors to the heat transfer efficiency [1, 7] as they directly affect quantities such as the dynamic Leidenfrost temperature [10], the residence time [11, 12], and the maximum spreading [10]. Although studies on these quantities have been reported in some detail, they have not addressed the effect of roughness (in particular controlled roughness) on the outcomes of droplet impact on heated surfaces.

The goal in this chapter is to investigate the effects of surface roughness, temperature, and impact conditions on the thermo-hydrodynamics of droplet impact on heated surfaces. With an emphasis on the effect of roughness, we use micro-structured surfaces with different size of structures. For each type of surface, we determine the dynamic Leidenfrost temperature. In the film boiling regime, we systematically vary the control parameters and determine their

Figure 4.1 – Scanning electron microscope (SEM) images of the structured silicon surfaces used in this chapter. (a) Structured surfaces having pillar interspacing $20\ \mu\text{m}$ and the pillar height being varied from $2\ \mu\text{m}$ to $8\ \mu\text{m}$. (b) Structured surfaces having pillar interspacing $4\ \mu\text{m}$ and the pillar height being varied from $2\ \mu\text{m}$ to $8\ \mu\text{m}$. The geometrical configuration of each structured surface is indicated by R_I^H , where H is the pillar height and I is the pillar interspacing. The pillar width W of all surfaces is roughly the same. The actual dimensions of the structures are listed in Table 4.1.

effects on the evolution of the contact area between the drop and the surface, the residence time, and the maximum spreading diameter of droplets. We also develop a scaling argument to account for the spreading factor in this regime and make predictions for both the vapor layer thickness and the vapor velocity under the drop. This scaling argument adds to the few known theoretical attempts to quantify the hydrodynamics and shape of the vapor layer under Leidenfrost droplets [4, 13–16]. In the contact boiling regime, we provide a qualitative description of the pronounced, upward-directed jets formed during spreading of droplets as a result of the vigorous boiling processes.

4.2 Experimental details

4.2.1 Fabrication of micro-structured surfaces

The microstructure arrays are fabricated via deep reactive ion etching (DRIE) on double side polished silicon wafers (p to p-type, Boron doped 5-10 Ohm cm

Surface	H (μm)	I (μm)	W (μm)
R_{20}^2	1.8	19.6	9.1
R_{20}^4	3.7	19.5	8.8
R_{20}^8	8.1	19.4	8.9
R_4^2	2.0	4.0	8.8
R_4^4	3.9	3.8	8.8
R_4^8	7.9	4.0	8.9

Table 4.1 – Size of the microstructures: height (H), interspacing (I), width (W).

resistivity, 100 mm diameter, 525 μm thickness, $\{100\}$ crystal orientation; Okmetic Finland). Olin 907-17 photoresist is spun on the wafer at 4000 rpm for 30 s to obtain a layer thickness of ≈ 1.7 μm . After a soft-bake step at 95 $^\circ\text{C}$ for 90 s, the photoresist layer is exposed for 3.5 s to mid UV light in an EVG 620 mask aligner through a photomask with the microstructure geometry, followed by development in OPD-4262 and hard-baking in air at 120 $^\circ\text{C}$ for 30 min. The actual pattern is eventually formed by reactive ion etching in a DRIE system (Adixen AMS100-SE ICP), with an RF generator at 13.56 MHz and a 1.5 kW ICP plasma source. The total chamber pressure is kept at 75 mTorr. The temperature of the electrode with the silicon substrate is kept at 10 $^\circ\text{C}$, using liquid nitrogen as a coolant. The etching time is varied from 53 s to 7 min to obtain pillar heights of approximately 2 μm , 4 μm , and 8 μm (see Table 4.1). SF_6 and C_6F_8 flows are kept constant during the etching process at 250 sccm (standard cubic centimeter per minute) and 200 sccm respectively. After the silicon etching, the remaining photoresist is removed with an O_2 plasma (Etser Tepla-300 system), followed by a nitric acid and a subsequent 1% HF treatment, to remove the SiO_2 grown during O_2 plasma etching. The resulting microstructures are shown in Fig. 4.1. Further details on the sample preparation were reported previously [17, 18].

4.2.2 Experimental method

Figure 4.2 shows the experimental setup used to study the impact of droplets on superheated, structured surfaces. The liquid used in all of our experiments is milli-Q water, having density $\rho_l = 998$ kg/m^3 , surface tension $\sigma = 72$ mN/m , and viscosity $\nu = 1.0$ mm^2/s (these properties are measured at room temperature). We generate single droplets of diameter D_0 by pushing water out of a fine needle at a small rate (≈ 0.05 mL/min). The droplet detaches from the

Figure 4.2 – Schematics of the experimental setup used to study droplet impact on heated structured surfaces. Water droplets of diameter D_0 impact a heated surface with velocity V_0 ; its spreading diameter during impact is denoted as D . The surfaces are heated by a plate P with cartridge heaters embedded inside. The impact dynamics and the boiling of the liquid are recorded from the side by high-speed camera C_1 . The heated plate P has a hole 2 cm in diameter allowing bottom-view recording when a transparent substrate (e.g. a sapphire plate) is used. In this case, we use another high-speed camera C_2 to record the impact from the bottom via a mirror M .

needle due to its own weight and falls on a heated solid surface with impact velocity V_0 . In our experiments $D_0 \approx 2.2$ mm and V_0 is varied between 0.4 m/s and 4 m/s by adjusting the release height of the droplet.

We use the above described silicon micro-structured surfaces as target substrates. The structures are arranged in a square lattice characterized through micro-pillar interspacing I , pillar width W , and pillar height H . In order to examine the effect of surface roughness on the impact outcome, we use two sets of structured surfaces: one has I fixed at 20 μm and the other one at 4 μm . The pillar height is varied between 2 μm and 8 μm in each set. The pillar width is kept fixed at $W \approx 9$ μm for all surfaces. The actual dimensions of the structures are listed in Table 4.1. For purposes of comparison, we also carried out some experiments using a smooth sapphire plate which, being transparent, enables us to record bottom views as well as side views.

We heat the surface by placing it on a brass plate that can be heated up to 600°C by six cartridge heaters embedded inside (Omega, Inc.); the temperature of the brass plate can be measured accurately to 1 K by a type K

thermocouple. We verified that the temperature difference between the heated plate (measured by the thermocouple) and the structured surface (measured by a surface sensor N-141-K made by Tempcontrol I.E.P. B.V.) is less than 5 K, and therefore can be neglected for the present purposes.

We use two high-speed cameras (Fastcam SA1.1 & SA2, Photron) to record the spreading and boiling processes of impacting droplets from the side and, for the sapphire plate, from the bottom. From the side-view recording of each impact experiment, we measure D_0 and V_0 , from which we calculate the Weber number $We = \rho_l D_0 V_0^2 / \sigma$. The Weber number is a measure of the drop's kinetic energy compared to its surface energy and is used as one of the control parameters. In our experiments, We is varied between 1 and 1000.

4.3 The dynamic Leidenfrost temperature

Typically, the behavior of droplets during impact on superheated surfaces can be specified as contact boiling or film boiling [1, 10, 19]. The differences between these two regimes are conveniently illustrated by using simultaneous side- and bottom-view snapshots of droplet impact on a smooth superheated plate, shown in Fig. 4.3. The bottom-view images in this figure are from interferometric recordings [10]. In the contact boiling regime (Fig. 4.3a), the spreading is accompanied by boiling at the wetted area. Note that the liquid does not wet the solid surface immediately, but first deforms to create a cavity due to the pressure build-up of vapor underneath (as revealed by the interferometric snapshot at 0.5 ms). The liquid then makes direct contact with the solid surface and starts boiling. Depending on the temperature of the solid surface, the liquid may display boiling characteristics from mild bubble formation to vigorous bubble expansion and droplet ejection. Increasing the surface temperature induces more and more vapor generated between the liquid and the solid surfaces that hinders the heat transfer rate. If the surface temperature is further increased beyond a critical point, i.e. the Leidenfrost temperature, a vapor layer develops and prevents the liquid to make any contact with the solid surface, and the impact is said to be in the film boiling regime. The superheated surfaces that cause impacting droplets in the film boiling regime are herein referred to as Leidenfrost surfaces. In Fig. 4.3b, we show a series of snapshots illustrating the behavior of droplets in this regime. Note that it is evident from the bottom view that the drop is separated from the solid surface during the entire impact time. Since vapor conducts heat poorly, an impacting drop in the film boiling regime interacts with the heated

Figure 4.3 – Representative series of snapshots taken from the side and the bottom views showing the spreading and boiling processes of droplet impact on a smooth sapphire surface in (a) the contact boiling regime and (b) the film boiling regime. In both cases, the diameter and velocity of the impacting water drop are 2 mm and 0.26 m/s, respectively, resulting in a Weber number of 1.9.

surface through a thermal-insulating layer and therefore does not exhibit the characteristic boiling behavior such as that in the contact boiling regime. The drop spreads and retracts as if it had fallen on a unheated superhydrophobic surface.

The transition temperature between the contact boiling and the film boiling regimes is called the dynamic Leidenfrost temperature [1, 10] to distinguish it from its quasi-static counterpart, i.e. the surface temperature at which the evaporation time of a deposited droplet is longest [4]. For smooth surfaces, it was shown that the dynamic Leidenfrost temperature T_L increases with the Weber number [10] (see Fig. 4.4a). Here, we follow Tran *et al.* [10] and determine the dynamic Leidenfrost temperature for each structured surface by repeating the drop impact experiment numerous times while varying the Weber number ($1 \leq We \leq 1000$) and the surface temperature ($200^\circ\text{C} \leq T \leq 550^\circ\text{C}$). In Fig. 4.4b, we show a typical phase diagram of boiling behavior on a structured surface with interspacing $I = 20\ \mu\text{m}$ and pillar height $H = 2\ \mu\text{m}$. In the phase diagram, the data points representing impacts in the contact boiling and film

Figure 4.4 – (a) Phase diagram for water droplet impact on a heated smooth surface showing that the contact boiling regime (red solid diamonds) is separated from the film boiling regime (blue solid circles) by a transition that marks the dynamic Leidenfrost temperature (violet dashed line). (b) Phase diagram for water droplet impacting a structured surface (R_{20}^2) having pillar interspacing $I = 20 \mu\text{m}$, height $H = 2 \mu\text{m}$, and width $W = 9 \mu\text{m}$. The solid black line represents the dynamic Leidenfrost temperature for this surface.

boiling regimes are marked by red diamonds and blue circles, respectively. Similar to the phase diagram obtained on smooth surfaces (Fig. 4.4a), there is a clear transition between the two regimes that marks the dynamic Leidenfrost temperature of this structured surface. The vertical bars indicate a transitional region that has behaviors in both boiling regimes.

Let us discuss the dependence of the dynamic Leidenfrost temperature T_L on the Weber number We . In Figs. 4.5a and 4.5b, we show T_L for two sets of structured surfaces respectively. In the first set, the pillar spacing is fixed at $20 \mu\text{m}$ while the height is varied from $2 \mu\text{m}$ to $8 \mu\text{m}$. The second set has the interspacing fixed at $4 \mu\text{m}$ and the same height variation. The dynamic Leidenfrost temperature for impact on smooth surfaces is also shown as a reference. It is evident that T_L increases with We for all structures. This result is consistent with the few known experimental studies of dynamic Leidenfrost temperatures [10, 20] and can be understood by comparing the vapor pressure (which increases with surface temperature) and the inertial pressure of the drop (which is proportional to We). To maintain a droplet impact in the film boiling regime, an increased We requires a higher vapor pressure (hence higher surface temperature), in accord with our experimental results.

On the other hand, increasing the pillar height effectively lowers T_L if the pillar interspacing I and width W are kept fixed. For instance, compared to

Figure 4.5 – (a) Dynamic Leidenfrost temperature for structured surfaces with pillar interspacing $I = 20 \mu\text{m}$: R_{20}^2 (upward triangles), R_{20}^4 (squares), R_{20}^8 (diamonds). The dynamic Leidenfrost temperature for smooth surfaces (solid line) is shown as a reference. (b) Dynamic Leidenfrost temperature for structured surfaces with pillar interspacing $I = 4 \mu\text{m}$: R_4^2 (downward triangles), R_4^4 (squares), R_4^8 (diamonds). (c) The quantity $(T_L - T_b)\alpha_e$ for structured surfaces with pillar interspacing $I = 20 \mu\text{m}$. (d) The quantity $(T_L - T_b)\alpha_e$ for structured surfaces with pillar interspacing $I = 4 \mu\text{m}$.

the smooth surface, the surface R_{20}^2 ($I = 20 \text{ } \mu\text{m}$, $H = 2 \text{ } \mu\text{m}$) reduces T_L by roughly 50 K for $6 \leq \text{We} \leq 270$, while the surface R_{20}^8 ($I = 20 \text{ } \mu\text{m}$, $H = 8 \text{ } \mu\text{m}$) causes a larger reduction in T_L , which is about 100 K for $10 \leq \text{We} \leq 890$.

As a possible explanation for the dependence of T_L on pillar height H , we first note that varying H modifies the solid's total surface area: for the geometrical configuration of our structured surfaces (see Fig. 4.1), the total area per unit projected area (herein referred to as the enhancement coefficient) is $\alpha_e = 1 + \pi WH/(W + I)^2$. If convective heat transfer is neglected, then the heat transfer rate to the liquid is proportional to the surface enhancement coefficient α_e and the superheat $\Delta T = T - T_b$ between the solid and the liquid surface, which is assumed at the saturation temperature T_b . Now consider two structured surfaces having different pillar heights (the corresponding enhancement coefficients are $\alpha_{e,1}$ and $\alpha_{e,2}$); the temperature of each surface (for the same Weber number) is set at its dynamic Leidenfrost temperature, i.e. $T_{L,1}$ and $T_{L,2}$. Given the same impact conditions (i.e. the same Weber number), we may further assume that the heat required to generate enough vapor to sustain an impacting droplet is insensitive to the pillar height. As a result, we can write $(T_{L,1} - T_b)\alpha_{e,1} = (T_{L,2} - T_b)\alpha_{e,2}$. In other words, for the same Weber number, the quantity $(T_L - T_b)\alpha_e$ is the same for surfaces having different pillar heights. To test our arguments, in Fig. 4.5c, we plot $(T_L - T_b)\alpha_e$ versus We for surfaces having the same interspacing $I = 20 \text{ } \mu\text{m}$, but different heights (from 2 μm to 8 μm). All of the individual data sets collapse onto a master curve.

For surfaces having pillar interspacing $I = 4 \text{ } \mu\text{m}$, reductions in T_L are also observed for surfaces with pillar heights from 2 μm to 8 μm , although with larger data scattering (Fig. 4.5b). If we compare the quantity $(T_L - T_b)\alpha_e$, there is an agreement between surfaces with pillar height $H = 2 \text{ } \mu\text{m}$ and $H = 4 \text{ } \mu\text{m}$ (Fig. 4.5d). However, the data for pillar height $H = 8 \text{ } \mu\text{m}$ (R_4^8) show considerable deviation from the cloud of data points obtained from surfaces with lower pillar heights (i.e. $H = 2 \text{ } \mu\text{m}$ and $H = 4 \text{ } \mu\text{m}$). We attribute this discrepancy to the overestimation of the area through which heat is transferred, that is, in the case that H is larger than I (as for surface R_4^8), the liquid may not fully penetrate the gap between pillars. Thus, the solid's total surface area is larger than the area through which the heat is transferred to the liquid. In order to determine the necessary condition for the liquid to penetrate the space between pillars, the inertial pressure of the liquid (which scales with $\rho_l V_0^2$) has to overcome the opposing capillary pressure (which scales with σ/I) [21]. Then, by invoking the Weber number definition, this condition can be written

as: $We \equiv \rho_l V_0^2 D_0 / \sigma > D_0 / I$. If we take the typical drop diameter in our experiments $D_0 \approx 2.2$ mm and $I = 4$ μ m for the surface R_4^8 , then the minimum Weber number for the liquid to fully wet the solid surface is $We \approx 550$, which is beyond the explored range of Weber number for this surface. As a result, the overestimation of the quantity $(T_L - T_b)\alpha_e$ of the surface R_4^8 compared to that of surfaces having smaller pillar heights does not contradict our argument presented above.

We note that there is a discrepancy between the quantity $(T_L - T_b)\alpha_e$ for smooth surfaces and that for structured surfaces, as shown in Figs. 4.5c and 4.5d. This discrepancy signifies that the reduction of T_L is not only resulted from the enhancement of the surface area, but also due to another mechanism that is not captured by our simple argument. This is most effectively demonstrated by comparing T_L for smooth surfaces and that for the surface R_{20}^2 : while the surface enhancement coefficient for R_{20}^2 is only 1.06 (i.e. an increase of 6% in surface area compared to that of smooth surfaces), a significant reduction in T_L (≈ 50 K) occurs. This observation suggests that a different physical process may be playing a role. One possibility is that the liquid may not penetrate the gap between pillars. In this case, the liquid would be separated from the top of the pillars by a very thin vapor layer through which heat conduction would be very large, while heat exchange over the rest of the surface would be relatively insignificant. The outward flow of the vapor generated under the drop is inhibited by the pillars, so that the vapor pressure sufficient to support the drop builds up at a lower surface temperature.

Even though the dominant physical mechanism is still unclear, the experimental evidence permits us to conclude that the dynamic Leidenfrost temperature on structured surfaces is reduced with increasing pillar height for given pillar interspacing and width. While results obtained on surfaces with uncontrolled roughness (e.g. particle-blasted surfaces, rough sanded surfaces, etc.) have not always shown consistent dependencies on the characteristics of surface features [20], our data show that structured surfaces offer a higher degree of control over the behavior of impacting droplets. This result suggests that T_L can be controlled accurately by manipulating the structure's geometry.

4.4 Film boiling regime: residence time

When the impact velocity is not too high, a drop impacting a superheated surface above the Leidenfrost temperature is observed to spread and then to bounce off the surface without splashing. For a certain time during this

Figure 4.6 – (a) Residence time measured for impact in the film boiling regime on different structured surfaces. (b) Residence time normalized by the period τ_0 of an oscillating drop as described in the text. The data show that τ_r/τ_0 is independent of the impact velocity. Inset: residence time as a function of the drop diameter D_0 in a log-log plot. The solid line represents the expression for the period of freely oscillating droplets by Rayleigh ($\tau_0 = (\pi/4)\sqrt{\rho_l D_0^3/\sigma}$).

process, the distance h between the bottom surface of the drop and the heated surface is below the optical resolution of our system. As an example, in Fig. 4.3b, this condition is fulfilled in all snapshots starting from the first shown snapshot to the last one. In analogy with literature on drop impact on unheated superhydrophobic surfaces, we refer to this time as the residence time τ_r . To estimate τ_r , it was observed [22], and as expected, that the spreading of droplets is generally opposed by both surface tension and viscosity. In the limit of low viscosity, the capillary effect becomes dominant. Thus τ_r can be approximated as the period of a freely oscillating drop, as calculated by Rayleigh [23]:

$$\tau_0 = (\pi/4)\sqrt{\rho_l D_0^3/\sigma}. \quad (4.1)$$

This estimate can directly be obtained (although without the prefactor $\pi/4$) by balancing inertia with capillarity. Equation (4.1) was experimentally verified for impact on unheated superhydrophobic surfaces [22].

Due to the apparent similarity between impact on Leidenfrost surfaces and impact on unheated superhydrophobic surfaces, it was suggested that the residence time of impact on Leidenfrost surfaces may also be approximated by Rayleigh’s expression for the period of a freely oscillating drop [23]. Indeed, it was shown in several studies [11, 12, 24, 25] that the measured residence time

can be approximately described by the expression $\tau_r = C\sqrt{\rho_l D_0^3/\sigma}$, where C is a constant. These studies were, however, limited to the case of superheated smooth surfaces or surfaces having uncontrolled roughness. In Fig. 4.6a, we present a plot of the residence time measured for impact on smooth and different structured surfaces in the film boiling regime under various impact conditions. The drop size was varied from 1.7 mm to 2.6 mm and the impact velocity from 0.5 m/s to 2 m/s. The impact velocity was limited to 2 m/s to prevent disintegration of small droplets during spreading (in which case Rayleigh's approximation of the residence time is not applicable). The variations in drop size and impact velocity cause τ_r to vary from 7 ms to 12 ms. However, when normalized by τ_0 , the data of residence time for impact on all different surfaces in the film boiling regime collapse on a horizontal line (Fig. 4.6b), implying that in this low velocity regime the impact velocity is an insignificant contributing factor to variations of the residence time. Further, the measured residence time on Leidenfrost surfaces is consistent with τ_0 for different drop sizes (as shown in the inset of Fig. 4.6). Thus, we conclude that the residence time of droplet impact on surfaces in the film boiling regime can be approximated by the period of a freely oscillating drop and is insensitive to the surface temperature, the impact velocity, and the structure's geometry.

4.5 Film boiling regime: spreading dynamics

In this section, we focus on the deformation of droplets impacting superheated surfaces in the film boiling regime without splashing and how it is affected by the structure's geometry and surface temperature. Upon impact, these drops spread and then retract. These deformation processes are best quantified using the diameter D of the deforming drop. Note again that the drop does not touch the solid surface, as shown in the interferometric observations in Fig. 4.3b. In Fig. 4.7, we show a plot of D/D_0 as a function of time t for different structured surfaces. The surface temperature was set at $T = 400^\circ\text{C}$, and the Weber number at $We = 33$, for which impacting droplets on all surfaces were in the film boiling regime. We also show the data measured for water droplets impacting an unheated superhydrophobic surface (with the same impact conditions) as a comparison. For impact on superheated surfaces, D/D_0 is not affected by changes in structured surfaces. However, compared to the spreading on unheated surfaces, it is significantly larger around the peak although the expansion time, defined as the time for the contact diameter to reach its maximum value, is only slightly larger. As a result, it is suggested

Figure 4.7 – Diameter D of the deforming drop normalized by the initial drop diameter D_0 versus time t measured for droplets impacting different surfaces with the diameter $D_0 = 2.4$ mm, velocity $V_0 = 1.0$ m/s, and Weber number $We = 33$. The structured surfaces (R_{20}^2 (solid upward triangles), R_{20}^4 (solid squares), R_{20}^8 (solid downward triangles)) have the same temperature $T = 400$ °C to bring droplet impact in the film boiling regime. The data for impact on an unheated superhydrophobic surface (solid circles) are collected under the same impact conditions.

that the maximum spreading diameter of impacting droplets on superheated surfaces in the film boiling regime is not strongly influenced by the structure's geometry and is higher than that on unheated surfaces.

We now verify the independence of the maximum spreading diameter D_m on the structure's geometry for droplets impacting on Leidenfrost surfaces with varying Weber number. Indeed, measurements of the spreading factor $\Gamma = D_m/D_0$ in the film boiling regime (Fig. 4.8) clearly show that it is not only independent of the structure's geometry, but also of the surface temperature. In Fig. 4.9, we show a log-log plot of D_m/D_0 versus We for droplet impact in the film boiling regime. The plot includes six sets of data obtained on six different structured surfaces (Table 4.1) and one on smooth surfaces [10]. All the data fall on the same curve despite wide variations in structured surfaces and temperature. Compared to the case of impact on unheated surfaces,

Figure 4.8 – Spreading factor D_m/D_0 versus Weber number for different structured surfaces and different temperatures in the film boiling regime. (a) Spreading factor measured for surfaces with pillar interspacing $I = 20 \mu\text{m}$. For each surface, we group data for different temperatures into two sets: ΔT_1 (240°C ≤ T < 315°C) and ΔT_2 (315°C ≤ T < 390°C). (b) Spreading factor measured for surfaces with pillar interspacing $I = 4 \mu\text{m}$. Data for each surface are grouped into four sets: ΔT_1 (240°C ≤ T < 315°C), ΔT_2 (315°C ≤ T < 390°C), ΔT_3 (390°C ≤ T < 465°C), and ΔT_4 (465°C ≤ T < 540°C). We show data in two figures for better clarification. All the data however collapse on a master curve as shown in Fig. 4.9.

the scaling of the maximum spreading diameter on Leidenfrost surfaces is steeper than the $1/4$ -scaling, which holds for unheated surfaces of various wettability and roughness [26–28]. Note that a scaling argument for the maximum spreading diameter of impacting droplets on an unheated post of the same diameter was also reported with experimental support and is in the form $D_m/D_0 - 1 \sim We^{1/2}$ [29].

To explain this universal behavior in our case, we seek to derive the spreading factor $\Gamma = D_m/D_0$ of droplets impacting on solid surfaces in the film boiling regime. The liquid during impact is modeled as a disc and spreads on a vapor layer generated by liquid evaporating from the bottom of the disc (see Fig. 4.10). If we further assume that the heat required to evaporate the liquid is conducted through the vapor layer of thickness $\sim h$ and area $\sim D_m^2$, it is then possible to approximate the rate of heat transfer to the liquid using Fourier’s law: $\dot{Q} = k_v \Delta T D_m^2 / h$, where k_v is the thermal conductivity of vapor, and ΔT is the temperature difference between the solid and the liquid surfaces (the liquid surface is assumed at boiling temperature). The rate of vapor generation is then $\dot{m} \sim \dot{Q} / L \sim k_v \Delta T D_m^2 / Lh$, where L is the latent heat of evaporation. This generation rate balances with the rate of vapor escaping the gap between

Figure 4.9 – Spreading factor $\Gamma = D_m/D_0$ for droplet impact on different structured surfaces in the film boiling regime. We also show the spreading factor for impact on smooth Leidenfrost surfaces as a comparison [10]. The dashed line represents the scaling $\Gamma \sim We^{1/4}$, which holds for unheated surfaces. The solid line represents the scaling $\Gamma \sim We^{3/10}$ resulted from the vapor-induced spreading mechanism (Eq. (4.11)). The dashed-dotted line represents the scaling $\Gamma \sim We^{1/2}$ resulted from the balance between the drop’s initial kinetic energy and the change in its surface energy at maximum deformation.

the liquid and the solid surfaces, $\dot{m} \sim \rho_v U h D_m$, where ρ_v is the vapor density, and U is the radial velocity of the vapor flow. Hence:

$$\frac{k_v \Delta T}{Lh} D_m^2 \sim \rho_v U h D_m. \quad (4.2)$$

The vapor flow is driven by a pressure increase ΔP under the drop. For an impacting droplet we take the dynamic pressure $\Delta P \sim \rho_l V_0^2$. Since the vapor thickness is very small (for a droplet impacting with $We \approx 3$, the vapor thickness is roughly $3 \mu\text{m}$ [10]), the vapor flow is viscous and can be described by the lubrication approximation $\partial_x P \sim \mu_v \partial_z^2 U$, where ∂_x and ∂_z are derivatives in the radial and vertical directions, respectively, and μ_v is the viscosity of the vapor. By taking D_m and h the typical length scales in the horizontal and

Figure 4.10 – Schematic to derive the spreading factor. A drop of diameter D_0 and impact velocity V_0 falls on a heated surface with temperature T . The drop spreads on a vapor layer of thickness h and takes the shape of a pancake. The vapor flows radially outward with velocity U due to the pressure increase ΔP (as compared to outside ambient pressure) and drags the liquid along. At maximum spreading, the diameter and thickness of this pancake are D_m and H respectively.

vertical directions respectively, we thus have:

$$\frac{\rho_l V_0^2}{D_m} \sim \mu_v \frac{U}{h^2}. \quad (4.3)$$

The viscous vapor flow exerts a drag force on the liquid. This drag force can be approximated as $\tau_v D_m^2 \sim \mu_v (U/h) D_m^2$, where τ_v is the viscous shear stress of the vapor flow. The drag force is then balanced by capillarity, $(\sigma/H_m) D_m^2$. Here, H_m is the thickness of the liquid pancake at its maximum spreading and is related to the maximum diameter D_m by volume conservation, $H_m D_m^2 \sim D_0^3$. Hence, the force balance becomes:

$$\sigma \frac{D_m^2}{D_0^3} \sim \mu_v \frac{U}{h}. \quad (4.4)$$

Equations (4.2), (4.3), and (4.4) allow us to determine the three unknowns D_m , U , and h . We can rewrite these equations in non-dimensional forms using the dimensionless variables $\Gamma = D_m/D_0$, $\tilde{U} = U/V_0$, $\tilde{h} = h/D_0$. The relevant dimensionless numbers are the Weber number We , the Stokes number $St = \rho_l D_0 V_0 / \mu_v$, and the ‘‘Peclet’’ number $Pe = \rho_v L D_0 V_0 / k_v \Delta T$. The mass balance (Eq. (4.2)) then reads

$$\Gamma^2 \sim \tilde{h}^4 St Pe, \quad (4.5)$$

the lubrication approximation (Eq. (4.3))

$$\Gamma \tilde{U} \sim \text{St } \tilde{h}^2, \quad (4.6)$$

and finally the force balance (Eq. (4.4))

$$\tilde{U} \sim \frac{\text{St}}{\text{We}} \Gamma^2 \tilde{h}. \quad (4.7)$$

This system of equations can be solved to obtain the final result

$$\Gamma \sim \frac{\text{We}^{2/5}}{\text{St}^{1/10} \text{Pe}^{1/10}}, \quad (4.8)$$

$$\tilde{h} \sim \frac{\text{We}^{1/5}}{\text{St}^{3/10} \text{Pe}^{3/10}}, \quad (4.9)$$

$$\tilde{U} \sim \frac{\text{St}^{1/2}}{\text{Pe}^{1/2}}. \quad (4.10)$$

If we now assume that all the dimensionless numbers are varied only by changing the impact velocity V_0 , then the velocity dependence of Γ , $\tilde{h}$, and $\tilde{U}$ can be expressed through the Weber number, resulting in

$$\Gamma \sim \left(\frac{\mu_v k_v \Delta T}{\rho_v \sigma L D_0} \right)^{1/10} \text{We}^{3/10} = \beta \text{We}^{3/10}, \quad (4.11)$$

$$\tilde{h} \sim \beta^{3/10} \text{We}^{-1/10}, \quad (4.12)$$

$$\tilde{U} \sim \left(\frac{\rho_l k_v \Delta T}{\rho_v \mu_v L} \right)^{1/2}, \quad (4.13)$$

where β in Eqs. (4.11) and (4.12) is a pre-factor that depends on the drop size D_0 , among other parameters. The dependence of β on D_0 is however very weak, and hence a small change in the drop size can be assumed not to affect the scaling law for the dependence of Γ on the Weber number (in our experiments, the mean diameter of droplets is 2.2 mm, with a standard deviation $\approx 10\%$).

For large We , the experimental result is consistent with the scaling exponent $3/10$ for the spreading factor Γ (see Fig. 4.9), whereas for smaller We , it deviates from the $3/10$ -scaling and in fact is closer to the $1/4$ -scaling for unheated surfaces. We attribute the discrepancy between the experimental data at low Weber number and the $3/10$ -scaling to the fact that the drag force induced by

Figure 4.11 – Jet formation during impact of a water droplet on a structured surface ($I = 4 \mu\text{m}$, $H = 2 \mu\text{m}$) heated to 300°C . The diameter of the drop is 2.2 mm and the impact velocity is 1.3 m/s .

the vapor flow is less dominant if the liquid is not strongly forced against the solid surface, which is the case in this low Weber regime.

Let us discuss the dependence of the spreading factor Γ on the superheat $\Delta T = T - T_b$, where T_b is the boiling point of the liquid. In our experiments, the surface temperature T is varied between 240°C and 540°C . Correspondingly, ΔT is varied from 140 K to 440 K . It is then predicted by Eq. (4.11) that increasing ΔT from 140 K to 440 K only causes Γ to increase 12% . This variation is within the experimental scatter of the data (see Fig. 4.9), and hence is consistent with the weak dependence of Γ on surface temperature that is observed experimentally.

The scaling laws for the normalized vapor thickness $\tilde{h}$ and the vapor velocity $\tilde{U}$ (Eqs. (4.9) and (4.10), respectively) are of great importance as they explicitly reveal the role of different parameters involved in the vapor flow dynamics. For instance, it is predicted by Eq. (4.10) and the resulting Eq. (4.13) that the vapor velocity U does not depend on the diameter of the drop and is linearly proportional to the impact velocity V_0 . This is a crucial prediction for applications such as cleaning of hot metal using sprays.

4.6 Contact boiling regime: jet formation

In this section, we describe the surprising formation of upward-directed liquid jets that emerge during the spreading phase of the droplets in the contact

Figure 4.12 – (a) Jet height of droplets impacting structured surfaces in contact boiling regime versus the pillar height H of the structure. The impact velocity $V_0 = 1.65$ m/s ($We = 88$) and the surface temperature $T = 300^\circ\text{C}$ were kept fixed. The error bars for each surface represent the standard deviation of 25 experiments of the same impact conditions. (b) Jet height versus the ratio H/I for all surfaces. (c) Schematic showing the structure’s geometry.

boiling regime on structured surfaces. We never observed similar jets in the case of smooth surface. The occurrence of the jet and its velocity vary depending on the surface structures, surface temperature, and impact velocity. That this type of jets occurs during the spreading stage makes the phenomenon very different from those that occur during the retracting stage of impact on unheated surfaces [30]. In Fig. 4.11, we show a series of images taken during impact of a water droplet falling with velocity 1.3 m/s on a structured surface heated to 300°C (the time origin $t = 0$ ms is taken as the moment the drop first touches the surface). Shortly after the initial contact, the liquid at the bottom of the droplet spreads out horizontally, whereas the top surface still remains spherical. At the same time, a stream of small droplets shoot up from the base of the spherical cap as shown in the image taken at $t = 0.83$ ms. These droplets are presumably caused by the bursting of vapor bubbles forming on the lower liquid surface.

The ejection of small droplets is then followed by a liquid jet shooting vertically upward from the center of the flattened drop. One possible explanation is that the expansion of vapor bubbles underneath the spreading drop applies a collective pressure to the liquid bulk and eventually causes the liquid in the middle to shoot up. On the other hand, the shape of the jet may suggest that it is caused by a converging liquid motion toward the axis of the flattened drop. A possible cause are vapor bubbles forming on the pillars which might penetrate through the lower surface of the liquid. Since, due to the geometry, more pillars would penetrate the liquid with increasing distance from the axis of the drop, a pressure gradient favoring an inward motion of the liquid might be generated in this way. Both mechanisms lead to the conclusion that the effect is more pronounced with increasing pillar height and decreasing spacing. These expectations are supported by Fig. 4.12, which show the maximum jet height h_{jet} for impacting droplets on different structured surfaces. The surface temperature and impact velocity are kept fixed. For the same interspacing, it is evident that the jet height is larger as the pillar height is increased. Further, when the jet height is plotted against the aspect ratio H/I of all the structured surfaces (see Fig. 4.12b), it is shown that h_{jet} increases with H/I .

4.7 Conclusions

In conclusion, we have determined the dynamic Leidenfrost temperature for various structured surfaces and compared it with that for smooth surfaces. For a fixed interspacing and pillar width, the dynamic Leidenfrost temperature decreases with increasing pillar height. This result shows that it is possible to control the dynamic Leidenfrost temperature of impacting droplets, hence their characteristic boiling behaviors, using structured surfaces.

We also investigated the hydrodynamic behaviors of impacting droplets on these structured surfaces in the film boiling regime. We show that the residence time of droplets is independent of the impact velocity, structures, or surface temperatures and can be approximated by Rayleigh's result for the period of a freely oscillating droplet, Eq. (4.1).

Regarding the spreading dynamics above the dynamic Leidenfrost temperature, we show experimentally that the maximum spreading factor follows a universal behavior regardless of changes in the surface temperature and structure geometry. We theoretically derive scaling laws for the spreading factor, the vapor thickness and velocity with the main assumption that the vapor escaping from the gap between the liquid and the solid surfaces drags the

liquid radially outward. The scaling law for the spreading factor $\Gamma \sim \text{We}^{3/10}$ was shown to be in accord with the experimental data at high Weber number where the vapor-induced mechanism becomes dominant. The scaling laws for the vapor thickness are still open to be tested experimentally as they may hold important implications for applications that utilize vapor flows.

In the contact boiling regime, the emergence of liquid jets shooting vertically upward is a surprising feature of impacting droplets on structured surfaces. We provide a detailed description of these liquid jets, and show that for a fixed temperature and Weber number, the jet shoots higher with increasing pillar height. The mechanism of the jet formation as well as the dependence of its intensity on the impact conditions, however, still remain open questions and need further investigations.

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5

Leidenfrost temperature increase for droplets impacting carbon-nanofibers*

Droplets impacting a superheated surface can either exhibit a contact boiling regime, in which they make direct contact with the surface and boil violently, or a film boiling regime, in which they remain separated from the surface by their own vapor. The transition from the contact to the film boiling regime depends not only on the temperature of the surface and the kinetic energy of the droplet, but also on the size of the structures fabricated on the surface. Here we experimentally show that surfaces covered with carbon-nanofibers delay the transition to film boiling to much higher temperature compared to smooth surfaces. We present physical arguments showing that, because of the small scale of the carbon fibers, they are cooled by the vapor flow just before the liquid impact, thus permitting contact boiling up to much higher temperatures than on smooth surfaces. We also show that, as long as the impact is in the film boiling regime, the spreading factor of impacting droplets is consistent with the $We^{3/10}$ scaling (with We the Weber number), as predicted for large We by a scaling analysis.

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5.1 Introduction

Spray cooling is an effective heat transfer mechanism as it is capable of delivering spatially uniform and high heat transfer rates [1–3]. An important new application of this technology is in electronic cooling, where the growing power consumption and decreasing sizes pose increasingly challenging heat dissipation demands [4, 5]. Other common situations in which cold drops impact hot surfaces are found in internal combustion engines [6, 7], quenching of aluminum and steel [8], fire suppression [9, 10] and others.

In all these applications a stream of fine droplets dispensed, e.g. from a nozzle impinges on a solid surface and cools it by a combination of sensible heat absorption and latent heat of vaporization. Due to the inherent complexity of the phenomenon and the large number of parameters involved, such as droplet size, velocity distribution, droplet number density and material properties, many aspects of the physical mechanisms involved still remain incompletely understood [1, 11, 12].

A fundamental understanding of the impact of an individual droplet on superheated surfaces is the first step toward a better understanding and eventual optimization of the process. Various aspects of this particular problem have been investigated, such as the effect of droplet size, velocity, physical properties [13, 14], and surface roughness [15, 16], the transition between different boiling regimes [16–22], the surface temperature change and heat transfer during impact [15, 23–25], the residence time of the impacting droplet [16, 26], the spreading factor [16, 21, 27] and others.

An important quantitative feature of the phenomenon is the transition temperature T_L between the contact boiling regime, where the liquid makes direct contact with the heated surface, and the film boiling regime, where a stable vapor layer between the liquid and the surface is formed during impact. As the rate of heat transfer in the film boiling regime is significantly reduced due to the poor thermal conductivity of the vapor layer, this regime should be avoided for applications that require high heat transfer rates. Methods to increase T_L , or delay the onset of the film boiling regime, are therefore of great interest for such applications.

Recently, surfaces covered with nanofibers were shown to effectively enhance the heat transfer from the surface to a liquid in contact with it [24, 28]. In particular, it was reported that for impacting ethanol droplets on surfaces covered with *nanofiber* mats, the film boiling behavior was not observed even when the surface temperature was as high as 300 °C [25], which implies

that the transition temperature to film boiling is *increased* compared to that observed on smooth surfaces. This is in marked contrast with the impact on surfaces covered with *microstructures*, for which the transition temperature is considerably *decreased* compared to a smooth surface [16]. Indeed, numerous questions regarding the effects of nanostructures on the transition temperature are still open. First of all, why do nanofibers cause a higher T_L compared to that on smooth surfaces? And, further, what is the transition temperature T_L on this type of surfaces? How does it change with the size of the nanostructures on the surfaces?

To answer these questions, in this chapter we study the impact of droplets on heated surfaces covered with carbon nanofibers (CNFs), which are carbonaceous structures grown by catalytic vapor deposition of hydrocarbons. This type of nanostructures is well-known for their unique physical and chemical properties with a tunable morphology (the diameter can be varied from a few to hundreds of nanometers, the height can be controlled from a few micrometers to millimeters), which in turn can be exploited for tuning the roughness, porosity, and surface area [29].

We use two types of CNF surfaces corresponding to two different typical fiber lengths and a smooth silicon surface. For each type of surface, we determine the transition temperature and its dependence on the impact velocity. We propose a quantitative explanation of the effect of nanofibers on the transition temperature T_L . Furthermore, for impact of droplets in the film boiling regime, we measure the spreading factor and compare our data with existing models.

5.2 Experimental details

5.2.1 Synthesis of carbon nanofiber layers

Carbon nanofibers (CNFs) were synthesized on oxidized silicon wafers (p-type, 5-10 Ohm cm resistivity, 100 mm diameter, 525 ± 25 μm thickness, {100} crystal orientation; Okmetic Finland) using nickel (Ni) thin film as catalyst. First, a SiO_2 layer of 220 nm thickness was grown via wet oxidation (45 min, 1000 °C) on these silicon substrates. Second, a pattern was defined in spin-coated photoresist (Olin, 906-12), resulting in unmasked squares of 8 mm $\times$ 8 mm, by means of standard UV lithography (EVG 620). Further, a 10 nm tantalum layer followed by a 25 nm nickel layer was deposited via electron-beam evaporation. Finally the samples were subjected to an ultrasonic lift-off step in acetone (> 20 min; VLSI 100038, BASF), followed by rinsing in water and spin drying.

Figure 5.1 – Scanning electron microscope (SEM) images showing side views of the carbon nanofiber (CNF) layers with a synthesis time of (a) 11 min and (b) 14 min. The arrow in (b) indicates the height H of the CNF layer. The corresponding top-view SEM images are shown in (c) for a synthesis time of 11 min and in (d) for a synthesis time of 14 min. The bar represents 1 μm in (a), (c), and (d), and 2 μm in (b).

These nickel-coated substrates were diced into 1 cm $\times$ 1 cm samples (Disco DAD-321 dicing machine). To remove organic contaminants, these samples were ultrasonically cleaned in acetone (10 min, Branson 200 ultrasonic cleaner) and de-ionized water (2 min, 25 $^{\circ}\text{C}$) [30].

After drying with synthetic air, the samples were placed centrally on a flat quartz boat inside a quartz reactor and were loaded into a horizontal oven equipped with three temperature controllers along it. Nitrogen (N_2 ; 99.999%, INDUGAS N.V.) was used as carrier gas during heating, pretreatment, CNF synthesis and cooling. First, the temperature was increased (5 K/min) to 500 $^{\circ}\text{C}$. Second, the samples were pretreated with 20 vol. % of hydrogen (H_2 ; 99.999%, INDUGAS N.V.) for 2 hours at a total flow rate of 50 mL/min in order to reduce the passivated Ni thin film. Subsequently the temperature was increased (5 K/min) to 635 $^{\circ}\text{C}$, at which temperature the CNF synthesis was

performed via catalytic vapor decomposition using 25 vol. % ethylene (C_2H_4 ; 99.95% Praxair, Inc.) and 6.25 vol. % H_2 in a total flow rate 100 mL/min. Finally the samples were cooled down to room temperature (10 K/min).

Two sets of samples were used for the droplet impact studies. One set was obtained after a CNF synthesis time of 11 min, resulting in a CNF layer thickness $H \approx 3.4 \pm 0.3 \mu\text{m}$. The other set was obtained after a CNF synthesis time of 14 min, resulting in a CNF layer thickness of $H \approx 7.5 \pm 0.7 \mu\text{m}$. More details of the influence of synthesis time on CNF layer thickness have been reported previously [30]. These samples will be termed as CNF(3.5) and CNF(7.5), respectively. Figure 5.1 shows representative scanning electron microscope (SEM) images with the side views (Figs. 5.1a and 5.1b) and top views (Figs. 5.1c and 5.1d) of the surfaces CNF(3.5) and CNF(7.5).

The thickness H of the CNF layers was determined using five representative cross-sectional SEM images taken at various positions on the sample (ten height measurements were averaged per SEM image). The width of the nanofibers ranges from 32 nm to 220 nm with an average value of 127 nm. Using the thickness of the CNF layers, the projected surface area of the samples ($A = 0.64 \text{ cm}^2$), the density of graphite ($\rho_n = 2267 \text{ kg/m}^3$, together with the total weight M_t of all the carbon nanofibers on each sample ($M_t \approx 120 \mu\text{g}$ for CNF(3.5) and $M_t \approx 190 \mu\text{g}$ for CNF(7.5)), we can estimate the porosity $\phi = 1 - M_t/(\rho_n l A)$ of each sample: $\phi \approx 0.76$ and $\phi \approx 0.83$ for CNF(3.5) and CNF(7.5), respectively.

5.2.2 Experimental method

A schematic diagram of the experimental setup is shown in Fig. 5.2. All droplet impact experiments were performed with FC-72 (3M Fluorinert Electronic Liquid), a dielectric fluid commonly used in electronics cooling applications. The liquid has a boiling point $T_b = 56^\circ\text{C}$, a density $\rho_l = 1680 \text{ kg/m}^3$, and a surface tension $\sigma = 10 \text{ mN/m}$. We generate droplets by using a syringe pump (PHD 2000 Infusion, Harvard Apparatus) to inject liquid into a small fused silica needle, where the droplets are formed at the tip. The flow rate is kept at a small value ($\approx 0.1 \text{ mL/min}$) so that droplet detachment from the needle is due only to gravitational force, hence keeping the droplet size uniform. After detaching from the needle, a droplet falls on the target surface placed on a brass plate with a cartridge heater and a thermocouple (Omega, Inc.) embedded inside. The surface temperature T was set by a controller and was varied between 60°C and 450°C . This temperature was also measured independently by a surface temperature probe (Tempcontrol B.V.). The difference between

Figure 5.2 – (a) Schematic of the experimental setup used to observe the characteristic behavior of droplets impacting heated surfaces. The surface of interest is placed on a heater, which can be heated up to 500 °C. FC-72 droplets of diameter D_0 impact the heated sample with impact velocity V_0 . The behavior of the impacting droplets is recorded from the side by a high-speed camera. From the recordings, D_0 , V_0 , and the maximum spreading D_m of the droplet can be measured. (b) Series of snapshots of an impacting droplet in the film boiling regime showing how D_m is measured as the maximum horizontal extension of the droplet.

the controller's set point and the surfaceprobe measurement was less than 3 K. Thus we take the set point of the controller as the surface temperature T of the surface.

Recordings of the impact events were made with a high-speed camera (Photron Fastcam SA1.1) (see Fig. 5.2). From these high-speed recordings, the boiling behaviors were analyzed, and the droplet diameter D_0 , the impact velocity V_0 and the maximum spreading diameter D_m (see Fig. 5.2) were measured. From the measured diameter and velocity, we calculated the Weber number $We = \rho_l D_0 V_0^2 / \sigma$, which is a dimensionless number that characterizes the droplet's kinetic energy compared to its surface energy. The impact velocity V_0 was varied by changing the needle's height. Impact events were repeated at least three times for every combination of V_0 and T to test reproducibility of the experiment.

Figure 5.3 – (a) Representative images showing the characteristic boiling behavior of an impacting FC-72 droplet on a 7.5 μm-thick CNF surface in the contact boiling regime, $T = 200^\circ\text{C}$. The diameter of the impacting droplet is $D_0 = 1.1$ mm, the impact velocity $V_0 = 1.0$ m/s, and the Weber number $We = 154$. (b) Representative images of an FC-72 droplet with the same diameter and velocity impacting the same surface as in (a), but at the higher surface temperature, $T = 400^\circ\text{C}$. In this case, the impact is in the film boiling regime.

5.2.3 Characterization of boiling behavior

By varying the surface temperature between 60 °C and 450 °C and the Weber number between 10 and 1000, we observed two characteristic boiling behaviors: contact boiling and film boiling. In Fig. 5.3 we show two series of images to illustrate the difference between these two regimes. The essential difference between the two is whether or not the liquid makes direct contact with the heated surface during impact [21, 22, 31]. In the contact boiling regime (Fig. 5.3a), as the pressure of the vapor generated underneath the droplet is not sufficient to support the droplet's dynamic pressure, the liquid touches the heated surface and quickly boils due to the high heat flux through the contact area. The recorded snapshots show the small droplets ejected as a result of the boiling process. In contrast, an impacting droplet in the film boiling regime is separated from the heated surface by a developing vapor layer (see Fig. 5.3b). This vapor layer insulates the droplet during the impact time, hence prevents the liquid from boiling violently.

By carefully analyzing the recorded movies of impacting droplets, we categorized the impact as being in the film boiling regime when droplet ejection or vapor bubble generation were not observed.

5.3 Results and discussions

5.3.1 Dynamic Leidenfrost temperature

In Fig. 5.4, we show phase diagrams of the characteristic boiling behavior of impacting droplets on smooth silicon surfaces, CNF(3.5), and CNF(7.5), respectively. The temperature ranges were 60 °C to 250 °C for the smooth silicon surfaces, 60 °C to 300 °C for the CNF(3.5) surfaces, and 100 °C to 450 °C for the CNF(7.5) surfaces. In each phase diagram, there is a clear transition between the contact and the film boiling regimes. This transition temperature is marked by a solid line, with the vertical bars indicating the intermediate region where both boiling behaviors were observed. The transition temperature, known as the dynamic Leidenfrost temperature T_L , increases with increasing kinetic energy of impacting droplets. This dependence of T_L on We is qualitatively similar to that found previously for droplets impacting on smooth and micro-structured surfaces [15, 16, 21], and is expected: The increasing momentum of the impact forces the droplet into contact with the surface at larger and larger temperature.

Figure 5.4 – (a) Phase diagram showing the characteristic boiling behaviors of impacting FC-72 droplets on smooth silicon surfaces. The contact boiling regime (red crosses) and film boiling regime (open blue circles) are separated by a transition band, indicated by the vertical bars, where both characteristic behaviors were observed. (b) Phase diagram for surfaces covered by a 3.5 μm -thick CNF layer. (c) Phase diagram for surfaces covered by a 7.5 μm -thick CNF layer. Note the much larger temperature ranges in (b) and (c).

Figure 5.5 – Dynamic Leidenfrost temperature (transition from contact to film boiling) for smooth silicon, and surfaces covered by a 3.5 μm - and a 7.5 μm -thick layer of carbon nanofibers.

These results, however, are in stark contrast with those found for smooth and microstructured surfaces in two respects, as can be seen from Fig. 5.5, in which T_L for the smooth and CNF surfaces is compared. The first unexpected finding is that, while T_L is lower for microstructured surfaces as compared with smooth ones [16], it is actually *higher* in the case of carbon nanofibers. For example, for $We = 100$, T_L for the smooth surface is 110 $^{\circ}C$, whereas for CNF(3.5) and CNF(7.5) it increases to 250 $^{\circ}C$ and 350 $^{\circ}C$, respectively. Secondly, T_L increases with nanofiber length, again in contrast with surfaces covered with micrometer-size pillars for which, for given shape and spacing, the microstructure height is inversely correlated with T_L [16]. The tentative explanation of that latter finding offered in Ref. [16] is that the surface of the impacting liquid tends to penetrate the space between the pillars. This causes the liquid surface area to increase, the more the higher the pillars. As a consequence, the vapor generation rate also increases and the film boiling regime sets in at a lower surface temperature.

As explanation of the opposite behavior found with carbon nanofibers we suggest that they are efficiently cooled by the vapor flow before the drop touches the CNF surface. To support this conjecture, in the following subsection we will estimate the time scale τ_c for the temperature of the nanofibers to cool, and compare it with the time scale τ_e the nanofiber is exposed to the vapor flow (which will be found to be somewhat larger), and also with the time scale τ_h for the heat flow inside the nanofiber (which will be found to be much larger).

5.3.2 Estimate of the relevant time scales

We start with the estimate for the time scale τ_c for the cooling of the nanofibers by the “vapor wind”. Since the cross section of the nanofibers is of the order of 100 nm, the time scale τ_c can be estimated by assuming their temperature to be uniform, which is the so-called lumped capacitance approximation (see e.g. [32]). This time scale can then be estimated to be

$$\tau_c \sim \frac{w\rho_n C_n}{h}, \quad (5.1)$$

in which w is the diameter of the nanofiber, ρ_n and C_n its density and specific heat, and h the heat transfer coefficient. The latter can be expressed in terms of a Nusselt number, $\text{Nu} = wh/K_v$, with K_v the vapor thermal conductivity, so that

$$\tau_c = \frac{\rho_n C_n w^2}{K_v \text{Nu}} = \frac{\rho_n C_n}{\rho_v C_v} \frac{w^2}{\kappa_v \text{Nu}}, \quad (5.2)$$

in which ρ_v , C_v , and κ_v are the vapor density, specific heat, and thermal diffusivity, respectively. The (approximate) proportionality of τ_c to the square of the fiber size is a particularly noteworthy feature of this expression. In standard correlations (see e.g. Ref. [32]), Nu is given as a function of the fluid Prandtl and Reynolds numbers. No measured value for the former seems to be available for FC-72 vapor, but it is well known that the Prandtl number of gases is close to 1 and we can safely use this estimate here. Estimation of the Reynolds number requires a value for the viscosity of the vapor which, again, does not seem to have been measured. The order of magnitude of the viscosity of many gases and vapors is 10^{-5} Pas, and this is the value we will use. The density of FC-72 vapor at the boiling point 56°C is about 11.5 kg/m^3 . Taking $w \sim 100 \text{ nm}$ and using these values we then find $\text{Re} \sim 0.1 V_v$, with V_v the vapor velocity in m/s. This quantity has been estimated in Chapter 4 of this

thesis (see Eq. (4.13)) where it was found to be of the order of

$$V_v \sim \left(\frac{\rho_l C_v \Delta T}{\rho_v L \text{Pr}_v} \right)^{1/2} V_0, \quad (5.3)$$

with ρ_l the liquid density, ΔT the liquid-surface temperature difference, L the latent heat and Pr_v the vapor Prandtl number. With $\rho_l = 1680 \text{ kg/m}^3$, $L = 88 \text{ kJ/kg}$, $C_v = 910 \text{ J/(kg K)}$, and $\rho_v = 11.5 \text{ kg/m}^3$ (values at 56°C), $\Delta T \sim 100 \text{ K}$, the impact velocity $V_0 \sim 1 \text{ m/s}$ and again taking $\text{Pr}_v \sim 1$, we find $V_v \sim 12 \text{ m/s}$ so that $\text{Re} \sim 1.2$. The Churchill-Bernstein correlation [32] then gives a Nusselt number of about 1. Use of Eq. (5.2) requires values of K_v or κ_v , neither of which seems to be available. For many gases and vapors κ_v is of the order of $10^{-5} \text{ m}^2/\text{s}$. With this estimate, taking $\rho_n \simeq 2267 \text{ kg/m}^3$, $C_n \simeq 709 \text{ J/(kg K)}$ and, again, $w \sim 100 \text{ nm}$, we find from Eq. (5.2) $\tau_c \simeq 150 \text{ ns}$.

This time scale has to be compared with the characteristic time τ_e during which the fiber is exposed to the cooler vapor until the liquid makes contact with it, which can be estimated as

$$\tau_e \sim \frac{H_v}{V_0}, \quad (5.4)$$

where $H_v \sim D_0 \text{St}^{-2/3}$ is the characteristic thickness of the vapor layer at which the drop starts being deformed due to the increasing pressure on its underside [33]. Here, as above, D_0 is the droplet diameter, V_0 is the impact velocity, and $\text{St} = \rho_l V D / \mu_v$ is the Stokes number, where μ_v is the viscosity of vapor. Hence we obtain the time during which the nanofibers are exposed to the cooler vapor flow $\tau_e \sim D_0 \text{St}^{-2/3} / V_0$. In the use of this estimate we again encounter the problem that μ_v is not available, but if we use the same estimate $\mu_v \sim 10^{-5} \text{ Pa s}$ as before and take $V_0 \simeq 1 \text{ m/s}$, $D_0 \simeq 1 \text{ mm}$, we find $\tau_e \simeq 330 \text{ ns}$, which is seen to be long enough to cause a substantial cooling of the fibers.

Of course, as the fibers are cooled by the vapor, heat flows towards their tips from the silicon substrate with a characteristic time

$$\tau_h = \frac{\ell^2}{\kappa_c}, \quad (5.5)$$

in which ℓ is the fiber length and κ_c is the thermal diffusivity of the carbon nanofibers. Since, in this experiment, the fibers had not been heat-treated, we can estimate their thermal conductivity on the basis of the results of Ref. [34] as $K_c = 4.6 \text{ W/(m K)}$ and, therefore, $\kappa_c \sim 2.86 \times 10^{-6} \text{ m}^2/\text{s}$. For

the shorter fibers $\ell \simeq 3.4 \mu\text{m}$ and, therefore, $\tau_h \sim 4 \mu\text{s}$, while for the longer fibers $\ell \simeq 7.5 \mu\text{m}$ and $\tau_h \sim 20 \mu\text{s}$. These times are much longer than both the cooling time and the exposure time to the vapor flow, which implies that the liquid encounters fibers at a much cooler temperature than the core silicon substrate. This circumstance would explain why the CNF surfaces require a higher temperature to achieve the film boiling regime compared to the smooth surfaces, and why the transition temperature increases with the fiber length.

The size of the cross section of the fibers in our experiment is close to the cross-over value at which cooling and exposure to the vapor flow have comparable time scales. It follows that fibers or, more generally, microstructures with a larger cross section would be insensitive to the cooling effect. As a check of this expectation we can apply the same estimates to the case of the microstructured surfaces studied earlier [16]. In that case the fluid was water for which, of course, all the required physical properties are well known. The microstructures had the form of silicon pillars with a square cross section of about $10 \times 10 \mu\text{m}^2$ and heights from $2 \mu\text{m}$ to $8 \mu\text{m}$. The vapor velocity estimated from Eq. (5.3), again with $\Delta T \sim 100 \text{ K}$ and $V_0 \sim 1 \text{ m/s}$, is found to be $V_v \sim 12 \text{ m/s}$. The corresponding Reynolds number is $\text{Re} \sim 6$ with a corresponding Nusselt number $\text{Nu} \sim 1.7$. In this case $\rho_n = 2330 \text{ kg/m}^3$, $C_n = 705 \text{ J/(kg K)}$, and Eq. (5.2) gives $\tau_c \sim 6.6 \text{ ms}$. The exposure time to the vapor is not very different from the previous estimate, and is therefore several orders of magnitude shorter than the cooling time. It is evident that, in this case, the vapor flow is just a small perturbation which does not have an appreciable effect on the pillar temperature.

5.3.3 Spreading factor

We devote this section to quantifying the spreading factor of impacting droplets in the film boiling regime. The spreading factor is defined as $\Gamma \equiv D_m/D_0$, where D_m is the maximum spreading diameter. In Fig. 5.6, we show a log-log plot of D_m/D_0 versus We for all the impact experiments obtained on smooth and CNF surfaces. All the data points were collected for impacts in the film boiling regime and in the course of which the droplets did not disintegrate during the expanding phase. The Weber number ranges from 5 to 600. All data sets collected from the three different surfaces collapse on the same curve, showing that the spreading dynamics does not depend on the features and temperature of the underlying substrate. This result is consistent with the recent study of impacting droplets on micro-structured surfaces [16], which showed that the spreading factor is independent of the microstructures and

Figure 5.6 – Spreading factor D_m/D_0 for impacting FC-72 droplets on three surfaces: smooth silicon, and silicon covered by a 3.5 μm - and a 7.5 μm -thick layer of carbon nanofibers. All the data points were obtained for impacts in the film boiling regime for which the impacting drop did not fragment in smaller droplets. The solid line represents the scaling relation $D_m/D_0 \sim \text{We}^{3/10}$ derived by taking the vapor flow as the major driving mechanism for the spreading of the liquid [16].

depends very weakly on the surface temperature. Moreover, the spreading factor for $\text{We} > 80$ is in agreement with the scaling $\Gamma \propto \text{We}^{3/10}$ derived in Ref. [16] for the large Weber number regime. This scaling law embodies the main assumption that the spreading of the liquid is driven by the vapor flow underneath the droplet [16]. Note that other studies have experimentally found that for $\text{We} < 100$, a scaling exponent ≈ 0.4 can be used to describe the impact of droplets on different type of surfaces, e.g. on hydrophobic powders [35], and on sublimating surfaces [36]. However, due to different ranges of the Weber number, these studies do not contradict our results of the spreading factor. As a result, we conclude that the presence of the carbon nanofibers only changes the transition temperature to film boiling of the impacting droplets, but does not affect the dynamics of the vapor flow in the film boiling regime or the liquid spreading.

5.4 Conclusions

In conclusion, we have explored the phase space (We, T) of impact of FC-72 droplets on heated smooth silicon surfaces and surfaces coated with carbon nanofibers (CNF) of different length. Unexpectedly, we have found that the dynamic Leidenfrost temperature T_L , i.e. the transition temperature between the contact and film boiling regimes, is higher on the CNF surfaces than on smooth silicon surface. Increasing the fiber length from $3.5\text{ }\mu\text{m}$ to $7.5\text{ }\mu\text{m}$ causes T_L to increase significantly due to the small time scale with which the nanofibers cool to the temperature of the vapor generated by the approaching liquid. Thus, the temperature of the fibers when contact with the liquid is established is much lower than their initial temperature. In other words, the temperature of the CNF surfaces has to be set higher than in the case of smooth silicon surfaces to bring the impact into the film boiling regime. In contrast, the silicon microstructured surfaces studied in Ref. [16] maintain their temperature during impact and T_L is lower, because the liquid surface area which generates the vapor is larger due to the curvature caused by the micro-pillars.

In spite of the effect on T_L , we have found that, as long as the impact is in the film boiling regime, the spreading factor of the droplet does not depend on whether the surface is smooth or covered with carbon nanofibers, nor does it depend on the surface temperature. The spreading factor is consistent with the scaling law $\Gamma \equiv D_m/D_0 \propto We^{3/10}$, which was derived based on the effect of vapor flow on the spreading dynamics [16].

The increase in the dynamic Leidenfrost temperature caused by nanofibers fabricated on silicon surfaces has a considerable implication for various applications that require high operating temperature, because CNF surfaces can operate at higher temperatures while still maintaining contact with the liquid.

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6

Phase diagram for droplet impact on superheated surfaces*

We experimentally determine the phase diagram for impacting ethanol droplets on a smooth, sapphire surface in the parameter space of Weber number We versus surface temperature T . We observe two transitions, namely the one towards splashing (disintegration of the droplet) with increasing We , and the one towards the Leidenfrost state (no contact between the droplet and the plate due to a lasting vapor film) with increasing T . Consequently, there are four regimes: contact and no splashing (deposition regime), contact and splashing (contact-splash regime), neither contact nor splashing (bounce regime), and finally no contact, but splashing (film-splash regime). While the transition temperature T_L to the Leidenfrost state depends weakly, at most, on We in the parameter regime of the present study, the transition Weber number We_C towards splashing shows a strong dependence on T and a discontinuity at T_L . We quantitatively explain the splashing transition for $T < T_L$ by incorporating the temperature dependence of the physical properties in the theory by Riboux & Gordillo [1, 2].

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6.1 Introduction

The transition to splashing, i.e. the disintegration of liquid droplets impacting solid surfaces, has been the subject of numerous studies ever since researchers were able to observe the impact process by high-speed imaging [3–7]. Although the splashing mechanism has not been fully understood, it was experimentally found by Xu, Zhang & Nagel [8] that the pressure of the ambient air is a key factor in the splashing process at room temperature, among others such as the liquid properties [9–11], the droplet’s kinetic energy [6, 12–15] and the properties of the surface [16–20]. In particular, the air layer under the droplet was thought to be responsible for splashing [21–25], but more recently it was suggested that rather than the gas under the whole droplet, the gas at the edge of the lamella plays a role in the transition to splashing [1, 2], finding good agreement with the experimental data for isothermal impact at room temperature.

Another transition that has received much attention is the dynamic Leidenfrost transition for droplets impacting heated surfaces [26–38]. When impacting a heated surface, the droplet either makes contact with the surface and boils violently or it is separated from the substrate by a layer of its own vapor for the entire duration of the impact process, the latter being the Leidenfrost state. The lowest surface temperature for which this lasting vapor layer exists is defined as the dynamic Leidenfrost temperature [33].

What both the transition to splashing and the Leidenfrost transition have in common is that the role of the gas phase between the droplet and the substrate is very relevant. Additionally, both transitions are crucially important in numerous technological and industrial applications; so it is of fundamental and also of practical interest to understand how the transition to splashing depends on the surface temperature and the kinetic energy of the droplet.

The experimental determination of the transition to the Leidenfrost regime is particularly challenging. The distinction of droplet behavior across the transition has normally relied on high-speed recording of the impact from side or top-angle views. In particular, the appearance of ejected droplets has been used as a criterion by many authors [26–30, 33, 35, 36] to exclude the Leidenfrost state, with the assumption that then there must exist a liquid/surface contact, leading to the disintegration of the droplet. Conversely, it is assumed that a droplet is in the Leidenfrost state when there are no signs of boiling (e.g. vapor bubbles or ejected droplets). However, it is not necessarily true that any liquid/solid contact during impact must produce vapor bubbles or ejected

droplets, so this way of classifying impact behavior might be unreliable. As the existence of a complete vapor layer between the impacting droplet and the solid surface demarcates the Leidenfrost regime from the contact boiling or transition regimes [37, 38], the most accurate means of determining the transition temperature is to measure the vapor layer directly.

In this chapter, we present a method based on interferometric high-speed imaging to quantify the Leidenfrost transition temperature in a wide parameter regime. We explore the behavior of droplets impacting heated surfaces across different regimes separated by the transition to splashing and the transition to the Leidenfrost state.

6.2 Experimental setup

Figure 6.1 shows the schematics of the experimental setup that allows us to observe and distinguish the different regimes of the droplets impacting the heated surfaces. We let ethanol droplets (density $\rho = 789 \text{ kg/m}^3$, surface tension $\sigma = 22 \text{ mN/m}$, viscosity $\mu = 1.1 \text{ mPa}\cdot\text{s}$, and boiling temperature $T_b = 78^\circ\text{C}$) fall on a polished sapphire plate (Goodfellow Cambridge Ltd.) from a height h . By adjusting h , the velocity U of the droplet immediately before impacting the surface can be varied between 0.5 m/s and 5 m/s . The droplets are generated by gently pushing the liquid out of a syringe with a syringe pump (PHD 22/2000, Harvard Apparatus), through a tube to a flat-tip, stainless steel needle (19 gauge, Hamilton Co.). The droplet forms at the tip of the needle and detaches when its weight overcomes the surface tension at the needle's tip. The pump is set at a sufficiently low flow rate (0.05 mL/min) to ensure that the droplet detachment is only due to gravity. As a result, all the droplets in our study have a uniform diameter $D = 2.5 \pm 0.1 \text{ mm}$.

The sapphire plate is heated by placing it on a brass holder (see Fig. 6.1 for the schematics), which radially embeds six cartridge heaters and a temperature probe (Omega Inc.). The surface temperature T of the sapphire plate can be varied between room temperature and 500°C and is measured independently with a surface temperature probe (N-141K, Anritsu) for each experiment. The brass holder has a hole in the center that, together with the transparent sapphire plate, allows for bottom-view recordings of the impacting droplets.

To study the impact behaviors of droplets, we use two high-speed cameras (Fastcam SA1.1 & SA-X, Photron) to make synchronized recordings of the impact events from the side and the bottom. From the side-view recordings, the droplet diameter D and velocity U immediately before impact are measured.

Figure 6.1 – Schematics of the experimental set-up, where a droplet of diameter D falls with velocity U on a sapphire plate P , which is placed on a temperature-controlled brass holder H . The impact is recorded by synchronized high-speed cameras from the side ($SA1.1$) and from the bottom ($SA-X$). Interferometric bottom-view recording of the impact is achieved by laser illumination from the bottom and a half mirror M .

To obtain interferometric recordings of the impact from the bottom, we use a continuous wave laser (iFlex-Gemini, Qioptic) as illuminating light (see Fig. 6.1). As long as the liquid is separated from the sapphire surface by a small distance, light reflected from the top surface of the sapphire plate and from the bottom surface of the droplet causes interference patterns, which consist of dark and bright fringes, that can be recorded by the high-speed camera via a half-mirror and a microscope of long working distance. In contrast, the area over which the liquid touches the surface appears dark in the recordings, because most of the light escapes through the liquid/solid interface. Based on this distinct difference, we can identify, without ambiguity, whether an impacting droplet is in the film boiling regime, in the contact boiling regime or in a transitional regime. Thus, the interferometric recording offers a unique tool to accurately determine the temperature T_L beyond which the impact is in the Leidenfrost regime, i.e. the droplet makes no contact with the plate during the entire impact [33].

6.3 Experimental observations

We investigate the droplet behavior while varying two control parameters: the surface temperature ($20^\circ\text{C} \leq T \leq 500^\circ\text{C}$) and the impact velocity ($0.5 \text{ m/s} \leq U \leq 5.0 \text{ m/s}$). The impact velocity is expressed in dimensionless form as Weber number $We = \rho DU^2/\sigma$ ($100 \leq We \leq 1500$), which measures the kinetic energy of the droplet in comparison to its surface energy. For fixed temperature, there is a critical Weber number We_C beyond which the impacting droplet makes a splash, i.e. disintegrates into smaller droplets during the spreading phase [1, 4, 8, 10, 16]. On the other hand, for each Weber number there also is a corresponding Leidenfrost temperature T_L . Hence, these two transitions naturally impose four typical behaviors of the impacting droplets in the (We, T) phase space: Contact and no splashing (deposition regime), contact and splashing (contact-splash regime), neither contact nor splashing (bounce regime) and finally no contact, but splashing (film-splash regime).

In the *deposition regime*, in which the temperature and the Weber number are relatively low, the impacting droplets are deposited on the surface and boiled at the same time, as exemplified in Fig. 6.2a. In this regime, the formation of vapor bubbles is clearly seen from the bottom view: The bubbles create dry patches on the surface which appear brighter in the bottom view, as opposed to the wetted areas that appear darker. The ejection of small droplets seen from the side view is clearly a result of the bursting of the vapor bubbles next to the surface. All the impacts in this regime are shown as (blue) diamonds in the (We, T) phase diagram (Fig. 6.3).

When increasing the Weber number, while keeping the temperature under T_L , the behavior of impacting droplets undergoes a transition to the *contact-splash regime* in which either a liquid sheet or smaller droplets are ejected from the lamella as a result of the high liquid inertia during the spreading phase of the impact. Note that there are two different mechanisms for the ejection of secondary droplets from the main droplet. One mechanism is associated with the impact itself (defined as splashing), while the other is connected with the boiling process at the liquid/solid interface (contact boiling). The former happens at the very early stage of impact (e.g. at 0.1 ms in Fig. 6.2b) and originates from the expanding lamella, whereas the latter happens at a much later time (e.g. at 2.7 ms in Fig. 6.2b) and originates upwards from the middle of the liquid puddle, due to bursting of vapor bubbles at the solid/liquid interface. We are thereby able to accurately distinguish the impacts in the contact-splash regime from those in the deposition regime. All of the impacts

Figure 6.2 – Typical sequences of ethanol droplets with diameter $D = 2.5$ mm impacting a sapphire plate for varying Weber number We and surface temperature T . All sequences have synchronized side-view and interferometric bottom-view recordings; the scale bars indicate 2 mm. (a) Deposition is observed for $We = 86$ and $T = 150^\circ\text{C}$. Dark areas in the bottom view indicate contact, as does the spray of small droplets due to boiling at the solid/liquid interface in the side view. (b) For the same temperature but a higher impact velocity ($We = 1156$) the droplet makes a contact-splash. (c) At low impact velocity ($We = 85$) and higher temperature ($T = 200^\circ\text{C}$) the droplet bounces off the surface. The interference pattern in the bottom view indicates that there is a lasting vapor film under the droplet during impact. (d) Now for the same temperature, but with high impact velocity ($We = 1190$), a film-splash is observed.

Figure 6.3 – Phase diagram of the outcome of the impact of an ethanol droplet on a sapphire plate with varying surface temperature and Weber number. Four regimes are identified from the high-speed recordings: deposition (blue diamonds), bounce (green circles), contact-splash (orange squares) and film-splash (red triangles). The thin solid line indicates the dynamic Leidenfrost temperature T_L , the dashed line is a guide to the eye for the transition Weber number We_C between regimes (c) and (d) and the thick solid line indicates We_C between regimes (a) and (b) as predicted by the model explained in section 6.4.

in the contact-splash regime are collected and shown as orange squares in Fig. 6.3.

Once the surface temperature is above the Leidenfrost temperature, the droplet and the surface are separated by a thin vapor film during the entire impact time. At a small Weber number, an impacting droplet spreads and rebounds from the surface as if the surface were superhydrophobic. Figure 6.2c shows such a bouncing droplet for $T = 200^{\circ}\text{C}$ and $We = 85$. From the bottom-view it is evident that there is no contact between the droplet and surface, as an interference pattern is observed for the entire impact duration, indicating a lasting vapor film. This regime is referred to as the *bounce regime* and is shown with green circles in Fig. 6.3.

With increasing impact velocity, while still keeping the surface temperature above T_L , the impact behavior undergoes a transition to the *film-splash regime*. Figure 6.2d shows a series of representative images of an impacting droplet in this regime. Side view measurements show that the droplet makes a splash at 0.1 ms. The interference pattern observed in the bottom-view recording during the entire impact process indicates that there is indeed a vapor film that separates the liquid and the surface. In the phase diagram shown in Fig. 6.3, this regime corresponds to the region with red triangles.

By identifying the characteristic behaviors of all experiments, out of the (We, T) parameter space we obtain the phase diagram for impacting ethanol droplets on a sapphire plate. The four well-separated regions correspond to the four aforementioned behaviors. Notably, the Leidenfrost transition marked by a dashed line, which separates the contact boiling regimes (deposition and contact-splash) and the film boiling regimes (bounce and film-splash), shows little dependence on the Weber number and can be approximated as $T_L \approx 165^\circ\text{C}$. This result is consistent with the value of T_L for ethanol on a smooth aluminium surface that was reported previously [30]. Note that the insensitive dependence of T_L on We found here is not inconsistent with the recently found, stronger dependence of T_L on We for water [33], because of the difference both in the working liquid and in the ranges of Weber number investigated: in our present study, the Weber number ranges from 100 to 1500, whereas in Tran et al. [33], it ranged from 0.5 to 600. Nevertheless, this insensitivity of T_L on We in the case of ethanol on sapphire is intriguing and deserves further studies for other combinations of materials.

In contrast to the, at most, weak dependence of T_L on We , the critical Weber number We_C , at which the transition to splashing occurs, is a strongly non-monotonic function of T . In the contact boiling regime, the transition to splashing separates the deposition regime from the contact-splash regime. The transition starts at $T = 20^\circ\text{C}$ and $We_C = 350$, which agrees with the previously reported value of the transition to splashing of ethanol droplets impacting a smooth surface at room temperature [10]. As the temperature increases, We_C also increases until it reaches $We = 850$ at a temperature close to T_L . This is striking because it shows that splashing is considerably *suppressed* (from $We_C = 350$ to $We_C = 850$) as the surface temperature increases, though both surface tension and viscosity decrease with increasing temperature.

As the surface temperature is increased beyond T_L , the We_C *suddenly drops* to a very small value $We_C = 110$ and only increases weakly to $We_C = 200$ when the surface temperature reaches $T = 450^\circ\text{C}$ in this regime. Thus, the transition

to splashing is not only discontinuous at T_L but also exhibits distinctively different behaviors in the film boiling and the contact boiling regimes.

To the best of our knowledge, the splash transition of a drop on a heated plate below T_L has not been reported previously, but the splash transition in the Leidenfrost state was reported by Wachters & Westerling [39] ($We_C = 80$ for various liquids) and by Biance et al. [40] ($We_C = 300 - 360$, various liquids). Although all studies show a weak temperature dependence, the results differ, so clearly the Weber number and plate temperature are not the only relevant control parameters for splashing in the film boiling regime.

6.4 Modeling the contact-splash transition

To explain the experimental observations in the preceding section, we make use of the theory by Riboux & Gordillo [1, 2]. The first step of this theory to describe the disintegration of the droplet during the initial phase after impact is to determine the ejection time t_e , i.e. the instant at which the lamella is first ejected. This time follows from the momentum balance [1, Eq. 1]

$$c_1 \text{Re}^{-1} t_e^{-1/2} + \text{Re}^{-2} \text{Oh}^{-2} = c^2 t_e^{3/2}, \quad (6.1)$$

with the Reynolds number $\text{Re} = \rho U R / \mu$, the Ohnesorge number $\text{Oh} = \mu / \sqrt{\rho R \sigma}$ and the drop radius $R = D/2$. The constants $c_1 \simeq \sqrt{3}/2$ and $c^2 = 1.2$ are adjusted to describe the experiments of [1]. Once t_e is calculated, the initial thickness of the edge of the lamella and its initial tangential velocity are determined as $h_t(t_e) \propto t_e^{3/2}$ and $v_t(t_e) \propto t_e^{1/2}$, respectively [1]. Here, the lower case variables indicate the dimensionless quantities constructed using R , U and R/U as the characteristic scales of length, velocity, and time.

For times larger than t_e , the edge of the lamella experiences a *vertical* lift force F_L per unit length given by the addition of the classical aerodynamic lift force and the projection in the vertical direction of the lubrication force exerted by the gas beneath the lamella [1, Eq. 2],

$$F_L = K_u \rho_g U^2 R v_t^2(t_e) h_t(t_e) + K_l \mu_g U v_t(t_e), \quad (6.2)$$

where the subscript g represents gas quantities, $K_u \simeq 0.3$ is a constant determined numerically and K_l depends logarithmically on the ratio $\lambda/(R h_t)$, with λ the mean free path of gas molecules. In Ref. [1] it is found that the critical lift force, above which the droplet disintegrates into smaller droplets, is given by

$$\left(\frac{F_L}{2\sigma} \right)^{1/2} = 0.14, \quad (6.3)$$

Figure 6.4 – Sketch of the lamella for an instant of time larger than t_e , illustrating the different regions in the flow and the temperature field deduced from the thermal boundary layer thicknesses. In the figure, blue and red represent low and high temperatures, respectively. Before the ethanol drop touches the plate, the drop is at room temperature $T_l \approx 20^\circ\text{C}$, while the surrounding air is at $20^\circ\text{C} \leq T_g \leq T$. After impact, a small spatial region in the liquid heats up to a temperature T and part of the gas surrounding the drop cools down to T_l . The widths of the regions where the liquid is heated up and the gas is cooled down are characterized by the thicknesses of their respective thermal boundary layers Δ and Δ_g .

from which the critical impact velocity or, equivalently, We_C is calculated using Eq. (6.2) (see Ref. [1] for details).

In order to make use of the splash criterion given by Eq. (6.3) and check whether the experimental observations in section 6.3 can be explained using the framework developed in Ref. [1], it is mandatory to use the correct temperature-dependent physical properties of the two fluids involved in the splashing process. Before the drop touches the substrate, the liquid is at room temperature $T_l \approx 20^\circ\text{C}$ and the gas temperature is $20^\circ\text{C} \leq T_g \leq T$. However, as soon as the drop impacts the substrate, the liquid heats up and the gas cools down in the regions characterized by their respective thermal boundary layer thicknesses, Δ and Δ_g (sketched in Fig. 6.4). To estimate both thicknesses, note first that the liquid particles feeding the lamella come from the region located to the right of the dashed line sketched in Fig. 6.4, which ends at the relative stagnation point present in the flow when the velocity field is described in a frame of reference moving at the wetting velocity $(1/2) \sqrt{3/t}$ [1, 2]. Since the relative stagnation point is located at a distance from the root of the lamella proportional to its thickness, $Rh_t \propto Rt^{3/2}$, and the liquid velocity feeding the liquid sheet is $Uv_t \propto Ut^{-1/2}$, the characteristic residence time of the fluid particles entering the lamella is $Rh_t(t_e)/(Uv_t(t_e))$, which coincides with the characteristic residence time of the gas particles flowing around the edge of the liquid sheet [1, 2]. Therefore, the ratios of the thicknesses of the

Figure 6.5 – Relative widths of the liquid and gas thermal boundary layers calculated using Eq. (6.4). The differences in the widths of the thermal boundary layers depicted in this figure are caused by the disparate values of the Prandtl numbers, $\text{Pr} \gtrsim 10$ for ethanol and $\text{Pr}_g(T) \simeq 0.7$ for air.

thermal boundary layers and the thickness of the lamella at the ejection instant, $Rh_t(t_e)$, are given by

$$\frac{\Delta}{Rh_t} \propto \sqrt{\frac{\nu(T)}{RUh_tv_t\text{Pr}(T)}} \quad \text{and} \quad \frac{\Delta_g}{Rh_t} \propto \sqrt{\frac{\nu_g(T)}{RUh_tv_t\text{Pr}_g(T)}}, \quad (6.4)$$

with $\text{Pr}(T)$ and $\text{Pr}_g(T)$ the temperature-dependent values of the Prandtl numbers for ethanol and air, respectively. Figure 6.5, where the ratios in Eq. (6.4) are represented, reveals that just a small region of the ethanol droplet in contact with the wall heats up to the temperature T and, therefore, most of the liquid flowing into the lamella is at room temperature. The width of the gas thermal boundary layer is, however, comparable to the width of the liquid sheet, as is sketched in Fig. 6.4. Consequently, most of the air located in between the lamella and the wall cools down to the temperature of the liquid, with the exception of the region closest to the substrate, where the air keeps its initial temperature T .

Taking this all into consideration, the term representing the viscous deceleration of the tip of the lamella in the momentum balance Eq. (6.1) is calculated using the following expression for the liquid viscosity:

$$\mu(T) = \exp\left(\sum_{i=0}^5 a_i T^i\right) \times 10^{-3} \text{ Pa s} \quad (6.5)$$

with $a_0 = 5.8942 \times 10^{-1}$, $a_1 = -2.2540 \times 10^{-2}$, $a_2 = 1.0283 \times 10^{-4}$, $a_3 = -8.8574 \times 10^{-7}$, $a_4 = 4.7884 \times 10^{-9}$, $a_5 = -9.7493 \times 10^{-12}$, and T in degrees Celsius [41]. Because most of the liquid feeding the lamella keeps its initial temperature, the liquid density and the interfacial tension coefficient in Eqs. (6.1) and (6.3) are evaluated at room temperature. The expressions for the air density and the mean free path of gas molecules in Eq. (6.2) depend on the wall temperature as $\rho_g = 10^5/(287 \times T)$ kg/m³ and $\lambda = 68 \times 10^{-9} \times T/293$ m, with the temperature in kelvin. However, since the gas located beneath the lamella cools down to the ethanol temperature, the value of the gas viscosity in Eq. (6.2) is evaluated at room temperature, $\mu_g = 1.86 \times 10^{-5}$ Pas. We now employ Eq. (6.3) using the expressions for the physical properties of both the ethanol and the air as detailed above, finding that the calculated critical velocity for splashing is in quantitative agreement with experiments, as Fig. 6.3 shows.

Recent work by Liu, Tan & Xu [42] shows that when the thickness of the lamella is equal to the fastest growing wavelength of a Kelvin–Helmholtz type instability, a droplet will splash. As this model does not give a prediction based on the impact parameters of either the lamella thickness, or the fastest growing wavelength, we cannot use this model to predict the critical Weber number for our experiments. With the somewhat older, but very similar model by Xu, Zhang & Nagel [8] we were able to fit a splash threshold to our experiments. However, the fitting parameter reported in Ref. [8], a universal 0.45, is not in accord with our experiments. The best fit of that model to our data is with a fitting parameter of 0.8, including the experiments at room temperature.

6.5 Conclusions

In conclusion, we have investigated the splashing and Leidenfrost transitions for ethanol droplets impacting a temperature controlled, sapphire plate. We have identified four different regimes in the explored $We - T$ phase space: deposition, contact-splash, bounce, and film-splash. While the dynamic Leidenfrost transition temperature T_L shows little dependence on We , the transition to splashing shows a strong and non-monotonic dependence on T . By incorporating the temperature dependence of the physical properties in the theory by Riboux & Gordillo [1, 2], we can quantitatively explain the splashing transition for surface temperatures below T_L . The splashing transition for droplets in the Leidenfrost state remains the subject of future research.

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7

Evaporation of picoliter droplets*

The evaporation of sessile droplets with picoliter volume is encountered in various industrial processes. In spite of the relevance of such tiny drops, many previous studies have only investigated the evaporation of nano- and microliter drops. In this paper, the evaporation of picoliter water droplets on non-absorbing substrates is studied. We find good agreement with the theoretical prediction based on vapor-diffusion-limited evaporation, provided that the underlying substrate has high thermal conductivity. In contrast, the rate of evaporation is strongly reduced on a substrate that is a poor thermal conductor. We can account for the reduction of the evaporation rate by considering the effect of evaporative cooling on the saturation vapor density close to the droplet. In addition, we explain why the reduction of the evaporation rate is larger as compared to what was observed for the evaporation of microliter droplets on a substrate with similar thermal properties.

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7.1 Introduction

The evaporation of a droplet on a flat substrate has received a lot of attention over the past years [1–11]. Besides being of fundamental scientific interest, drop evaporation is relevant for many technological applications, such as inkjet printing, spray cooling and microfabrication. The efficiency obtained in these applications relies on knowledge of the droplet lifetime and the ability to accurately predict the evaporation rate aids directly in the optimization of the associated industrial processes.

In spite of the strong connection to applications in which the volume of the droplets is of the order of picoliters, the vast majority of sessile droplet evaporation studies were reported on the evaporation of microliter [1, 4, 5, 9, 12–23] or nanoliter [2, 24–27] drops. Here, we investigate the evaporation of picoliter water droplets on a non-absorbing substrate and compare our results with the evaporation of the aforementioned larger drops.

It was discovered over a century ago that the evaporation rate of a spherical drop scales linearly with the radius of the droplet rather than with its surface area [28]. A few years later, it was demonstrated that the diffusion of vapor in the surrounding gas is the mechanism that limits the evaporation rate, which explains the linear dependency on the radius [29]. A few decades later, Picknett & Bexon [12] identified three modes in which a sessile drop can evaporate; one in which the drop’s footprint radius remains constant (CR mode), another one in which the contact angle is constant (CA mode) and a mixed mode, which was later named ‘Stick-Slip’ [14] or ‘Stick-Slide’ [23], in which the drop first evaporates in the CR mode before it starts a phase of CA evaporation when it reaches a critical contact angle. Recently, a fourth mode called ‘Stick-Jump’ was observed [27, 30], in which the evaporation, or in that case dissolution, is always in the CR mode, but the radius suddenly jumps to a smaller value each time the contact angle reaches a critical value. As long as convection in the surrounding gas can be neglected, the vapor diffusion is the rate-limiting mechanism, regardless of the evaporation mode. Therefore, for isothermal evaporation, the droplet lifetime can be calculated directly for any sessile drop [11, 23, 27].

Deviations from these predictions arise when the drop locally cools down due to the latent heat of evaporation. This is the case when the liquid is highly volatile [2, 19] or when the substrate is a poor thermal conductor [8, 9, 17, 18, 21, 31, 32]. For a microliter water drop it was reported that an insulating substrate (PTFE, thermal conductivity $k_s = 0.25 \text{ W/(m K)}$) reduces

the evaporation rate by up to 20% as compared to aluminum [17], which can be considered isothermal due to its high thermal conductivity. In the same study it was mentioned that the difference in evaporation rate between droplets deposited on aluminum and PTFE substrates decreases consistently with decreasing drop size. Does this mean that thermal effects do not play a role in the evaporation of very small drops, regardless of the substrate's thermal conductivity? The answer to this question is especially relevant in the case of inkjet printing, where the underlying substrates are poor thermal conductors, e.g. uncoated or glossy paper, or vinyl. In this chapter we will seek for this answer first by monitoring the evaporation of picoliter droplets, then by comparing the results to the theory of isothermal evaporation, and finally by identifying the relevant time scales of the system.

7.2 Experimental observations

In order to study the evaporation of picoliter water droplets, we deposited the droplets on a substrate with a drop-on-demand printhead (Dimatix Materials Cartridge, Fujifilm), illuminated the droplet with a continuous, metal-halide arc light source (ILP-2, Olympus) and measured the droplet volume from side-view recordings made with a high-speed camera (V311, Phantom). Heating of the

Figure 7.1 – High-speed recording of a water droplet with an initial volume of 19 pL, evaporating on a vinyl substrate at ambient temperature $T_\infty = 22^\circ\text{C}$ and humidity $H = 0.72$. After the droplet is deposited ($t = 0$ s), it spreads to its maximum diameter ($2R = 55\ \mu\text{m}$) at $t = 0.25$ s, and begins evaporation in the CR mode. From $t = 1.1$ s onwards, both $R(t)$ and $\theta(t)$ decrease until the droplet vanishes a few seconds later.

Figure 7.2 – Volume-time curves of evaporating droplets on a vinyl substrate at $T_{\infty} = 22^{\circ}\text{C}$ and varying relative humidity H . In the first tenth of a second the volume decreases faster than during the remainder of the droplet lifetime, where it experiences an almost constant evaporation rate. The dashed lines show linear fits of the volumes after the transient period. For increasing humidity the slopes of these linear fits are -12.8 , -10.9 , -7.9 , -5.8 , and -4.7 pL/s.

droplets due to light exposure was avoided by using an optical fiber and by placing it far away from the droplet. A polymeric, self-adhesive vinyl (MPI 2000, Avery Dennison) was used as a substrate, because it is non-absorbing, easy to handle and widely used in graphics inkjet printing. A revolving metal disk with a radius that is large compared to the scale of the droplet acted as the holder for the substrate for convenience. The entire experimental setup was placed in a custom-built climate chamber, in which the relative humidity H and ambient temperature T_{∞} were controlled: The temperature was kept at $22 \pm 1^{\circ}\text{C}$ for all experiments and the relative humidity ranged from 0.40 to 0.80 with an uncertainty of 0.02. Figure 7.1 shows a typical high-speed recording made with this experimental setup. The droplet was deposited at $t = 0$ s, reached its maximum spreading diameter of $55\text{ }\mu\text{m}$ at $t = 0.25$ s and began a period of CR mode evaporation until $t = 1.1$ s. From here onwards, both the radius and the contact angle decreased before the droplet has completely disappeared after 4 s.

In Fig. 7.2 we show representative examples of the volume-time curves of water droplets with initial volumes between 16 and 20 pL that evaporate on

the vinyl substrate with varying relative humidity. In the early stage (≈ 0.15 s) the evaporation is faster than in the remainder of the droplet lifetime, where it follows an approximately constant evaporation rate. A linear relation fitted to each evaporation curve after this period of faster evaporation results in evaporation rates of -12.8 , -10.9 , -7.9 , -5.8 , and -4.7 pL/s for $H = 0.42$, 0.51 , 0.60 , 0.72 , and 0.80 , respectively.

7.3 Diffusion-limited evaporation

To compare the observed evaporation rates with those of larger drops, we must evaluate the dependency of the evaporation rate on the drop geometry, the liquid properties, and the ambient conditions. When a sessile drop is small enough for gravitational effects to be negligible, its shape is that of a spherical cap with a footprint radius R and a contact angle θ . Its corresponding volume is

$$V(R, \theta) = \frac{\cos^3 \theta - 3 \cos \theta + 2}{3 \sin^3 \theta} \pi R^3. \quad (7.1)$$

If the gas that surrounds the droplet is quiescent, the diffusive transport of vapor is the mechanism that limits the evaporation rate [12], which implies that the vapor concentration c in the gas in close vicinity of the droplet surface is at the saturation level, i.e. $c = c_s$. The reference value is the concentration far away from the droplet, i.e. $c = c_\infty$. For water vapor in air this value is set by the relative humidity H as $c_\infty = H c_s$. Because the droplet lifetime is always much longer than the characteristic diffusion timescale R^2/D , with D the mass diffusion coefficient, we can assume that the vapor diffusion is a quasi-steady process and hence that the vapor concentration therefore satisfies Laplace's equation. The evaporative flux can then be calculated analytically with the proper boundary conditions, resulting in an expression for the evaporation rate [2, 4, 12, 20]

$$\frac{dV}{dt} = -\frac{\pi R D (c_s - c_\infty)}{\rho} f(\theta), \quad (7.2)$$

with ρ the liquid density and $f(\theta)$ given by [4]

$$f(\theta) = \frac{\sin \theta}{1 + \cos \theta} + 4 \int_0^\infty \frac{1 + \cosh 2\theta\tau}{\sinh 2\pi\tau} \tanh [(\pi - \theta)\tau] d\tau. \quad (7.3)$$

Dividing both sides of Eq. (7.2) by $RD(c_s - c_\infty)/\rho$ and defining a nondimensional volume and time, respectively, as

$$\hat{V} = \frac{V}{R^3}, \quad \hat{t} = \frac{c_s - c_\infty}{\rho} \frac{t}{R^2/D}, \quad (7.4)$$

Figure 7.3 – Dimensionless evaporation rate of evaporating water droplets on a vinyl substrate at $T_\infty = 22^\circ\text{C}$ and varying relative humidity. The evaporation rates collapse on a single curve by non dimensionalization as given in Eq. (7.5), but this universal curve falls well below the theoretical expectation for isothermal surfaces (right-hand side of the same equation).

gives a universal expression for the dimensionless evaporation rate

$$\frac{d\hat{V}}{d\hat{t}} = -\pi f(\theta), \quad (7.5)$$

for which very good agreement was found with experimental data of the evaporation of microliter drops [20].

We use the properties of water ($\rho = 998 \text{ kg/m}^3$, $D = 24.6 \text{ mm}^2/\text{s}$, values taken from Ref. [33]) to plot our experimental data in dimensionless form, as given by Eq. (7.5). In Fig. 7.3 it is seen that while the data collapse on a single curve, this curve lies well below the predicted evaporation rate based on the right-hand side of Eq. (7.5) (black line).

What causes the observed reduction in evaporation rate? Could it be due to evaporative cooling of the droplet? Although the thermal conductivity of the vinyl substrate is low ($k_s = 0.25 \text{ W/(m K)}$), the observed reduction of the evaporation rate by more than a factor of 2 is much larger than the 20% that was reported for microliter water drops evaporating on a substrate with similar thermal properties [17, 18]. In addition, the trend is opposite to the reported

observation that the influence of the substrate's thermal properties reduces for decreasing drop size [17].

In order to check the influence of the thermal conductivity of the substrate on the evaporation rate of picoliter droplets, we performed the very same experiments using an aluminum foil as a substrate. Water drops ($V_0 = 18$ pL, $R = 40$ μm , $\theta_0 = 20^\circ$, $T_\infty = 22^\circ\text{C}$, and $H = 0.40$) evaporated on the aluminum foil at a rate of $dV/dt = -46$ pL/s. From Eq. (7.2) we obtain the theoretical prediction as $dV/dt = -49 \pm 4$ pL/s for the same initial conditions, while taking the experimental uncertainty of the ambient conditions into account. This implies that the evaporation of picoliter water droplets on aluminum is consistent with isothermal diffusion-limited evaporation, in accordance with previous studies [17, 18]. Thus, the thermal properties of the underlying substrate greatly influence the evaporation rate of picoliter drops.

7.4 Thermal effects

To further investigate the effect of the substrate's thermal properties on the evaporation rate, we look into the mechanism that causes the temperature change. The phase transition from liquid to vapor requires energy and it is well-known that the liquid will cool itself locally if it can not acquire the needed energy from its surroundings. The saturation vapor density c_s strongly depends on the local temperature T and since the difference between the vapor concentration close to the drop (where $T = T_d$) and far away (where $T = T_\infty$) determines the evaporation rate, it is clear that a lower droplet temperature will greatly reduce the evaporation rate. The amount by which the droplet temperature decreases depends on the volatility of the liquid and the supply of heat to the drop from either the underlying substrate or the surrounding gas.

The effect of the temperature on the saturation vapor density is incorporated in the isothermal diffusion-limited evaporation rate of Eq. (7.2) as [8, 18]

$$\frac{dV}{dt} = -\frac{\pi R D (c_s(T_d) - H c_s(T_\infty))}{\rho} f(\theta), \quad (7.6)$$

where we use the following polynomial relationship for the temperature dependence of the saturation vapor density [32, 34]:

$$c_s(T) = \sum_{i=0}^4 a_i T^i, \quad (7.7)$$

Figure 7.4 – The influence of the local temperature T just above the droplet on the evaporation rate for varying humidity (solid lines) and the experimentally determined values (dashed lines), all at $T_\infty = 22^\circ\text{C}$. The droplet temperature is found from the intersections of the lines (black dots): They are at $T_d = 14.8, 15.9, 16.7, 18.5$, and 19.7°C for increasing humidity: Larger humidity implies less evaporation and therefore less cooling.

with T in $^\circ\text{C}$ and the coefficients $a_0 = 5.460 \times 10^{-3}$, $a_1 = 1.64924 \times 10^{-4}$, $a_2 = 2.12226 \times 10^{-5}$, $a_3 = -1.00126 \times 10^{-7}$ and $a_4 = 4.64274 \times 10^{-9}$ computed to fit the experimental data of Ref. [35].

To study whether we can account for the reduction of the evaporation rate with the droplet’s self-cooling, we first need to calculate the temperature of the droplet, as clearly the droplet is too small to directly measure its temperature. We use Eq. (7.6) with the experimentally determined values of dV/dt from the linear fits in Fig. 7.2 and the corresponding values of R and θ at $t = 0.2$ s, i.e. just after the start of the constant evaporation rate. The solid lines in Fig. 7.4 show the effect that the local temperature has on the evaporation rate for varying humidity. The droplet temperature is found by equalizing this result with the experimentally determined dV/dt (dashed lines), from which we find $T_d = 14.8, 15.9, 16.7, 18.5$, and 19.7°C for $H = 0.42, 0.51, 0.60, 0.72$, and 0.80 , respectively. The larger temperature decrease at lower humidity reflects the corresponding larger evaporation rate, leading to stronger cooling.

An energy balance of an evaporating droplet gives an estimate of the

droplet temperature without the need for input of experimental parameters. For a perfect thermal insulating substrate this can be done analytically for an evaporating hemispherical droplet [32] and we obtain a lower bound for the temperature of the droplet

$$DL_{fg}(c_s(T_{d,a}) - Hc_s(T_\infty)) = k_g(T_\infty - T_{d,a}), \quad (7.8)$$

with $L_{fg} = 2454$ kJ/kg the latent heat of evaporation and $k_g = 0.0259$ W/(m K) the thermal conductivity of air (values taken from Ref. [33]). We find that if the substrate were a perfect thermal insulator, the droplet temperature on this adiabatic substrate would be $T_{d,a} = 13.8, 15.2, 16.6, 18.3,$ and 19.4°C for the same values of H as before. These temperatures are lower than those we calculated above, albeit by only a small amount, which means that the self-cooling of the droplet combined with the poor thermal conductivity of the substrate can account for the observed reduction of the evaporation rate of picoliter droplets.

It is striking that there is no length scale associated with Eq. (7.8). This means that the effect of a perfect thermal insulating substrate on the evaporation rate should be the same, regardless of the droplet size. Of course we do not use a perfect insulator, but how can we explain the observed difference in the case of a substrate with low thermal conductivity? As the evaporation rate scales linearly with R , this also holds for the internal heat absorption rate of the droplet. The heat *flux* through the surface area then scales with $1/R$, which means that the temperature gradient inside the substrate becomes larger for smaller droplet size, resulting in a significantly lower droplet temperature.

Another observation that needs more explanation is the initial faster evaporation of the droplets. Let us look at the characteristic time scale for thermal conduction in the substrate $\tau_c = d^2/\alpha$. With a thickness $d = 120$ μm and a thermal diffusivity $\alpha \approx 0.1$ mm^2/s this gives $\tau_c = 0.1$ s. This means that the time it takes to reach steady conduction within the substrate is comparable to the observed more rapid evaporation at start. Thus, the droplet temperature changes during this initial stage, then stays constant in the remainder of the droplet lifetime.

The same calculation can be performed in the case of the aluminum substrate, with $k_s = 237$ W/(m K), $\alpha = 84.2$ mm^2/s , and $d = 16$ μm . With these values we find $\tau_c = 3$ μs , which means that steady conduction is achieved instantly. Equation (7.8) can also be used to estimate the temperature gradient within the aluminum substrate when the air is considered a perfect thermal insulator. The temperature of the substrate changes by only 0.003°C , which

supports the assumed isothermal behavior of the aluminum substrate in our experiments.

7.5 Conclusions

In conclusion, we have shown that the evaporation rate of a picoliter-sized water droplet on a non-absorbing substrate with poor thermal conductivity is significantly lower than expected based on the diffusion-limited model for isothermal evaporation. When the substrate is replaced by a good thermal conducting material, we find good agreement with the model, so the substrate's thermal properties are key to this problem. We can explain the observed differences by considering the evaporative cooling of the droplet and its effect on the saturation vapor density. From an energy balance we find that the temperature of the droplet that is required to fully account for the observed (lower) evaporation rate is close to, yet slightly higher than that of a droplet deposited on a perfectly insulating substrate. In addition, the evaporation rate is reduced by a larger amount than was previously reported for microliter water drops on a substrate with similar thermal properties, which can be explained by noting that the heat flux is inversely proportional to the droplet radius, i.e. it diverges for the droplet radius going to zero. Thus, in that limit the assumption of isothermal evaporation can no longer be sustained.

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8

Conclusions and Outlook

8.1 Conclusions

An ultrafast imaging technique to measure the surface tension and viscosity of picoliter droplets at a very short time after their ejection from a printhead was presented. It was shown with this technique that the surface tension of a picoliter droplet that contains a surfactant is significantly higher when the droplet is in flight than the equilibrium value. This is because the characteristic time scale of surfactant adsorption at the liquid-air interface is larger than the flight time of the droplet.

The impact studies in this thesis aimed at gaining a better understanding of the dynamic Leidenfrost effect. With a systematic study of the outcome of droplet impact on smooth, superheated surfaces, it was shown that the dynamic Leidenfrost temperature increases with the kinetic energy of the drop. This is explained by considering that the stability of the vapor layer that is needed for the Leidenfrost state results from a competition between the evaporation rate and the drop's kinetic energy. The momentum of the drop squeezes the vapor layer under the drop, so a higher plate temperature is required to achieve the evaporation rate that is needed to sustain the vapor layer. This means that when the evaporation rate is increased, the dynamic Leidenfrost transition temperature goes down. This is exactly what was observed when

the substrate had an increased effective area due to the manufacturing of pillars. In the situation of extremely large effective area (a substrate with a layer of carbon nanofibers), it was expected to see an even further decrease of the dynamic Leidenfrost temperature, but the opposite was observed, the dynamic Leidenfrost temperature on this substrate is higher than for a smooth substrate. This is explained by comparing the typical time that is needed to change the temperature of the fibers and the typical time they are exposed to the vapor flow, which is cold compared to the substrate. It was shown that the cooling time scale of the fibers is shorter than the time the fibers are exposed to the vapor flow before drop impact, resulting, locally, in a lower substrate temperature at the moment of impact and thus a lower evaporation rate.

In addition to the dynamic Leidenfrost transition temperature, the spreading and splashing of droplets on heated surfaces was studied. The normalized maximum spreading diameter of drops in the film boiling regime is larger than for drop impact at room temperature, even when the substrate at room temperature is superhydrophobic. This is caused by the vapor flow under the droplet that is directed radially outward, which promotes droplet spreading. Although the maximum deformation of drops is larger in the Leidenfrost state as compared to drops that impact a cold, superhydrophobic substrate, the typical time scale to reach the maximum deformation is the same and scales with the capillary time scale.

The critical velocity for which a drop makes a splash upon impact increases with the substrate temperature, until it suddenly decreases at the dynamic Leidenfrost temperature. By incorporating the effect of the temperature on the relevant parameters, a good agreement was found with the theory by Riboux & Gordillo [1, 2] for the splash threshold below the dynamic Leidenfrost temperature. The splash threshold for drops on a substrate above the Leidenfrost temperature depends, at most, weakly on the substrate temperature, the reason for this remains the topic of future research.

The evaporation rate of picoliter droplets on a substrate with poor thermal conductivity was found to be less than half of that of a droplet that evaporates on an isothermal substrate. This decrease in evaporation rate is much larger than the expected decrease of $\approx 20\%$ on a substrate with similar thermal properties reported before for microliter drops [3]. The larger reduction in evaporation rate for picoliter droplets can be explained by comparing the heat flux due to evaporative cooling for microliter and picoliter droplets. The rate of evaporation scales linearly with the droplet radius, i.e. the heat flux is inversely proportional to the radius. Thus, a smaller droplet will reach a lower

temperature, resulting in a slower evaporation.

8.2 Outlook

With the experimental technique described in chapter 2 we can measure the surface tension and viscosity of tiny droplets by analyzing their shape oscillation at a short time after droplet formation. The challenge in the imaging of these droplets is that they are of micrometer size and move with several meters per second, which means that a large magnification and a short illumination time are needed to resolve the droplet shape during oscillation. The large magnification as a result, dictates that the time that the droplet is in the view of the camera is limited. A way to circumvent this trade-off is to mount the printhead on an xyz-stage and move it every time the delay of the stroboscopic imaging is changed. This way, the droplet is always in the view of the camera, even at large magnification, but this requires precise control of the printhead.

This improvement also enables the study of the shape oscillation a longer time after droplet generation, so the surfactant adsorption dynamics can be investigated. However, the origin of the shape oscillations that we analyze is the natural break-up of a liquid jet and as the shape oscillations are damped with a characteristic time that scales with the kinematic viscosity ν and droplet radius R as $\tau \sim R^2/\nu$, a picoliter water droplet will be spherical after a few oscillation cycles. It was mentioned in chapter 1 that the droplet can be kicked with an acoustic field to initiate the shape oscillations, so by placing an acoustic transducer at a fixed distance from the printhead, the experimental setup can be used to measure the time dependence of the surface tension and viscosity in more detail.

In chapter 7 we investigated the evaporation of picoliter water droplets on non-absorbing substrates. The next step would be to study either the evaporation of droplet on an absorbing substrate or the evaporation of droplets of a liquid mixture. Droplets that sit on a porous material will not only evaporate, but also enter the pores of the substrate. Therefore, measurement of the volume evolution from side-view recordings of the droplet is not sufficient to measure the evaporation rate, instead the mass loss should be directly measured with an analytical balance. The small mass of the droplets makes this experiment challenging for microliter drops and very challenging for picoliter droplets. Therefore the absorption of picoliter droplets should first be investigated using non-volatile liquids.

The evaporation of droplets of liquid mixtures has been reported in the scientific literature for mixtures of volatile liquids, e.g. water mixed with ethanol and/or methanol. However, in the case of inkjet printing there is at least one component in the ink that is non-volatile, as there is a residue after drying. How does the addition of a non-volatile component to water change the evaporation rate of droplets? What is the effect of a surfactant added to this mixture on the evaporation rate? Does the addition of particles change the evaporation rate? These questions are not only interesting from a scientific point of view, but since inks are a mixture of solvents, surfactants and pigment particles, their answers are very relevant for inkjet printing.

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Summary

Droplets are everywhere around us in our daily life; rain droplets impacting a window, a dripping faucet, but they can also be found in inkjet printers and dish washers. Droplets are also used in many industrial and medical applications, such as the cooling of hot objects with sprays, the spraying of crops in agriculture, or the administration of drugs via an inhaler. In this thesis, we study droplets during flight, impact, and evaporation in order to get a better understanding of the underlying, physical mechanisms, which aids to improve the efficiency of the processes involved in the applications.

In chapter 2 we use an ultrafast imaging technique to record the axisymmetric shape deformation of inkjet printed droplets of picoliter volume during flight. By expansion of the droplet shape in normal modes in a way similar to the early work of Lord Rayleigh, we can directly determine the surface tension and viscosity of the liquid from the shape oscillation of the droplet. The values of the surface tension and the viscosity of a picoliter-sized, purified water droplet that we measured with this technique show good agreement with the literature values. However, many droplets used in industry are not of a pure liquid, but are at least a mixture of a solvent and a surfactant. The surfactant lowers the surface tension, but by how much depends on the age of the liquid-air interface. The surface tension of a freshly formed liquid-air interface equals that of the solvent and decreases over time due to the adsorption of surfactant molecules at the interface, until an equilibrium is reached. With the previously described technique we show that the surface tension of an inkjet printed droplet in flight is indeed significantly higher than the equilibrium value. On the other hand, the viscosity of an inkjet printed droplet was found to be lower for shorter surface age, which we attribute to the Gibbs elasticity that is associated with the adsorbed surfactant molecules.

In chapters 3–5 we study the impact of droplets on superheated surfaces. In chapter 2 we show that three regimes with different outcomes of droplet impact on superheated surfaces can be identified. The first is the contact boiling regime, in which the droplet makes direct contact with the substrate upon

impact and boils; the visible signs of which are the formation of vapor bubbles and the ejection of secondary droplets due to the bursting of these bubbles. The second regime is gentle film boiling, in which the droplet is separated from the substrate by a vapor film that is stable when the temperature of the substrate is sufficiently high. This phenomenon is called the dynamic Leidenfrost effect and the temperature that marks the transition from contact to gentle film boiling the dynamic Leidenfrost temperature. The last identified regime is spraying film boiling, in which secondary droplets are ejected from the droplet, but not due to contact as the droplet is separated from the substrate by a vapor film. We show experimentally that the dynamic Leidenfrost temperature increases with the kinetic energy of the droplet, which is explained by considering that the stability of the vapor film is the result of a competition between the evaporation rate and the kinetic energy of the droplet. When the droplet has a higher kinetic energy, a higher evaporation rate is required to sustain the vapor layer, which means that a higher plate temperature is needed to achieve the dynamic Leidenfrost effect. Another way to increase the evaporation rate is by enlarging the effective area of the substrate by the fabrication of micro-pillars. In chapter 4 we show that the dynamic Leidenfrost temperature decreases for these micro-structured surfaces in comparison with a smooth surface of the same material. However, increasing the effective area even further, as we do in chapter 5 by covering a silicon substrate with a layer of carbon nano-fibers, leads to an increase of the dynamic Leidenfrost temperature. This can be explained by noting that the fibers are only about 100 nm thick, which makes them easy to cool down by the vapor that flows in between the fibers prior to droplet impact. When we compare the timescale needed to cool down the fibers with the time the fibers are exposed to the vapor flow, we find that these times are comparable, so a higher initial surface temperature is required for an impacting droplet to be in the film boiling regime.

When a droplet impacts a substrate, there is a critical velocity above which a droplet disintegrates after impact, which is also known as splashing. The dependence of this critical velocity on the temperature of the substrate is studied in chapter 6. We show that the critical velocity increases with the temperature of the plate, if the plate temperature is below the dynamic Leidenfrost temperature. By incorporating the effect of the temperature on the relevant liquid and gas properties in the theory by Riboux & Gordillo, we quantitatively explain the critical velocity of droplet impact on heated surfaces below the dynamic Leidenfrost transition. When the plate temperature is at the dynamic Leidenfrost temperature, the critical velocity suddenly drops. For

higher plate temperatures, the critical velocity depends, at most, weakly on the temperature of the substrate.

In chapter 7 we investigate the evaporation of sessile droplets of picoliter volume. The rate of evaporation of sessile droplets of a pure liquid in a quiescent gas is limited by the diffusion of vapor through the surrounding gas. The rate of vapor diffusion is set by the difference in vapor concentration close to the droplet, which is at the saturation value, and the vapor concentration far away, which is set by the ambient conditions. The saturation vapor concentration strongly depends on the temperature of the gas, which makes that the evaporation rate also depends on this local temperature. The temperature of the gas close to the droplet changes when the temperature of the droplet reduces due to the evaporation process. The change of phase from liquid to vapor requires energy and if the droplet is not supplied with the needed energy by its surrounding, it will cool down. Therefore, when the droplet is very volatile or when the underlying substrate has a low thermal conductivity, the evaporation rate will be lower than the isothermal, diffusion-limited evaporation model predicts. This reduction of the evaporation was observed previously for microliter droplets, but has never been studied for smaller droplets. We show that the reduction of the evaporation rate due to evaporative cooling is even larger for picoliter droplets than was previously reported for microliter droplets. This is explained by the dependence of the heat flux due to evaporative cooling on the size of the droplet. The evaporation rate is proportional to the droplet radius, which means that the heat adsorption is also proportional to the droplet radius. Then it follows that the heat flux is inversely proportional to the droplet radius, which explains the stronger cooling effect for smaller droplets, thus the stronger reduction in evaporation rate. In addition, this means that isothermal evaporation can not be sustained for the limit of droplet radius going to zero.

Samenvatting

Druppels komen we overal tegen in ons dagelijks leven; regendruppels die inslaan op een raam, een druppelende kraan, maar ook in inkjet printers en in vaatwassers zijn ze te vinden. Druppels worden ook gebruikt in industriële en medische toepassingen, zoals bij het koelen van hete objecten met sprays, het besproeien van gewassen in de landbouw en het toedienen van medicatie middels een inhaler. In deze thesis hebben we gekeken naar druppels in hun vlucht, tijdens inslag en verdamping om zo de onbegrepen onderliggende, fysische mechanismen beter te kunnen begrijpen. Deze nieuwe inzichten leiden direct tot een verbeterslag die de processen in bovengenoemde toepassingen vele malen efficiënter maakt.

In hoofdstuk 2 gebruiken we een ultrasnelle beeldvormingstechniek om oscillerende druppels met een volume in de orde van picoliter op te nemen. Door de veranderende vorm van de druppel tijdens zijn vlucht door de lucht te analyseren, zijn we in staat om de oppervlaktespanning en de viscositeit van de vloeistof te bepalen. Met deze techniek vinden we waarden voor de oppervlaktespanning en viscositeit van een druppel van puur water in overeenstemming met de literatuurwaarden. Veel druppels die je in de industrie tegen komt zijn echter niet van een pure vloeistof, maar op zijn minst een mengsel van een oplosmiddel (zoals water) en een oppervlakte-actieve stof. De oppervlakte-actieve stof verlaagt de oppervlakte spanning van de druppel, maar hoe groot de reductie is, hangt af van de leeftijd van het oppervlak. De oppervlaktespanning van een vers gevormd oppervlak is gelijk aan die van het oplosmiddel en neemt af naarmate er meer oppervlakte-actieve moleculen adsorberen aan het oppervlak, totdat er na enige tijd een evenwicht is bereikt en de oppervlaktespanning constant blijft. Met de eerder genoemde techniek laten we zien dat de oppervlaktespanning van een water druppel waaraan een oppervlakte-actieve stof is toegevoegd inderdaad lager is dan de evenwichtswaarde voor een korte leeftijd van het oppervlak.

In de hoofdstukken 3–5 bestuderen we de inslag van druppels op verwarmde oppervlakken, waarvan de temperatuur hoger ligt dan het kookpunt van de

vloeistof. In hoofdstuk 2 laten we zien dat er drie verschillende uitkomsten van de inslag van een druppel op een verwarmd oppervlak geïdentificeerd kunnen worden. De eerste mogelijkheid is “contact boiling”, waarbij de druppel op het moment van inslag in contact komt met het substraat en begint te koken. Het kookproces is zichtbaar door de formatie van dampbellen in de druppel en de uitwerping van kleine druppeltjes veroorzaakt door het barsten van deze bellen. De tweede mogelijkheid is “gentle film boiling”, waarbij de druppel afgeschermd wordt van het substraat door een laagje damp, die stabiel is als het oppervlak heet genoeg is. Dit wordt ook het dynamische Leidenfrost effect genoemd en de laagste temperatuur waarbij de damp laag stabiel is, de dynamische Leidenfrost temperatuur. De laatste uitkomst is “spraying film boiling”, waarbij er een stabiele damp laag tussen de druppel en het substraat is, maar er toch kleine druppeltjes uit de druppel komen. Door systematisch de temperatuur van het substraat en de snelheid waarmee de druppel inslaat te variëren, vinden we dat de dynamische Leidenfrost temperatuur toeneemt met de inslagnsnelheid van de druppel. Een verklaring hiervoor is dat de stabiliteit van de damp laag wordt bepaald door een competitie tussen de verdampingssnelheid en de kinetische energie van de druppel. Een hogere kinetische energie zorgt ervoor dat de damp sneller wegstroomt, dus dat een hogere temperatuur nodig is om de verdampingssnelheid hoog genoeg te maken. Een andere manier om de verdampingssnelheid te verhogen is door het effectieve oppervlak van het substraat te vergroten. In hoofdstuk 4 laten we zien dat de dynamische Leidenfrost temperatuur omlaag gaat als een glad oppervlak wordt vervangen door een oppervlak met micro-pilaren van hetzelfde materiaal. Als we echter het effectieve oppervlak extreem groot maken, zoals we doen in hoofdstuk 5, waarin we een silicium oppervlak bedekken met een laagje carbon nano fibers, zien we juist een hogere dynamische Leidenfrost temperatuur. Dit komt doordat in dit geval de fibers slechts 100 nm dik zijn en dus gekoeld kunnen worden door de damp die langs de fibers stroomt voordat de druppel inslaat. Als we de tijd die de druppel blootstaat aan de damp vergelijken met de tijd die nodig is om de fibers af te koelen, vinden we dat deze tijdschalen vergelijkbaar zijn. De fibers kunnen dus significant gekoeld worden voordat de druppel inslaat, dus een hogere initiële temperatuur is nodig om een stabiele damp laag te krijgen.

Wanneer een druppel inslaat op een substraat, is er een kritieke inslagnsnelheid vanaf wanneer de druppel uit elkaar spat gedurende de inslag. Hoe deze kritieke snelheid afhangt van de temperatuur van het substraat wordt bestudeerd in hoofdstuk 6. We laten zien dat de kritieke snelheid toeneemt met

de temperatuur van de plaat, als deze temperatuur lager ligt dan de dynamische Leidenfrost temperatuur. Wanneer we het effect van de temperatuur op de relevante eigenschappen van de vloeistof en de lucht opnemen in de theorie van Riboux & Gordillo, kunnen we kritieke inslagsnelheid van druppels die inslaan op verwarmde oppervlakken kwantitatief verklaren. Als de temperatuur van het substraat op het Leidenfrost punt ligt, resulteert dit in een abrupte verlaging van de kritieke snelheid. Voor nog hogere temperaturen, neemt de kritieke snelheid, op zijn meest, zwak toe met de temperatuur van het substraat.

In hoofdstuk 7 onderzoeken we de verdamping van druppels met een volume in de orde van picoliters op een substraat. De verdampingsnelheid van druppels van een pure vloeistof in stilstaand gas is gelimiteerd door de diffusie van damp door het omringende gas. De mate van damp diffusie wordt bepaald door het verschil in de concentratie van damp dichtbij de druppel, waar het gas verzadigd is met damp, en de concentratie van damp ver van de druppel vandaan. Wat de concentratie van damp in verzadigd gas is, hangt sterk af van de temperatuur van het gas, wat ervoor zorgt dat de verdampingsnelheid ook afhangt van deze lokale temperatuur. De temperatuur van het gas dichtbij de druppel verandert als de temperatuur van de druppel afneemt door het verdampingsproces. De faseverandering van vloeistof naar damp kost energie en als de druppel deze energie niet kan opnemen van zijn omgeving, koelt hij af. Dus als de druppel erg vluchtig is of als de thermische geleiding van het onderliggende substraat laag is, zal de verdampingsnelheid lager zijn dan het isotherme, diffusie gelimiteerde verdampingsmodel voorspelt. Deze afname in verdampingsnelheid is eerder gezien voor microliter druppels, maar is nooit bestudeerd voor kleinere druppels. Wij laten zien dat de afname van de verdampingsnelheid nog groter is voor picoliter druppels dan was eerder gerapporteerd voor de microliter druppels. Een uitleg hiervoor is te vinden in het verband tussen de warmteflux die veroorzaakt wordt door verdamping en de grootte van de druppel. De verdampingsnelheid is evenredig met straal van de druppel, dus de mate van warmteabsorptie door de druppel is dit ook. Omdat de warmteflux gelijk is aan de mate van warmteabsorptie gedeeld door het geleidende oppervlak, is de warmteflux omgekeerd evenredig met de straal van de druppel. Dit verklaart de sterkere koelingseffect voor kleinere druppels en de daaruit volgende langzamere verdamping. Dit betekent bovendien dat isotherme verdamping niet mogelijk is in de limiet van een druppelstraal die naar nul gaat.

List of publications

Scientific publications

Drop impact on superheated surfaces

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Droplet impact on superheated micro-structured surfaces

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Leidenfrost temperature increase for impacting droplets on carbon-nanofiber surfaces

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Ultrafast imaging method to measure surface tension and viscosity of inkjet printed droplets

H. J. J. Staat, A. van der Bos, M. van den Berg, H. Reinten, H. Wijshoff, M. Versluis, and D. Lohse
In preparation

*Equally contributing authors.

Evaporation of picoliter droplets

H. J. J. Staat, H. Wijshoff, M. Versluis, and D. Lohse
In preparation

Contributed talks

Dynamic Leidenfrost temperature for impact of droplets on micro-structured surfaces

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68th Annual Meeting of the APS/DFD, Boston, MA, USA (2015)

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Inkjet printing

H. J. J. Staat and M. Versluis
Arago Focus **45**-1 (2015)

Inkjet flight 20

Winner MESA+ jury award in the Twente Seconds Science video competition

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Let us first go back to the moment when my PhD adventure started. It was a cold day in December of the year 2011 when Detlef sent me an e-mail stating that we should discuss my future after my master thesis. When I entered Detlef's office he asked me what I wanted to do after my Master graduation, which was a few weeks later.

"I was thinking about doing a PhD", I said.

"Good.", Detlef replied, "There is a project together with Océ, which I think would really suit you. We should go to Venlo and meet with them."

There was already a progress meeting planned, so that was the ultimate opportunity to tag along. A few weeks later, we drove to Venlo and met the people at Océ and I immediately knew that these were the people that I wanted to work with during the next four years. This was the first of many meetings in Venlo and the start of a fantastic time in my life, the extension of my stay at the Physics of Fluids group as a PhD researcher.

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both conferences run smoothly.

Since I did my PhD at the same place as the rest of my studies, the past four years felt like an extension of my life as a student. Although I didn't have as much time as before to participate in all the activities, it was still a lot of fun to hang out with people from S.V. Arago, het BACO, de MEK, de Vestingbar, and B.S.V. de Stoottroepen. Stomme Mongool II, Elvis, Jaap, Gert, Stapelpants, Remkows, Jenkins, Smink, Kwiebus, Bennie, Marijke, F5, Kanye, Stomme Mongool III, Dikkop, Jaco, Mark, Bibi, Janneke, Wuis, Ruud, Kaas, Sikh, Brutus, Denise, Marcel, Hidden, Gwijde, Floris, and all the others, you ensure that the BACO remains so much better than de BRAK.

To the (former) occupants of the MEK I want to say that I find it very special that you have always treated me as one of your own, even though I was not. Thanks a lot for this Jaap, Quincy, Hannah, Marina, Heidi, Nico, Ötzi, Piena, Joost, Truus, Karim, Annika, Tommie, Ed, Jaldert, Tony, Arie, and Ollie. I hope that the Grolsch MEKscursie, the celebration of new year's eve, and playing singstar in the living room will be great traditions for many generations of students to come.

My love for playing football was reignited by the MEK's very own Futsal team MEK Mek Mek ft. Arie, which was later renamed MEK Mek Mek ft. Old School. Playing legendary opponents, such as FC Schultenbräu, Bruine Ster Drienerlo, and West Henk United did not always result in a win, but at least we won the third half on the couch at the MEK.

Later I also joined Physics of Fluids very own futsal team: POF United. Pascal, Maarten, Ruben, Enrique, Ivan, Alvaro, Yaxing, Bart, Bram, Bram, Mathias, Erwin, Arjan, Ivo, Stefan, Gert-Wim, Minori, Mark-Jan, Michiel, Aram, Maurice, Stef, Luuk, Lammert, Ivan, Jacco, Chao, Tuan, and many others, we had a lot of fun playing together in orange. Thank you for letting me be your captain.

I would like to thank my closest family, my parents Koos and Liesbeth, my sisters Margriet and Welmoed, and my brother-in-law Michel for their never-ending support. Last but not least, Karin, mein Schätzchen, thank you for being part of my life and standing by me through thick and thin. You are amazing, I love you.

Erik-Jan Staat
Enschede, March 2016

About the author

Hendrik Johannes Jacobus Staat was born on the 5th of June in 1986 in Munnekezijl, Friesland, the Netherlands. On his second birthday, he moved to Yerseke, where he attended the elementary school ‘C.B.S. Het Kompas’. He relocated to Haarlem in 1993, where he attended ‘de Dreefschool’ for two years, before moving to Rijnsburg, where he finished his elementary education at the ‘Koningin Emmaschool’ and attended the high school ‘Visser ’t Hooft college’ in Leiden. He received his high school diploma from ‘Damstede’ in Amsterdam, after attending that school in the two years that he lived in Zunderdorp. He then decided he wanted to move again and study Applied Physics at the University of Twente in Enschede. On the 13th of January 2012, he received his master’s degree in Applied Physics for his work on droplet impact on superheated surfaces in the Physics of Fluids group under the supervision of Detlef Lohse and Chao Sun. He continued his PhD in the same research group on the flight, impact and evaporation of droplets in collaboration with Océ Technologies. During his time at the University of Twente, he was involved in many extracurricular activities, including boardmember of S.V. Arago, chairman of the BACO, head of security at ‘De Vestingbar’, member of the organization committee of two international conferences, and captain of PoF United. Apart from organizational efforts, he takes an interest in playing football, cooking, playing pool, and is a proud supporter of AFC Ajax.