LIQUIDS UNDER TENSION

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Liquids under tension

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LIQUIDS UNDER TENSION

PROEFSCHRIFT

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About the cover

Figure 1: Canorgraphy machine designed by Roos Meerman. It consists of a marker pen hanging from a long wire so that its tip rests under an angle on a stretched canvas. When the canvas is actuated by for example a loudspeaker, the pen starts walking in the indicated direction. The photographs show a typical example of the resulting chaotic ink patterns left behind by the pen.

A little bit of public exposure can lead to surprising collaborations. After my name had appeared for about 3 seconds in a science quiz on Dutch national television I was promptly contacted by Roos Meerman. She designs and builds machines to freeze physical processes in order to turn them into products that people would like to buy. An interesting viewpoint which is not so often encountered in science. How to discover/invent physical phenomena that you can permanently store, and whose frozen shape is useful and/or esthetic at the same time? The molten tin experiment mentioned in the introduction was one of the ideas that came forth from our conversations.

When Roos came to visit me, she had already build some intriguing machines that satisfied the above criteria. One of those machines is shown schematically in figure 1. Conceptually the setup is fairly simple. It consists of a marker pen hanging

from a long wire, so that its tip rests on a framed canvas. Below the canvas a big loudspeaker is placed which makes the cloth vibrate up and down. The surprising result is that the angled pen starts walking over the canvas, leaving behind beautiful patterns of lines and loops as the wire tries to swing it around. The precise outcome is different every time the experiment is repeated, even if all the settings are kept the same. In scientific terms: it displays chaotic behavior. The qualitative features of the drawing can be controlled by changing the length of the wire, the mass and length of the pen, the tension in the canvas and the frequency and amplitude of the sound.

It is a challenging fundamental question for a scientist, and of great practical importance to a design-artist, whether it is possible to predict the (qualitative) outcome given the machine's settings. So I started a series of simulations. First a detailed 3D simulation which closely resembled the actual setup, and later a fast, highly simplified 2D model which only contained the bare minimum to produce the chaotic line and loop patterns. Figure 2 shows how the latter produced the cover of this thesis. I found this simulation result particularly appealing because of the vague circular structure that starts to appear after running the simulation for a sufficient long time.

Figure 3 shows that if one slightly increases the friction coefficient μ_c of the canvas, the pattern becomes completely regular. Interestingly, increasing μ_c slightly *more* makes it chaotic again. The next challenge will be to understand this behavior and to reproduce it experimentally.

The mechanism behind the cover pattern has many common grounds with the topics discussed in this thesis, such as the continuous build up and periodic release of tension, and the friction controlled motion. Above that, the picture can be interpreted as an abstract representation of a charging, evaporating, impacting or bursting droplet (chapters 3, 4 and 5) or a bubble growing in a gas saturated solution (chapter 2). On an even higher level it can be related to the scientific process itself. It stands for the interplay between simulations, models and experiments, and for the often long and chaotic path of scientific inquiry, wandering around a central theme. Only by looking at it from a distance, can one start to see the emerging patterns.

Figure 2: Development of the cover pattern in time.

Figure 3: Final results of three simulations ran with slightly different friction coefficients μ_c of the canvas. The simulation on the left corresponds to the cover image and in each subsequent image μ_c is increased by 3%.

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1

Introduction

When you step into a swimming pool, the force that is exerted on the water makes it smoothly flow out of the way. Quite the opposite happens when one accidentally lands flat on the water after a dive. In this case the water has no time to flow and the *incompressible*, solid-like, nature of a liquid is experienced very vividly.

What is perhaps less well known from daily experience is that liquids are also *inextensible* when they have no opportunity to flow. In this case one can pull, or more precisely, exert a negative pressure or *tension* on a liquid, without the liquid giving in. This distinguishes a liquid from a gas, which can only withstand positive pressures. The origin of this difference can be traced back to the relative importance of attractive and repulsive intermolecular forces in liquids and gases. In a liquid, molecules are held together by attractive forces, which are then (on average) balanced by repulsive collision forces. In gases the average interaction forces are very weak and the motion of the molecules is dominated by collisions with the walls of the container. A gas will therefore always expand to fill the whole available volume, while in a liquid molecules prefer to stick together. If one pulls strong enough on a liquid its bonds can be “broken” and it will snap like a wire under tension. In the case of a liquid this sudden breaking is called *cavitation*. It is often an explosive event, because of the large amount of tension energy that is suddenly released. For example, some people like to make the liquid in their knuckles cavitate by pulling on their fingers (see figure 1.1(a)). The sudden release of energy is accompanied by a loud popping sound, hinting at the short time scales involved (figure 1.1(b)). The precise origin of

Figure 1.1: Cavitation in the joint of an index finger caused by pulling on it. (a) MRI scans before and after the knuckle popped. The cavity is visible as a dark contrast in between the bones. (b) Recording of the typical popping sound produced. Both the MRI scans and the sound recording were kindly provided by chiropractor Jerome Fryer [1] and reproduced here with permission.

the sound is still an open question in this case [1].

Cavitation always occurs at a weak spot in the liquid, called a nucleus. These nuclei can be present in the liquid before the tension is applied, for example in the form of small gas pockets, they can be introduced in the system by some external action, using for example a focused sound or light pulse [2, 3], or they can be formed spontaneously due to density fluctuations [4]. The latter situation is referred to as *homogenous nucleation* and the first two cases are examples of *heterogeneous nucleation*. Homogenous nucleation sets an upper limit for the time and tension for which the liquid can be stable. At room temperature the formation rate of spontaneous nuclei is extremely low and therefore cavities are usually most readily nucleated from heterogeneous sites. In many circumstances the precise qualities of these nucleation sites are unknown. Depending on the method by which a liquid was put under tension the resulting cavity can be (practically) empty, or be filled with gas and/or vapor. The dynamics will be different in each case.

From a thermodynamics point of view, a liquid under tension is a *metastable*

Figure 1.2: “Cavitation” on a tape measure. In (a) the curved metal tape is put in a metastable state. At some extension the tape snaps under its own weight and displays a bend as shown in (b). The different regions referred to in the text are identified in (c). The flat, plate-like part is analogue to a cavitation bubble in a liquid.

system. To clarify this concept and to show its generality, the following section starts with an example from structural mechanics [5] in which the reason for metastability is more tangible. By a direct analogy this will then be related to the fluid state.

1.1 Metastability and phase transitions

The extended tape measure shown in figure 1.2(a) is an example of a metastable system. It consists of a thin sheet of metal with a slightly bended cross section. This design makes that the tape can be pulled out from its container over a substantial distance without buckling (typically 2 meters, if done carefully). However, anyone who has used this handy tool knows that this rigid, rod-like state of the tapeline is not the most stable state under these conditions. It is metastable. Close to its maximum extension, a small perturbation of the preformed shape is enough to make the tape lose its rigidity and fall to the floor. This transition is accompanied by a loud snapping sound. Figure 1.2(b) shows what the fold looks like after buckling. It consists of two straight, almost undeformed legs, connected by a circular bend in

Figure 1.3: Elastic free energy and bending moment of a piece of tapeline as a function of its longitudinal bending curvature. The black lines in (b) are calculated by taking the derivative of the rod-like and sheet-like energies in (a). The gray line in (b) represents the full analytical solution worked out by Wuest (1954).

which the tape is flat. A schematic of the different regions is shown in figure 1.2(c). The bend and the straight legs are separated by two interfacial regions with a more complicated structure.

1.1.1 Free energy and equation of state

Although it sounds like the snapping is quite violent, everything happens in the elastic regime of the stainless steel tape measure. No permanent, plastic deformations are visible after straightening the tape again. When the tape is straight it behaves like an elastic rod. The elastic energy, or more precisely *free energy*, of a rod u_{rod} per unit length as a function of the bending curvature κ can be written as [6]

$$u_{\text{rod}} = \frac{1}{2} EI_r \kappa^2, \quad (1.1)$$

reminiscent of Hooke's law for simple springs. Here $E \approx 200 \text{ GPa}$ is the Youngs modulus of the metal and $I_r \approx 1 \text{ mm}^4$ is the area moment of inertia of the tape's cross section about the bending axis, which together determine the spring constant. κ refers to the bending curvature along the length of the tape, not to be confused with the almost constant transverse curvature $\kappa_t \approx 100 \text{ m}^{-1}$. After buckling, the tape is flat in the bend region. The free energy per unit length of this flat, flexible sheet can be

expressed as [6]

$$u_{\text{sheet}} = \frac{EI_s}{2(1-\sigma^2)} \left[\kappa^2 + \kappa_t^2 + 2\sigma\kappa\kappa_t \right] \quad (1.2)$$

where $\sigma \approx 0.3$ is the metal's Poisson ratio and the flat sheet's area moment is $I_s \approx 10^{-3} \text{ mm}^4$, three orders of magnitude smaller than that of the rod. In figure 1.3(a) both free energies are plotted as a function of the amount of bending κ . From thermodynamics we know that for a given κ , a piece of tape will take the shape that minimizes its free energy. For small amounts of bending the rod shape has the lowest free energy. But around $\kappa \approx 3 \text{ m}^{-1}$ the lines cross and the sheet-like state becomes more favorable. When the tapeline bends beyond this point, it snaps.

The mechanical properties of the rod-like state and the sheet-like state are very different. Figure 1.3(b) shows the bending moment of the tape, which by the principle of virtual work can be directly obtained from the free energy as $m = \partial u / \partial \kappa$. When the tape buckles, this can be felt as a sharp drop in its resisting bending moment. In reality the transition is not as sharp as sketched here. The limiting behaviors for small and large κ are captured well by the simple models, but the maximum moment is somewhat overestimated. The gray line represents a detailed calculation of the moment of a small bended piece of cylindrical shell, carried out by Wuest in 1954 [7]. This detailed model predicts the critical moment to be about $m_{\text{max}} \approx 0.25 \text{ Nm}$. We can compare this to the moment exerted by gravity on a tape pulled out of its container over a horizontal distance L : $m_g \approx \rho g A_c L^2 / 2$, where $g \approx 9.8 \text{ m/s}^2$ is the gravitational acceleration, $A_c \approx 1.6 \text{ mm}^2$ is the cross sectional area of the tape and $\rho \approx 8000 \text{ kg/m}^3$ is its density. The two moments become equal when $L = L_{\text{max}} \approx 2 \text{ m}$, close to what is observed experimentally if the extraction is done very carefully.

1.1.2 Phase transition and coexistence

When the rigid tapelines snaps, it is not the whole tape that becomes flat. The above analysis only holds for a very small piece of tape (say, smaller than the size of the interface regions, see figure 1.2). For longer tapes a highly curved sheet-like phase *coexists* with an almost straight, rod-like phase and the system as a whole can no longer be described by a single curvature κ .

Upon increasing or decreasing the angle θ between the legs, the curvatures κ_s and κ_r in respectively the bend and the legs remain constant, while the interface between them moves to accommodate the change in angle. When the interfaces move, their shape and associated energy remain constant (as long as they don't touch). This implies that the bending moment m of the tape remains constant during this *phase change*. As can be easily verified experimentally [5]. For such a system, it is not the

Figure 1.4: Maxwell construction for (a) a tape measure and (b) an ideal liquid. The phase equilibrium condition is obtained by moving up or down the vertical line until the shaded areas are equal, giving the two phases as the left- and rightmost intersection points. The inset in (a) shows that for a tape measure the longitudinal curvature in the bend closely matches the preformed transverse curvature of the rod-like state, which is an universal feature of buckled tapelines.

free energy $U = u(\kappa)L$ that is minimized, but a quantity called the Gibbs free energy $G = \mu(m)L$ [8], where L is the length of the tape measure and $\mu(m) = u(m) - \kappa m$ is the Gibbs free energy per unit length. In molecular thermodynamics μ is often referred to as the *chemical potential*. For a tapeline with a bend region of length L_s and legs of total length L_r , one can write $G = \mu_s L_s + \mu_r L_r + 2\Gamma$, where Γ is a *constant* energy contribution from each interface. In equilibrium we must have $\delta G = \mu_s \delta L_s + \mu_r \delta L_r = 0$, and because the lengths of the rod and sheet regions are related as $\delta L_r = -\delta L_s$, we find $\mu_s = \mu_r$. This is a general condition for thermodynamic phase equilibrium [8]. Together with the condition for mechanical equilibrium $m_s = m_r$, we have two equations which can be solved for the two equilibrium curvatures κ_s and κ_r . In 1875 Maxwell demonstrated a neat geometrical construction to obtain the equilibrium condition directly from the graph of m versus κ , which was originally derived in the context of the liquid-vapor phase transition [9]. As depicted in figure 1.4(a), Maxwell's construction amounts to finding a horizontal line m_{eq} through the curve $m(\kappa)$ such that the shaded areas above and below the line are equal. That the line is horizontal ensures that $m_s = m_r$, while the 'same area rule' can be proven to be equivalent to $\mu_s = \mu_r$. From the left and rightmost intersection points one can then read off the equilibrium curvatures: $\kappa_r \approx 0$ for the legs and $\kappa_s \approx 90 \text{ m}^{-1}$ for the bend

region. That the latter is very close to the preformed curvature $\kappa_t \approx 100 \text{ m}^{-1}$ is not a coincidence, but an universal feature of thin curved strips (for which $I_s/I_r \ll 1$).

1.2 Liquids under tension

Around 1870 Van der Waals conceived the idea “that there is no essential difference between the gaseous and the liquid state of matter” (Nobel Lecture of Van der Waals in 1910). He used this idea to successfully explain deviations from the ideal gas law ($p\nu = R_g T$) observed for pressurized gases, and got the liquid state for free. Using density functional methods introduced by Laplace, he arrived at the following equation of state for an “ideal liquid” [10]:

$$\left(p + \frac{a}{\nu^2}\right)(\nu - b) = R_g T, \quad (1.3)$$

in which p is the pressure, ν is the volume per mole of molecules, $R_g \approx 8.31 \text{ J/mol K}$ is the gas constant, T is the temperature in degrees Kelvin, and a and b are two constants that model the (average) attractive and repulsive forces, respectively. In figure 1.4(b) this relation between p and ν is plotted for $T = 375 \text{ K}$ (100°C). The parameters a and b were chosen such that the behavior is roughly that of water. For small volumes (i.e. large densities) the steep slope indicates that large pressures or tensions are required to change the volume by a small amount, corresponding to the incompressible and inextensible nature of liquids. At large volumes (for the same number of molecules) the pressure behaves like that of an ideal gas.

Basically, the $p(\nu)$ curve for a liquid is the upside-down version of the $m(\kappa)$ relation for a tape measure, and indeed the behavior of a liquid under tension is similar to that of a tapeline. In this analogy the rigid, rod-like parts of the tape correspond to the liquid phase and the flexible, sheet-like state corresponds to the gas phase.

A gas that consists of the same molecules as the liquid it is in contact with, is called a *vapor*. The condition for stable liquid-vapor coexistence can again be found from the Maxwell construction (see figure 1.4(b)). For water at 100°C the equilibrium pressure p_{eq} is equal to the atmospheric pressure at sea-level $p_a \approx 0.1 \text{ MPa}$. This means that the vapor phase can exert enough force from inside the liquid to overcome the pressurisation by the surrounding air: in other words the water can start to *boil*. That is, *if* nucleation sites are present in the liquid or on the container walls. In the absence of weak spots in the liquid, the surrounding pressure can be lowered substantially without the liquid starting to boil or cavitate. The liquid becomes metastable. For the ideal liquid in figure 1.4(b) the minimum pressure is about -60 MPa , that is, a tension of 600 times atmospheric pressure! Although this might seem extreme, there are many examples in which highly metastable liquids are encountered in practice.

Figure 1.5: High speed recording of cavitation near the bottom of a water filled beer bottle, after firmly hitting it on the top. About 2 ms later, the collapse of the cavities results in cracks in the glass. The dashed lines are a guide to the eye to compare the liquid and glass levels. The last frame shows how the bottom part of the bottle finally completely comes off.

The highest tensions can be found in small amounts of water trapped in natural or artificial mineral inclusions. In these systems tensions as high as 140 MPa are routinely observed [11–13]. An interesting application of these natural occurring fluid inclusions is to infer the paleogeologic conditions under which they were formed [14–16]. High tensions can also develop when a continuous column of liquid is pulled up over great heights, similar to a tape measure that becomes metastable under its own weight. This happens for example for the sap transported up through the wooden channels (xylem) in tree trunks. Tensions between 1 and 10 MPa are observed in real and synthetic trees [17, 18]. Cavitation of the liquid in the xylem is a serious threat to trees [19] and in the course of evolution they have developed several advanced defense strategies, like filtering of small bubbles and particles in their root channels [20], mechanical safety valves between the interconnected xylem chambers [21, 22], and refill pumps in the case of a failure [23, 24].

It is also possible to generate high tensions dynamically. A popular example is shown in figure 1.5. In the first frame a beer bottle partly filled with water is struck firmly on the top, so that the bottle moves down with a large acceleration. Initially the mass of water cannot keep up with this acceleration, and we see large cavities form near the bottom of the glass. Finally, the water catches up and forms sharp jets inside the cavities directed toward the glass, which upon impact exert enough pressure to locally fracture it. The whole sequence from hitting the bottle to the first cracks, takes about 2 milliseconds. The last frame shows the final fate of the bottle about 60 milliseconds later. Note that this trick does not work as well with

beer inside the bottle. The large number of CO_2 gas nuclei in beer weaken the liquid and damp the implosion. However, other interesting effects can be observed in this case [25]. Although this is a playful example, the study of how cavitation can lead to damage is of great importance in the design of ship propellers [26], which generally accelerate the fluid beyond its tensile strength. Another example of dynamically induced cavitation can occur in lubricated ball bearings. Here the motion and weight of the ball lead to large viscous stresses in the thin film of liquid below it. In this case a (stable) cavity helps to break the symmetry of the flow, preventing the ball from touching the wall [27].

1.3 Surface tension

For the tape measure the interfacial regions contributed a constant amount $U_i = 2\Gamma$ to the free energy, which was therefore not important for calculating the condition for mechanical equilibrium. For a cavity in a liquid, which generally exists in three dimensions, this contribution takes the form $U_i = \gamma A$, where A is the surface area of the cavity and γ now has units of J/m^2 or, equivalently, N/m and is called the *surface tension*. This energy penalty causes that small bubbles and droplets “want” to be spherical to minimize their surface area. From a molecular point of view this tension originates from an imbalance (on average) between attractive and repulsive intermolecular forces along the liquid-vapor interface [28]. For water the surface tension changes from about $\gamma \approx 72 \text{ mN/m}$ at room temperature to $\gamma \approx 0 \text{ mN/m}$ around the critical temperature $T_c = 374^\circ\text{C}$. Above this point there is no longer a clear distinction between liquid and vapor.

Although surface tension is often a not so important force on a human scale, it dominates the world of small animals like birds and insects (see figure 1.6). If one compares for example the typical gravitational body force on a puddle of liquid of linear dimension L , giving $F_g \sim \rho g L^3$, with that of surface tension, $F_\gamma \sim \gamma L$, one finds that F_γ becomes larger for $L \sim \sqrt{\gamma/\rho g}$. For water this length scale is about $L \sim 3 \text{ mm}$. The competition between body forces and surface forces will be a recurring theme throughout this thesis.

The existence of surface tension also has important implications for the ultimate fate of cavities in a liquid. Consider a spherical cavity of radius r . A small change δV in its volume will lead to a change $\delta A = 2\delta V/r$ in its area. Using again the principle of virtual work, $\delta U_i = \gamma \delta A = 2\gamma \delta V/r \equiv \Delta p_\gamma \delta V$, we see that the surface tension must result in a pressure drop of

$$\Delta p_\gamma = \frac{2\gamma}{r}, \quad (1.4)$$

Figure 1.6: Four examples of small animals dealing with surface tension. From left to right, top to bottom: a drinking bird, a water strider on a pond, a bee drinking some sugar water and a spider dismantling his web covered with dew drops.

in going from the inside of the cavity to the outside. This pressure drop is called the *Laplace pressure* and in general it can be written as $\Delta p_\gamma = 2\gamma\kappa$, where κ is the mean local curvature of the interface. Now suppose that we somehow managed to make an empty cavity of radius r which is in static mechanical equilibrium with the surrounding liquid at a uniform pressure $p_\infty = -2\gamma/r$ (i.e. the liquid must be held under tension). This equilibrium is not stable with respect to small changes in r . If r is slightly decreased, the pressure just outside the cavity also decreases (inside it remains zero). This pressure difference sets up a flow toward the cavity, decreasing the cavity size even further, and so forth, until the cavity has finally completely collapsed. If r is slightly *increased* just the opposite happens, and the cavity will grow without bounds (the liquid is torn apart). The rate of collapse or growth is determined by the inertia (or viscosity) of the surrounding liquid, or by the rate at which gaseous content (gas or vapor) is transported across the interface. Whichever is the limiting factor. For example, a millimetric cavity filled with air in a glass of tap water (i.e.

Figure 1.7: (a) Equation of state of an ideal liquid for three different temperatures $T = 100^\circ\text{C}$, 200°C , and 300°C . For each curve the dashed line indicates the liquid-vapor equilibrium pressure. (b) Phase diagram for water. Here the dashed lines represent the coexistence conditions for the different phases as function of temperature. The arrows indicate three typical pathways to put the liquid in a metastable state in an experiment.

a gas bubble) can persist for days due to the slow rate of gas transport through the liquid. Note that the above instability argument only holds for cavities which are completely surrounded by liquid. If it is lodged in a crevice on the container wall or on some solid particle, it can be stable, depending on the geometry of the crevice and the adhesion properties of the solid [29–31].

Surface tension also greatly influences the behavior of small droplets. It determines for example how they deform upon collision with a solid surface. Detailed knowledge of this process is of great importance in many applications, from optimizing the ink coverage and resolution in inkjet printing [32] to blood spatter analysis in crime scene reconstructions [33]. Chapter 4 raises some of the fundamental questions that still exist in this widely studied field.

1.4 Super heating, cooling, saturating and charging

1.4.1 Superheating

As is clear from equation (1.3) the state of a liquid is not only a function of the pressure, but also strongly depends on the temperature. Figure 1.7(a) shows p versus v for three different temperatures T : 100°C , 200°C , and 300°C . The dashed lines cor-

Figure 1.8: High speed recordings of droplets of hot, molten tin impacting onto a pool of water at room temperature. The same experiment is repeated for three temperatures of the tin $T_{\text{tin}} = 300\text{ }^{\circ}\text{C}$, $330\text{ }^{\circ}\text{C}$, and $400\text{ }^{\circ}\text{C}$. As shown in the three frames on the right, the result is different in each case.

respond to the equilibrium pressures obtained from the Maxwell construction. With an increase in temperature both the minimum pressure and the equilibrium pressure increase. This means that for higher temperatures the liquid becomes more susceptible to cavitation. It also means that a liquid can be put under tension, with respect to its equilibrium liquid-vapor pressure, simply by increasing the temperature. In other words, a liquid can be heated to above its boiling point, without boiling. In this state a liquid is said to be *superheated*. From a thermodynamic point of view, heating the liquid above its boiling point or lowering its pressure below its equilibrium pressure are two sides of the same coin. Many people will have had some experience with superheated liquids in their kitchen, for example when small water droplets from rinsed or frosted vegetables enter hot cooking or frying oil. In contrast to the relatively gentle boiling in a kettle, highly superheated liquids boil explosively.

Figure 1.8 illustrates some of the different behaviors of (locally) superheated liquids often encountered in industry when processing hot metals. In the experiment a small droplet of hot, molten soldering tin is dropped from a height of 6 cm into a pool of water at room temperature. The final outcome of the experiment strongly depends on the degree of superheating of the tin with respect to the boiling point of water. When the temperature of the tin is around $300\text{ }^{\circ}\text{C}$ a stable layer of water vapor is formed around the droplet, completely encapsulating it as it falls through the liquid. The effect of this stable vapor film is two-fold: first, it thermally insulates the tin from the water, keeping it in its molten state till the very end where it impacts onto the bottom of the container. Second, it dramatically reduces the friction between the

tin droplet and the surrounding water, it slices through as if the liquid was not there. Depending on the industrial application this so called *Leidenfrost effect* is detrimental or beneficial.

When the temperature of the tin is slightly increased to 330 °C, the behavior completely changes. Instead of slicing through the water, the tin droplet now “pops” open like pop-corn and cools down quickly below its melting point because of the larger exposed surface area. The frozen chunk of metal slowly sinks to the bottom. The precise mechanism which causes the liquid metal to pop open is unknown as far as the author knows, but it is likely that during its impact with the pool small water droplets are encapsulated in the hot melt, making the tin droplet explode like a fire-cracker when these droplets vaporize from within. For tin of 400 °C the explosion is even more violent and the droplet is completely shattered. This example highlights the difference between confined and unconfined liquids under tension, which is another theme in this thesis.

1.4.2 Supercooling

By plotting the equilibrium liquid-vapor coexistence pressure $p_{eq}(T)$ as a function of the temperature, one obtains what is called a *phase diagram*. Figure 1.7(b) shows a part of the phase diagram of water. Within the shaded area, liquid is the most stable form of water. If one increases the temperature at a constant pressure, or decreases the pressure at constant temperature, one will eventually cross the liquid-vapor line (see arrows). At this point the liquid becomes metastable and it will (partly) turn into vapor upon nucleation.

Of course it is also possible to *decrease* the temperature of a liquid. It is a well known fact that if the temperature of water drops below 0 °C, it wants to turn into ice. Also in this case the liquid first becomes metastable, it becomes *supercooled*. Effective nuclei are often solid particles with a molecular lattice structure close to that of ice, although the question of what constitutes a good nucleation site for ice formation is still actively debated [34–38]. Supercooled droplets are commonly observed in high altitude clouds, but the precise role of these droplets in the overall cloud dynamics is a big “known unknown” in current climate models [39].

Compared to other liquids that freeze, water is very special. Instead of shrinking, water expands. This means that if water freezes in confinement, it will exert large stresses on its container walls. In nature this can for example cause the sudden fracturing of large rocks containing fluid inclusions [40, 41] (see figure 1.9). One can also experience these large stresses when stepping onto a lake covered with a thick layer of fresh ice. The ice compresses itself by pushing on the sides of the lake, and the release of this stress when one steps onto it is accompanied by loud sounds of crack

Figure 1.9: Fractured rock on mountain plateau the Hardangervidda in Norway. The initial crack could have been caused by stresses built up on the inside by the freezing of liquid water inclusions.

propagation, reminiscent of the sounds in an arcade spacecraft shooter. Chapter 5 of this thesis treats an example of ice under tension.

1.4.3 Supersaturating

In many circumstances of practical interest the phase diagram in figure 1.7(b) is still not quite complete. Often the liquid is (or has been) in contact with a gas other than its own vapor. In this case the phase diagram needs an extra dimension to take into account the equilibrium between the dissolved and gaseous phases of the gas molecules.

Suppose that we have somehow created a situation in which some amount of pure liquid water is in contact with an atmosphere of air. At first the air will exert a pressure on the water and very slightly compress it. However, it is thermodynamically favorable for some of the gas molecules to go in between the liquid molecules. This dissolved air will exert a kind of internal pressure, trying to push apart the water from the inside. When finally a dynamic equilibrium is reached between molecules entering and leaving through the gas-liquid interface, the internal and external gas pressures will be equal. To a good approximation, doubling the external gas pressure results in a doubling of the final concentration of dissolved gases. Now suppose that we close the chamber and quickly remove the gas above the liquid with a vacuum pump. The gas dissolved in the liquid will have had no time to escape and still exerts an internal pressure on the liquid, putting the liquid under tension. In this situation the

Figure 1.10: Two spherical droplets sitting on a grounded plate are drawn up in a cone when a statically charged teflon rod is held above them.

water is said to be *supersaturated* with gas. If the gas concentration is high enough the liquid (given some nuclei) will cavitate and bubbles filled with gas form inside it. This happens for example when removing the lid from a carbonated soft drink. In this case the external pressure is suddenly lowered from typically 3 atm to 1 atm.

In the above considerations we assumed that the temperature was kept constant. Interestingly, if instead of removing the gas above the liquid we had decided to suddenly raise the temperature of the liquid, we would have observed a very similar behavior. In general, the effects of heating and internal gas pressure have to be added in order to calculate the internal pressure, and nucleated cavities will be filled with both gas and vapor. One can observe this effect for example when heating up some water in a pot. Even before the liquid starts to boil, a lot of small bubbles appear on scratches in the bottom of the pot. At some point the bubbles grow large enough so that they detach. Initially the liquid higher up in the pot will still be relatively cold. When a bubble filled with a mixture of gas and vapor enters this colder liquid, the vapor quickly condenses back, leaving the gas behind in a smaller bubble (gas diffusion is a much slower process). Oscillations of these remaining gas bubbles cause that familiar noisy sound, tricking many people (including the author) into thinking that their water is already fully boiling. In chapter 2 the growth dynamics of mixed gas-vapor bubbles is described in more detail.

1.4.4 Supercharging

Already in the year 1600 William Gilbert noticed how small spherical droplets of water sitting on a conducting plate are “drawn up in a cone” [42] when a piece of statically charged amber is held above them (see figure 1.10). The effect is caused by charges of one sign that are pulled into the droplet from the plate (or pushed out of it). Because like charges repel, they will be concentrated in a thin layer at the liquid-gas interface, leaving the interior of the drop electrically neutral. This in turn allows one

to pull on the interface with an electrical field.

While the intermolecular forces in the liquid keep the spherical droplet together, the charges do just the opposite. When the amount of charge exceeds some critical value, the spherical shape of the droplet becomes unstable with respect to the cone shape. Also this transition exhibits some metastable characteristics [43], and one could call the droplet *supercharged* in the regime where it remains spherical while the cone-shape is more stable. Increasing the charging even further, the cone tip destabilizes and starts to eject small charged droplets.

1.5 In this thesis

The arrows drawn in figure 1.7(b) give the liquid a central position in the phase diagram. However, similar arrows could have been drawn from the ice or vapor phase into the liquid (melting, condensation), or from the ice into the vacuum (fracturing). All cases exhibit metastability and have nuclei of different kinds. But although on a high level thermodynamics unifies all forms of metastability, the phenomena observed after the tension is released can be quite diverse. This thesis can be seen as a melting pot of different kinds of metastable systems and their dynamical interaction after the tension in one of the systems breaks. The common divider will be the presence of a liquid as one of the metastable systems.

Chapter 2 deals with gas saturated, heated liquids that cavitate when a brittle solid material fractures inside it. The initial cavities can grow to visible bubbles when the conditions are such that gas and vapor enters them. This process is dubbed *tribonucleation*, because this fracturing can happen on a small scale when two solids are rubbed together.

In chapter 3 it is shown that small, hypermobile *Leidenfrost droplets* (droplets that hover on their own vapor on a hot metal plate) can be trapped in an external electrical field. Here they spontaneously start to jump higher and higher as if they were dribbled like a basketball. In this process regular supercharging of the droplet plays an important role to transfer charge through the electrically and thermally insulating vapor layer.

While the droplets in chapter 3 have small velocities and therefore bounce almost *elastically*, in chapter 4 it is discussed what happens at high impact velocities, when the droplets deform to a large extent and behave *plastically*.

Finally, in chapter 5, experiments are presented in which initially supercooled water droplets freeze from the outside-in, resulting in a sudden explosion when the build up stresses get too high.

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2

Tribonucleation: Writing with bubbles *

We report on the nucleation of bubbles on solids that are gently rubbed against each other in a liquid. The phenomenon is found to depend strongly on the material and roughness of the solid surfaces. For a given surface, temperature and gas content, a trail of growing bubbles is observed if the rubbing force and velocity exceed a certain threshold. Direct observation through a transparent solid shows that each bubble in the trail results from the early coalescence of several microscopic bubbles, themselves detaching from microscopic gas pockets forming between the solids. From a detailed study of the wear tracks, with Atomic Force and Scanning Electron Microscopy imaging, we conclude that these microscopic gas pockets originate from a local fracturing of the surface asperities, possibly enhanced by chemical reactions at the freshly created surfaces. Our findings will be useful for either preventing undesired bubble formation, or, on the contrary, for ‘writing with bubbles’, i.e. creating controlled patterns of microscopic bubbles.

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2.1 Introduction

Microscopic gas-vapor bubbles play an important role in various processes in nature, industry and medicine. Sometimes they are desired: to lower the temperature at which a liquid starts to boil, or to enhance the contrast in medical ultrasound applications. In other cases bubbles are harmful: they cause damage when expanding and collapsing near the propeller blades of ships, and sickness upon expanding in the veins of plants and animals. In spite of their ubiquity, the *nucleation* of bubbles, i.e. the mechanism responsible for their initial formation, has remained mysterious for a long time and, even today, it is not fully understood. Here we show that bubbles can nucleate when two solids are gently rubbed together in a liquid: ‘tribonucleation’.

Elementary considerations show that a bubble will spontaneously disappear unless its radius r is larger than a critical value $r_c = 2\gamma/\Delta P$, where γ is the surface tension of the liquid and ΔP is the difference between the pressure of the bubble contents and the surrounding liquid [1]. Only bubbles larger than r_c can persist and grow by gas diffusion and liquid evaporation. The classical kinetic theory of nucleation [2] shows that, for water, the *spontaneous* formation of critical bubbles requires either superheats of 212 °C or negative pressures (i.e. tensions) of 140 MPa. Recent experiments have come close to the quantitative verification of these predictions [3, 4], but only at the cost of a great deal of sophistication and ingenuity. It must therefore be concluded that a different mechanism is responsible for the exceedingly commonplace occurrence of bubbles.

The seed for the currently accepted explanation was planted by Gernez [5] who, in 1867, hypothesized that bubbles start from a pre-existing gaseous nucleus lodged in solid impurities or the walls of the container. An explanation for the stability of these heterogeneous nuclei was later supplied by Harvey et al. [6] who pointed out that the curvature induced by contact with a hydrophobic solid surface would be able to stabilize a gas pocket even in an under-saturated liquid. This ‘crevice model’ of bubble nucleation explains a large number of observations and has been applied to the development of so-called enhanced boiling surfaces [7, 8]. Gas bubbles can be further stabilized by the formation of organic skins at their surface [9, 10].

In spite of these advances, the nucleation phenomenon still exhibits obscure facets, one of which – tribonucleation – is studied in this chapter. It has been known for at least half a century that, as noticed by Hayward in 1967 [11], “extremely gentle rubbing” of two solid objects inside a liquid under tension, which is otherwise stable against most forms of mechanical action (e.g. knocking on the container wall or stirring), readily induces nucleation. This tribonucleation is often cited as a plausible source of the microbubbles found in the limbs of humans and animals after physical exercise [12, 13]. Campbell [14] and Ikels [15] attributed the nucleation

Figure 2.1: (a) Schematic of the rubbing experiment. (b) Photograph of one of the authors writing a ‘P’ with a trail of slowly growing bubbles by gently rubbing the tip of a pair of metal tweezers over a piece of unpolished silicon wafer submerged in ethanol.

observed in these conditions to the pressure drop induced by the viscous flow in the space between two separating solid surfaces. Indeed, in highly viscous liquids bubble formation compatible with this picture has been reported [16–18]. However, this explanation cannot easily account for the nucleation observed in low viscosity fluids like water and ethanol, because in many cases the theoretical gap between the solids would have to be smaller than the surface roughness. More strikingly, it cannot account for the key observation by Hayward that bubbles do not nucleate in the case of a rolling motion, but only in the case of a sliding motion between the solids [11], although for the same force and velocity the pressure drop is expected to be twice as large for rolling than for sliding [19]. Another instance of bubble nucleation upon solid-solid contact in a low viscosity liquid was reported by Theofanous et al. [20]. These authors were able to reliably nucleate single bubbles by gently bringing into contact two stainless steel wires in Freon superheated by up to 60 °C.

Here we present experiments in which we rub a bead against a wafer submerged in a low viscosity liquid. We vary the rubbing force and velocity, the temperature, and the materials of the solids. Our approach is to combine macroscopic observations, revealing a threshold for the rubbing induced nucleation, with microscopic observations at the smallest scales of the problem: that of the apparent (Hertz) contact between the solids and that of the roughness tips where the actual contact is realized.

Figure 2.2: Experimental setup. It consists of a lever to control the normal force on the bead, a linear slide (connected to a linear motor) to control the rubbing velocity and a heater to set the temperature at the bottom of the liquid cell. The wafer surface can be closely monitored from the side (dashed rectangle) or from the top with a long-distance microscope.

2.2 Preliminary findings

This study was prompted by a recent observation in one of our experiments with heated liquids: bubbles are formed when the tip of a pair of stainless steel tweezers is gently rubbed against a submerged piece of unpolished silicon wafer (see figure 2.1). When the temperature of the liquid is below the boiling point, the bubbles appear as a trail behind the tweezers, where they slowly grow until they detach. After the detachment, no new bubbles are formed, indicating that the rubbing does not create permanent nucleation sites.

This tribonucleation phenomenon occurred in all fluids we have tried so far (ethanol, water, acetone, pentane and perfluorohexane), whether polar or not, and whether they wet the solids or not. Conversely, it depends strongly on the material of the wafer being rubbed. Bubbles appear on silicon and aluminum under mild rubbing conditions, but remain absent on copper, glass and sapphire even upon vigorous rubbing.[†]

2.3 Setup and method

In order to obtain quantitative information about the rubbing conditions for bubble formation, we used the setup sketched in figure 2.2. A smooth sapphire bead (average roughness $\mathcal{R}_a < 0.025 \mu\text{m}$ from Ceratec; radius $R = 4 \text{ mm}$) attached to a movable lever

[†] Bubbles did appear at high loads on glass and sapphire with the tweezers, but not when the tweezers were replaced by a glass or sapphire bead. We think that this is because the tweezers material itself promotes the tribonucleation to some extent.

Figure 2.3: Side view of the experiment. Bubbles (and their reflection in the silicon wafer) appear as black disks against a lighter background. (i) A smooth sapphire bead, submerged in ethanol, is rubbed from left to right against an unpolished silicon wafer at 70°C . (ii) The bubble trail left behind the bead slowly grows by gas diffusion. (iii–v) When two bubbles touch (see white circle), they merge, jump up and then slowly settle down again due to the temperature gradient near the surface (Marangoni effect). (vi) Eventually, buoyancy overcomes the downward Marangoni force and the bubbles rise to the free surface.

arm, replaces the tweezers. A heater was placed underneath the wafer being rubbed. This allowed us to precisely control the nominal geometry of the contact, the normal force F applied to the bead, the rubbing velocity V and the temperature T of the submerged surfaces. Ethanol (99.8% from Assink Chemie; boiling point 78°C) was used as the liquid.

2.4 Bubble trails

Figure 2.3 shows a typical experiment, observed from the side through a long-distance microscope. At $t = 0\text{ s}$ (i) the bead rubs against the *unpolished* side of a silicon wafer held at a temperature of 70°C . Subsequently (ii–vi), small bubbles (black spots) appear behind the bead and slowly grow by gas diffusion. A theoretical estimate of the relevant timescales of this growth is provided in appendix 2.A. Although ethanol wets

Figure 2.4: Threshold velocity for the formation of a trail of bubbles as a function of the normal force, for a sapphire bead and an unpolished silicon wafer. The wafer temperature is 70 °C and the fitted lines correspond to $FV = \text{const}$.

the silicon wafer, the bubbles do not immediately detach. They are pulled down by a ‘Marangoni force’ induced by the temperature gradient close to the wafer surface [21]. Snapshots (iii–vi) show how two bubbles in the row merge, jump up and then settle down again. The jumping is driven by a release of surface energy during their merger, as described for droplets in reference [22]. As the bubbles grow bigger, the upward buoyancy force eventually overcomes the downward Marangoni force and they rise to the free surface (vi).

2.5 Force-velocity dependence

The experiment was repeated for different rubbing velocities and loads (figure 2.4). In each experiment, we fixed the normal force on the bead and then increased the velocity step by step, while monitoring the bubble trail behind the bead. We distinguished between a ‘full trail of bubbles’, a ‘partial trail of bubbles’ and ‘no bubbles’. The data shows that the higher the load, the lower the rubbing velocities required to generate bubbles. As indicated by the lines in figure 2.4, the thresholds we measured are well described by

$$FV = \text{const}, \quad (2.1)$$

with $\text{const} = 17 \mu\text{W}$ and $53 \mu\text{W}$ for the lower and upper thresholds, respectively.

Figure 2.5: Comparison between the force-velocity thresholds for unpolished silicon and sandblasted aluminum submerged in ethanol at 70 °C and having similar roughness $\mathcal{R}_a \sim 0.5 \mu\text{m}$. The solid lines correspond to $FV = \text{const}$. In the shaded area we still observe a partial bubble trail, see figure 2.4.

2.6 Influence of the material and surface roughness

The fact that no sharp transition exists from no bubbles to a full trail suggests that bubble formation depends, somehow, on the varying conditions along the rubbing track. Indeed, when the *polished* side of the silicon wafer was rubbed, the generation of bubbles became significantly harder and less regular. Moreover, when the bead was continuously rubbed back and forth over the same track on the unpolished wafer, bubble formation stopped after typically 10 to 20 strokes, suggesting that rubbing locally changes the surface. If, subsequently, the bead was slightly displaced from the deactivated track during the rubbing, bubbles formed again.

Besides silicon, bubbles are also readily formed on aluminum. In figure 2.5 we compare the tribonucleation threshold for aluminum with that for silicon. To give aluminum a macroscopic roughness similar to that of the silicon wafer ($\mathcal{R}_a \sim 0.5 \mu\text{m}$), the surface was sandblasted with a fine grain before the experiment. The threshold for aluminum turns out to be significantly lower than for silicon ($9 \mu\text{W}$ as compared to $53 \mu\text{W}$). Moreover, in contrast to the quick deactivation of the rubbing tracks on silicon, the tracks on aluminum kept on generating bubbles even after more than 1000 strokes (the largest value we tried), although after typically 20 strokes a polished wear track became clearly visible on the roughened aluminum. Lastly, when the

Figure 2.6: Threshold temperature for bubble formation as a function of the normal force, for a smooth sapphire bead rubbed against a polished aluminum surface with velocity $V = 2.8 \text{ mm s}^{-1}$. The dots represent the experimental data, and the lines represent equation (2.6). The single fitting parameter h can be interpreted as a measure of the typical roughness height in the wear track (see text).

sandblasted surface was replaced by a smooth layer of aluminum (vapor-deposited on a glass slide, $\mathcal{R}_a \sim 2 \text{ nm}$), no bubbles appeared during the first rubbing stroke, but did appear in subsequent passes over the same spot, hinting that the steady state wear track on aluminum is not smooth and promotes nucleation (as will be further discussed below).

2.7 Influence of the temperature

In all the experiments described so far, the temperature was kept unchanged at 70°C (about 8 degrees below the boiling point of ethanol). In order to determine if and how temperature affects the generation of bubbles, we did experiments in which we ramped the temperature from 25 to 70°C , while continuously rubbing back and forth over the same track on a polished aluminum wafer. We choose aluminum because, on it, tracks do not deactivate but keep forming bubbles as long as the force-velocity threshold is overcome, as reported above. We fixed the velocity at 2.8 mm s^{-1} (which at 70°C is enough to generate bubbles at very low loads) and varied the normal force between each temperature ramp. The results are shown in figure 2.6. They reveal

that the lower the temperature, the higher the load required to generate bubbles. As with the force-velocity threshold (figure 2.4), there is a finite transition region from no bubbles to a full trail.

2.8 Origin of the threshold for bubble trail formation

We envision the trail formation to depend on two steps: (1) the inception of bubble nuclei in the contact area and (2) the subsequent growth of these nuclei after the contact area has moved. To see how these steps determine the observed thresholds (figure 2.5 and 2.6), we set up the experiment shown in figure 2.7(a). A piece of aluminum foil was tightly wrapped around the sapphire bead, which was then rubbed against a glass substrate submerged in ethanol. This allows for a direct observation of the contact area through the glass. To enhance the wear of the foil by the substrate, the latter was equipped with protrusions in the form of micro-pillars.

The direct observation of the contact area provided some crucial insights. First, as shown in figure 2.7(b), rubbing can trigger the nucleation of bubbles on aluminum even at room temperature. During the rubbing, gas continuously comes out of solution and collects in microscopic gas pockets trapped between the two solids. As the substrate moves on, these pockets are ejected in the form of small bubbles. At room temperature, these bubbles do not grow, but dissolve as soon as they reach the bulk of the liquid. Similarly, the gas pockets trapped in the contact area slowly dissolve when the substrate motion is stopped. Second, at temperatures for which the pressure inside the bubble is large enough to make them persist, the microscopic bubbles merge, resulting in a regular trail (figure 2.3). This indicates that in figure 2.6 it is the supersaturation condition (and not the bubble inception) which dictates the trail formation.

We can quantify this idea with a model in which the size of the microscopic bubbles is set by the space available in the contact area (see figure 2.8). First we use Hertz's contact theory to estimate the radius a of the apparent contact area

$$a \sim \sqrt{\epsilon R}, \quad (2.2)$$

where the indentation depth ϵ is related to the normal force F as [23]

$$\epsilon \sim \left(\frac{3}{4} \frac{F}{E^* R^{1/2}} \right)^{2/3}. \quad (2.3)$$

Here E^* is the effective elastic modulus of the particular bead-substrate combination, which is dominated by the softer of the two. Combining the contact radius a with a

Figure 2.7: (a) Schematic of the setup: a transparent glass surface covered with micro-pillars is rubbed against a bead covered with aluminum foil ($F = 7 \times 10^{-2}\ \text{N}$, $V = 4.7\ \text{mm s}^{-1}$). (b) Bottom view of the experiment through a microscope. Gas pockets are trapped between the two solids in the contact area and microscopic gas bubbles (red arrows) are observed downstream. The spacing between the pillars, their diameter and their height are $10\ \mu\text{m}$, $9\ \mu\text{m}$ and $0.3\ \mu\text{m}$, respectively.

Figure 2.8: Geometry used for the model. Gas (yellow) completely fills the gap in the apparent contact area and collects in a single bubble with radius r . For clarity the bead is shown indented here, while in reality the indentation is essentially concentrated on the aluminum surface which is much softer than the sapphire bead.

typical roughness height h gives the volume available for all the gas pockets

$$\Omega \sim \pi a^2 h. \quad (2.4)$$

If we suppose that all this gas ends up in a single bubble of radius $r = (3\Omega/4\pi)^{1/3}$, then, as is mentioned in the introduction and elaborated on in appendix 2.A, this unstable bubble will grow in the bulk if its radius is larger than

$$r_c = \left(\frac{3\Omega_c}{4\pi} \right)^{1/3} \sim \frac{2\gamma}{\Delta P}. \quad (2.5)$$

Prior to being heated, the liquid used in the experiments was equilibrated for a long time with air (i.e. gas + vapor) at a temperature of $T_0 = 20^\circ\text{C}$; under a total pressure $P_{atm} = P_g + P_v(T_0) = 1$ bar. During the heating to a temperature T , the gas content of the liquid, i.e. $P_g \simeq P_{atm} - P_v(T_0)$, did not change appreciably (since the relevant gas diffusion timescale is much longer than that of the heating, and the gas solubility only changes by 10% over the temperature range). The excess pressure ΔP in the heated liquid therefore comes down to the increase in the vapor pressure from T_0 to T , that is, $\Delta P \simeq P_v(T) - P_v(T_0) = \Delta P_v(T)$. Combining equations (2.2) – (2.5) yields an expression for the critical force as a function of temperature

$$F_c(T) \sim \frac{4E^*}{3R} \left(\frac{4}{3h} \right)^{3/2} \left(\frac{2\gamma}{\Delta P_v(T)} \right)^{9/2}, \quad (2.6)$$

with a pre-factor ~ 1 .

Equation (2.6) is plotted in figure 2.6 for $h = 50$ and 300 nm, using the surface tension $\gamma = 0.02 \text{ N m}^{-1}$ of ethanol, the elastic modulus $E^* = 70 \text{ GPa}$ of aluminum, and an empirical relation for the ethanol vapor pressure [24]. The roughness parameters of 50 and 300 nm correspond, in order of magnitude, to the large and small scale roughnesses we measured by Atomic Force Microscopy (AFM) on the steady state wear track on aluminum. The experimental data in figure 2.6 therefore seems to be consistent with our model. One crucial question however remains: what controls the *nucleation* of these gas pockets?

2.9 Microscopic mechanism for gas pocket formation

As mentioned in the ‘Preliminary findings’, tribonucleation is observed on aluminum, but not on copper. This prompted us to closely analyze the wear tracks left on each surface. Figure 2.9 shows photographs and detailed Scanning Electron Microscopy (SEM) recordings of wear tracks on aluminum and copper. Although the two tracks look very similar optically, they can be easily distinguished in the SEM images. Indeed, for both aluminum and copper, the asperities in the wear tracks got flattened by the rubbing bead. However, on aluminum this flattening seems to result from a continuous breaking off of small parts of the rough surface (as for a brittle material). The top surface of the flattened asperities has small scratches throughout and a lot of small wear particles are observed around, in the troughs. In contrast, for copper the top surface has a relatively low roughness, material is plastically squeezed out at the sides of the asperities, and no wear particles are observed around (as for a ductile material).

The comparison of the wear tracks suggests that the fracturing of the surface is an essential ingredient for a material to provoke tribonucleation. To test whether it is the fracturing itself, or its products (i.e. the wear particles left on the track) which are responsible for the creation of gas pockets, we realized the experiment shown in figure 2.10. A piece of aluminum (soft Al99.5%, Salamon’s Metalen) or copper (Cu99.95%, Salamon’s Metalen) foil was immersed in hot ethanol and then torn apart at a constant velocity of about 9 mm s^{-1} . Consistent with the rubbing experiments, bubbles did appear in the case of aluminum, but *not* in the case of copper[‡]. Since wear particles play no role here, this experiment shows that the fracturing itself can generate gas nuclei.

[‡]Sometimes, a single bubble appeared in the very last stage, when the two ends of the copper foil completely separated at much higher velocity.

Figure 2.9: Wear tracks formed by rubbing a sapphire bead 50 times back and forth against (a,b,c) sandblasted aluminum and (d,e) sandblasted copper. Rubbing parameters: $T = 70^\circ\text{C}$, $F = 7 \times 10^{-2} \text{ N}$ and $V = 1 \text{ mm s}^{-1}$. (a,d) The wear tracks are clearly visible under racking lighting and look very similar to the naked eye. (c,e) SEM imaging however reveals important differences at the scale of a single asperity. (c) On aluminum, the scratches on top of the flattened asperities are relatively deep ($R_a \sim 50 \text{ nm}$ from AFM measurements) and many small wear particles are collected in the troughs around the asperities (as for a brittle material). (e) On copper, the tops of the asperities are much smoother ($R_a \sim 5 \text{ nm}$), they seem to be plastically squeezed, and no wear particles are observed (as for a ductile material).

Figure 2.10: Snapshots of the tearing of thin foils of (a) aluminum and (b) copper submerged in ethanol at around 78 °C. The foils are respectively 12.0 μm and 12.5 μm thick, and the two sides of the foil are torn apart with a velocity of about 9 mm s^{-1} . For aluminum, bubbles form at the tip of the tear, while for copper no bubbles form.

2.10 Discussion

A possible scenario for the nucleation by fracturing is that the gap formed when a micro-crack opens, fills with gas and vapor before the liquid can enter it. This embryo can then act as a nucleus for the formation of a visible bubble. Only in a brittle material this crack opening would be rapid enough.

While bulk aluminum is ductile, it has a thin ($\sim \text{nm}$) oxide layer on its surface, which might explain its brittle behavior. A similar layer exists on the surface of silicon. Note that this ‘passivation layer’ forms because the bare materials readily react with any oxidizing molecules in their environment. In particular, in the presence of water this chemical activity causes the generation of hydrogen gas, which might be at the root of, or at least contribute to, the initial nucleation process. This idea is supported by experiments with degassed water, in which we still observed the formation of microscopic gas bubbles, which quickly dissolved after the rubbing had stopped. On the other hand we should stress that we could also create bubble trails in perfluorohexane (FC72), a liquid that should be inert in most circumstances. Also in the work by Theofanous et al. [20], which involved polished stainless steel and Freon, chemical reactions are very unlikely.

The embryos formed by the mechanism of fracturing and, possibly, chemical reactions may not grow individually, but only if they merge with others before dissolving. The force-velocity threshold $FV = \text{const.}$ would then be a manifestation of the

competition between generation, merging and dissolution and could be interpreted as a minimal frictional power input required for abundant local fracturing.

2.11 Conclusion and outlook

We have found that bubbles are readily and reliably generated upon gentle rubbing of certain solid surfaces. An intriguing demonstration of the phenomenon is the “writing” example shown in figure 2.1. It is somewhat surprising that, in spite of its robustness and repeatability, this phenomenon has been the object of so little attention in the literature.

We observed that bubbles can nucleate and form a trail on submerged solids under gentle rubbing conditions (normal force $F = 1 - 200$ mN and relative velocity $V = 0.1 - 20$ mm s⁻¹). At room temperature, small bubbles are observed to form and detach, but they dissolve as they move away from the contact area. As the temperature is increased, the bubbles persist and grow, forming a trail. On silicon and aluminum, measurements in ethanol at 70 °C and above indicate the existence of a threshold for the trail formation of the form $FV = \text{const.}$, with a constant 6 times larger for silicon than for aluminum.

Bubble formation strongly depends on the materials being rubbed. On silicon, tribonucleation stops after typically 20 strokes over the same spot, while on aluminum a steady state wear track forms from which bubbles keep appearing upon rubbing. Bubbles do not form on copper, although the wear tracks on copper and aluminum look very similar optically. SEM imaging shows that aluminum asperities are abraded by a fracturing, brittle-like mechanism, while copper asperities are flattened by plastic, ductile-like deformations. Additional experiments on the slow rupture of aluminum and copper foils indicate that fracturing alone (in the absence of wear) is sufficient to create gas nuclei.

The above observations evidence that trail formation by tribonucleation involves two steps: (1) bubble nucleation in the contact region and (2) subsequent growth of these nuclei in the bulk. Both steps need to be satisfied in order to see a trail. Our experiments show that fracturing is essential for the first step. We hypothesized that a void created by the rapid fracturing of the surface asperities, possibly in combination with chemical reactions forming gas at the freshly created surfaces, can explain the nucleation of bubbles at the low loads and velocities used in the experiments. When there is abundant local fracturing, the amount of gas that comes out of solution is limited by the space available between the asperities of the surfaces in contact, and it is this volume that sets the threshold for trail formation in this case.

We hope that the present exploratory work may motivate further studies to look

into the fundamental mechanism(s) involved in tribonucleation, and to explain, for example, the emergent dependence of the phenomenon on the rubbing force and velocity.

Appendix

2.A Diffusive bubble growth in a hot liquid

In the experiments described in the main text, a liquid saturated with dissolved air at room temperature T_0 is heated to a higher temperature T below its boiling point T_B . The growth of bubbles nucleated in this hot liquid hinges on the fact that the equilibrium condition $r = r_c$, with $r_c = 2\gamma/\Delta P$, is unstable when the amount of gas and vapor in the bubble is not constrained to be constant. Here we provide a more detailed description of how this instability leads to the bubble growth that we observe.

For $T < T_B$ the growth process is sufficiently slow so that inertia can be neglected, as in the classic paper by Epstein and Plesset on the diffusive growth of gas bubbles [25]. We also assume for now that surface tension can be neglected, which will be justified below. With these assumptions, the sum $P_g + P_v$ of the gas and vapor partial pressures in a bubble (however nucleated), will essentially be equal to the ambient atmospheric pressure P_{atm} at all times.

Before raising the temperature, the liquid had been in contact with the surroundings long enough to ensure that it was uniformly saturated with dissolved air at the initial room temperature T_0 . According to Henry's law, this initial dissolved gas concentration would have been $C^{(0)} = P_g^{(0)}/k(T_0) = [P_{atm} - P_v(T_0)]/k(T_0)$, in which k is the temperature-dependent Henry's constant. Once a bubble is nucleated in the hot liquid, the constraint $P_g + P_v = P_{atm}$, together with the fact that $P_v(T) > P_v(T_0)$, implies that the gas partial pressure inside it will be lower than $P_g^{(0)}$. As a consequence, again by Henry's law, the dissolved gas concentration at the bubble surface would take a value $C^{(i)} = [P_{atm} - P_v(T)]/k(T) < C^{(0)}$ while, in view of the slowness of the mass diffusion process (compared to the heating rate), the bulk concentration in the liquid (i.e. far from the bubble surface) remains at the initial value $C^{(0)}$. This circumstance sets up a concentration difference between the bubble surface and the bulk liquid given by

$$\Delta C = C^{(0)} - C^{(i)} = \frac{P_{atm} - P_v(T_0)}{k(T_0)} - \frac{P_{atm} - P_v(T)}{k(T)} \approx \frac{\Delta P_v}{k}, \quad (2.7)$$

where $\Delta P_v = P_v(T) - P_v(T_0)$ and, in the last step, we have neglected the small temperature dependence of the Henry's constant, which is inconsequential in the temperature range of present concern.

According to ref. [25], the radius r of a bubble in a gas-supersaturated liquid grows at the approximate rate

$$\dot{r} = \frac{D\Delta C}{\rho_g} \left(\frac{1}{r} + \frac{1}{\sqrt{\pi Dt}} \right), \quad (2.8)$$

where ρ_g is the density of the gas in the bubble, D is the gas diffusivity in the liquid, t is time, and concentration is expressed in kg/m^3 . The asymptotic solution of this equation, valid for radii much larger than the initial value, takes the form [25]

$$r^2 = 2 \left[\lambda + \sqrt{1 + \lambda^2} \right]^2 \frac{D\Delta C}{\rho_g} t, \quad (2.9)$$

with $\lambda \equiv \sqrt{\Delta C / (2\pi\rho_g)}$.

For air in ethanol at $T = 70^\circ\text{C}$ we have $k = 3 \times 10^5 \text{ m}^2/\text{s}^2$ (an order of magnitude smaller than for water), $\rho_g = 0.3 \text{ kg/m}^3$, $D = 10^{-8} \text{ m}^2/\text{s}$ and $\Delta P_v = 70 \text{ kPa}$. Making use of these values and of equations 2.7 and 2.9, we find that a bubble grows to the typical detachment radius $r = 0.15 \text{ mm}$ observed in the experiments in approximately 0.8 seconds. This duration corresponds in order of magnitude to the growth time observed in the experiments ($\sim 3 \text{ s}$, see figure 2 of the main text), but it represents an under-estimation of the actual growth time as it neglects the hindrance to diffusion caused by the solid surface and the competition for dissolved gas due to the growth of the neighboring bubbles. The real situation is further complicated by the merging and jumping of the bubbles.

Lastly, we can estimate the influence of surface tension, which we neglected above. Surface tension is important close to the nucleation threshold $r_c = 2\gamma/\Delta P_v$, and we thus consider a bubble with radius $r = (1 + \epsilon)r_c$, where $\epsilon \ll 1$ is a small parameter. The bubble grows only if $\epsilon > 0$, because in this case the gas partial pressure inside the bubble, which balances the external atmospheric pressure, is smaller than that required for thermodynamic equilibrium by

$$\Delta P_\gamma = 2\gamma \left(\frac{1}{r_c} - \frac{1}{r} \right) \simeq \frac{2\gamma}{r_c} \epsilon = \Delta P_v \epsilon. \quad (2.10)$$

Gas diffusion is also the limiting mechanism here. We thus make use of equation 2.8 with the effective concentration difference $\Delta C_\gamma = \Delta P_\gamma/k = 2\gamma\epsilon/r_ck$, and taking into account the compressibility of the gas via the effective gas density $\rho_g^* = \rho_g +$

$4\gamma/3R_gTr_c = 0.7 \text{ kg/m}^3$ [25], where $R_g = 290 \text{ J/kgK}$ is the specific gas constant of the gas, to find

$$\dot{\epsilon} = \frac{2D\gamma}{\rho_g^* r_c^2 k} \left(\frac{1}{r_c} + \frac{1}{\sqrt{\pi Dt}} \right) \epsilon. \quad (2.11)$$

This yields the following exponential growth

$$\epsilon(t) = \epsilon_0 \exp \left(\frac{t}{\tau_1} + \sqrt{\frac{t}{\tau_2}} \right), \quad (2.12)$$

in which the timescales are $\tau_1 = \rho_g^* k r_c^3 / 2D\gamma$ and $\tau_2 = \pi \rho_g^{*2} k^2 r_c^4 / 16D\gamma^2$. With $\gamma = 18 \text{ mN}$ at $T = 70^\circ\text{C}$, this gives $\tau_1 \simeq 0.1 \text{ ms}$ and $\tau_2 \simeq 0.3 \text{ ms}$, which means that the delay induced by surface tension on the growth time derived from equation 2.9, is indeed negligible.

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3

Dribbling Leidenfrost droplets in an electric field *

Leidenfrost droplets, i.e. droplets whose mobility is ensured by a thin vapour film between the droplet and a hot plate, are exposed to an external electric field. We find that in a strong vertical electric field the droplet can start to bounce progressively higher, defying gravitational attraction. From the droplet's trajectory we infer the temporal evolution of the amount of charge on the droplet. This reveals that the charge starts high and then decreases in steps as the droplet evaporates. After each discharge event the charge is in a fixed proportion to the droplet's surface area. This behaviour can be accurately modelled by treating the droplet as a conducting sphere that occasionally makes electrical contact with the hot plate, at intervals dictated by an electro-capillary instability in the vapour film.

*To be submitted as: Sander Wildeman, Chao Sun, *Leidenfrost droplets in an electric field*

3.1 Introduction

Four hundred years ago William Gilbert noticed how a water droplet sitting on a dry surface is “drawn up into a cone” when a piece of statically charged amber is held above it [1]. Important progress on this topic was made a few centuries later: by Lord Rayleigh [2] in his work on the stability limits of charged droplets and by Millikan [3], who showed in his famous oil-drop experiments that charge is quantized. Closely after, Zeleny [4] published beautiful photographs of how droplets suspended from thin glass capillaries, destabilize when a high voltage is applied between the liquid and a nearby grounded plate. The change of shape of the droplet from a spherical cap to a cone and the subsequent jetting of small charged droplets from the cone tip, were later put on firm theoretical grounds by Taylor [5]. The curious behaviour of charged liquid is further exemplified by phenomena like floating water bridges [6, 7], whipping jets [8, 9], and the non-coalescence of oppositely charged drops [10, 11].

An equally curious effect, with uncharged droplets, was demonstrated by Leidenfrost in 1756 [12]. He showed that water droplets can survive for seconds on a glowing hot iron spoon, without the instant evaporation one might expect. The effect, occurring above a critical temperature T_L of the spoon, is explained by a thin vapour film sustained below the droplet, which thermally insulates it from the hot metal. The vapour film also enables Leidenfrost droplets to move with very little friction [13]. It was recently demonstrated that these hyper-mobile droplets can be conveniently trapped and steered by equipping the hot surface with ratchet-like structures [14–16] or, in the case of a paramagnetic liquid, by using a magnet [17]. For an overview of the work on Leidenfrost droplets we refer to the recent review by Quéré [18].

In this study we bring together the classic experiments of Gilbert and Leidenfrost, and investigate how Leidenfrost droplets behave in a strong electric field. Previously Celestini & Kirstetter [19] showed that the Leidenfrost state can be suppressed by applying a voltage directly between the hovering droplet and the hot plate. In our experiments we apply the electric field externally, so that the forces are determined by a capacitive coupling between the electrodes and the droplet. A similar idea was recently employed to guide droplets through microfluidic devices [20, 21]. Here we will show that for Leidenfrost droplets, electrical forces can cause the droplet to bounce progressively higher, until it finally impacts onto the top electrode (§3.3). By combining high speed recordings of the free flight trajectories with a detailed model of the electric forces, we will first infer the amount of charge on the droplet after each rebound, and then show how it can be predicted (§3.4). We demonstrate how charging and evaporation, together with the elastic behaviour of small Leidenfrost droplets [22], allow the droplet to escape from the hot plate (§3.5), while the observed discharge behaviour can be understood by considering the electrical field in the vapour

Figure 3.1: (a) Schematic of the setup. A droplet hovering on a hot plate ($T > T_L$) is trapped under a spherical electrode set to a high voltage V_s between 2 and 5 kV. (b) Image captured by the high speed camera just after deposition. It shows a millimetric droplet of ethanol and its reflection in the polished aluminium plate. In the magnification of the contact region (c) the thin vapour gap, which insulates the drop from the hot surface is clearly visible.

film during impact (§3.6). Finally, we will discuss how the different control parameters, plate temperature, the type of liquid, and electrode voltage, affect the drop's behaviour (§§3.7–3.10).

3.2 Setup and method

The setup, shown in figure 3.1, consists of a stainless steel ball ($\varnothing$ 24 mm) mounted a distance $d = 7$ mm above a polished aluminium plate. The sphere is connected to a high voltage DC power supply and the bottom plate is grounded. The temperature of the plate can be set via an external temperature controller. In each experiment the plate had a constant temperature $T > T_L$, and the top electrode was set to a potential V_s between 2 and 5 kV. With a grounded stainless steel needle (not shown) we then gently deposited a millimetre sized droplet of demi-water, ethanol or perfluorohexane (FC72) on the hot plate (see table 3.1 for an overview of the relevant liquid properties). The spherical shape of the top electrode ensures that a charged Leidenfrost droplet experiences a small horizontal force that traps the droplet below the centre of the sphere (see appendix 3.A). The droplet's motion was recorded with a high speed camera and the captured frames were further processed with an image analysis script to obtain the centre-of-mass (CM) trajectory ($X_{cm}(t)$, $Y_{cm}(t)$) and the volume $\Omega \equiv 4\pi R^3/3$ of the droplet, defining an effective droplet radius R .

<i>Property</i>	<i>Symb.</i>	<i>Unit</i>	Ethanol	Water	FC72
Boiling temperature	T_b	$^{\circ}\text{C}$	78	100	56
Surface tension	γ	mN/m	17	59	10
Dielectric permittivity (l)	ϵ_r	-	19	55	1.7
Density (l)	ρ	kg/m^3	730	950	1594
Density (v)	ρ_v	kg/m^3	1.6	0.6	12.5
Viscosity (v)	μ_v	$\mu\text{Pa s}$	10	12	12
Thermal conductivity (v)	k_v	W/(mK)	0.02	0.02	0.01
Latent heat of evaporation	L	kJ/kg	900	2260	88

Table 3.1: Vapour (v) and liquid (l) properties used throughout the text. All material parameters are taken at the boiling temperature.

3.3 Droplet trajectory and radius

Figure 3.2 shows a recording of an ethanol Leidenfrost droplet in a field of 2.9 kV/cm ($V_s = 2\text{ kV}$) on a hot plate of $T = 220^{\circ}\text{C}$. Here the first frame was taken about 10 seconds after deposition. Initially the droplet bounces with a small amplitude $\Delta Y_{\text{CM}} \ll R$, which decreases slowly with time for most parts, but occasionally shows a sudden increase (indicated by the upward arrows). Interestingly, near the end of the sequence in figure 3.2(b) this behaviour reverses. In this final stage the jump height steadily increases in time, now with an occasional drop in amplitude (downward arrows). Finally, it bridges the gap and impacts onto the top electrode (figure 3.2(d)). The full time series of the extracted CM trajectory and the effective radius are shown in figure 3.5(a).

For most parts the droplet radius R decreases approximately linear in time. This suggests that the mass flux can be captured by a simple convective mass transfer model of the form $\dot{m} = -4\pi R^2 \Delta\rho_v h$, where h is a mass transfer coefficient and $\Delta\rho_v$ is the difference between the vapour density at the droplet surface and that in the surrounding air. On the other hand we have $\dot{m} = 4\pi\rho R^2 dR/dt$, where ρ is the density of the liquid, so that

$$\frac{dR}{dt} = -\frac{\Delta\rho_v}{\rho} h. \quad (3.1)$$

If we make the assumption that the droplet reaches its boiling temperature T_b at its surface, then the vapour pressure here is equal to the atmospheric pressure $P_a = 1\text{ atm}$ and we can use the ideal gas law to estimate $\Delta\rho_v \approx P_a/C_v T_b$, where C_v is the vapour's specific gas constant (this was done in table 3.1).

Figure 3.2: Typical dynamics of a small Leidenfrost droplet in a strong electric field. Figures (b) and (c) were obtained by taking from each subsequent frame in the high speed recording a thin vertical strip through the centre of mass of the droplet (shown in (a) for the first frame) and then merging all these strips. The total time covered by (b–c) is about 9 seconds with a gap of 1 second between the initial stage (b) and the final stage (c). The up- and downward arrows in (b) and (c) indicate the times for which there is a sudden increase or decrease in the jumping amplitude, respectively. In (d) the droplet has just impacted on the unheated top electrode, ejecting a small secondary droplet.

Figure 3.3: Evaporation behaviour of the different types of liquid used in the experiments. (a) Radius versus time. (b) Extracted mass transfer coefficients (local slope in (a), multiplied by $-\rho/\Delta\rho_v$). The horizontal axis shows the time with respect to the time of impact onto the top electrode ($t \equiv 0$), which is well defined for all cases and allows for an easier comparison of the final radii.

In figure 3.3(a) the radius evolution of the ethanol droplet is plotted together with those of a water and an FC72 droplet. Although the evaporation rates are very different for the three cases (water has a lower volatility, while FC72 has a higher volatility), the extracted mass transfer coefficients are very close in magnitude (see figure 3.3(b)). Note that for the ethanol droplet h somewhat decreases in the final stage. As seen from figure 3.5(a) this is probably because the droplet here spends less of its time near the hot plate.

3.4 Charge on the droplet

When the droplet is free from the surface the only external forces acting on it are gravity $F_g = -mg$, air drag F_d and electrical forces F_e from the electrodes and image charges, where m is the mass of the droplet and g is the gravitational constant. For the small velocities considered here, we can safely neglect the air drag. The vertical component of the equation of motion then takes the form

$$m\ddot{Y}_{CM} = -mg + F_e(Y_{CM}, R, V_s, Q_d), \quad (3.2)$$

in which Q_d is the charge on the droplet. Since we can measure m , $\ddot{Y}_{CM}$ (see inset figure 3.5(a)), Y_{CM} and R , and we control V_s , we can solve equation (3.2) to infer Q_d , given the function $F_e(Y_{CM}, R, V_s, Q_d)$. The simplest form of this function is obtained by assuming that the droplet is a point charge in an external electric field of

Figure 3.4: Canonical electrostatic problems to calculate the capacitance coefficients in our experiment. The height Y and radius R of the droplet are varied. From (a) we get $c_{dd}(Y, R) = Q_d$ and $c_{sd}(Y, R) = Q_s$ and in (b) we have $c_{ds}(Y, R) = Q_d$ and $c_{ss}(Y, R) = Q_s$.

strength V_s/d , so that $F_e \approx -Q_d V_s/d$. This point charge model can be extended by including forces $\sim Q^2/(4\pi\epsilon_0 Y_{CM}^2)$ from image charges in the top and bottom electrode. Although this approach can capture most of the charging trends, it fails when the droplet is close to the electrodes, where it can no longer be considered to be a point. In this case we can view our system as consisting of three finite conductors: a grounded plate, a spherical top electrode with a fixed potential and a small sphere, the droplet, which acts as a floating potential (i.e. it is in general not connected to any of the electrodes). It can be shown that for any configuration of conductors at potentials V_i one can write the charge on conductor i as $Q_i = \sum_j c_{ij} V_j$, where the capacitance coefficients c_{ij} only depend on the geometry of the problem, and $c_{ij} = c_{ji}$ [23]. The total potential energy for the system can then be written as $U_e = \frac{1}{2} \sum_i Q_i V_i - \sum_n Q_n V_n$. The first sum runs over all conductors and the second sum over all conductors connected to a constant voltage supply.

In our experiment the geometry is fully specified by Y_{CM} , R , and the (fixed) position and radius of the top electrode (see figure 3.4). We can therefore write $Q_d = c_{dd} V_d + c_{ds} V_s$ and $Q_s = c_{ss} V_s + c_{sd} V_d$, where the subscripts s and d refer to the top electrode and the droplet, respectively. The charge Q_p on the bottom plate is not relevant here, as $V_p = 0$ and it therefore does not contribute to the potential energy. Using these relations to express $U_e = (Q_d V_d - Q_s V_s)/2$ in terms of Q_d and V_s (which are constant during each flight) we find

$$U_e = \frac{1}{2c_{dd}} Q_d^2 - \frac{c_{ds}}{c_{dd}} Q_d V_s + \frac{1}{2} \left(\frac{c_{ds}^2}{c_{dd}} - c_{ss} \right) V_s^2. \quad (3.3)$$

Finally, the force needed to vary the droplet height Y_{CM} can be obtained from the usual relation

$$F_e = -\partial_{Y_{CM}} U_e. \quad (3.4)$$

The required coefficients $c_{ij}(Y_{\text{CM}}, R)$ can be obtained analytically only in some special cases (which will be discussed later). For the remaining configurations the coefficients were determined numerically (see appendix 3.B).

Combining equations (3.2) through (3.4) we find a quadratic equation for Q_d , which we solve for each maximum in the droplet's flight trajectory. The result of this analysis is shown in figure 3.5(b). The amount of charge on the droplet starts high and then decreases in time as the droplet evaporates. Initially, there is a large scatter in the inferred charge (left of first dotted line). This is mostly related to the initial scatter in the measured droplet volume and in the tracking of the centre of mass (cf. figure 3.5(a)). We expect the extracted charge to be most reliable in the later stages, when the drop is further from the surface and its shape better satisfies the axisymmetry assumed in the analysis. In the final stage, about 6 seconds before impact, the charge decreases in a step-like manner, perfectly correlated with the sudden changes in the jumping amplitude (as indicated by the vertical lines in region (II) of figure 3.5).

The fact that the charge on the droplet decreases with time, indicates that there is occasionally electrical contact between the droplet and the plate, most likely during a rebound. Irrespective of how this contact occurs we can model the droplet during this stage as a small conducting sphere adhered to a grounded plate, corresponding to the situation in figure 3.4(b) with $Y_{\text{CM}} = R$. This problem is mathematically equivalent to the problem of two adhering spheres aligned with an external electric field, and has been solved by Smith & Rungis [24] using the method of images. They give the

Figure 3.5 (*preceding page*):

(a) Extracted radius R and vertical trajectory Y_{CM} as a function of time ($V_s = 2\text{ kV}$, $T = 220^\circ\text{C}$). The data for R were smoothed (black line) to remove (non-physical) fluctuations in the tracking (grey shading) due to deviations from axisymmetry. The inset shows a magnified region of 70 ms of the trajectory. Parabolas (see black line in inset) were fitted to obtain the free-fall acceleration $\ddot{Y}_{\text{CM}}$ at each peak.

(b) From R , Y_{CM} and $\ddot{Y}_{\text{CM}}$ the charge on the droplet can be inferred (dots). The solid line shows the prediction by equation (3.5), using the smoothed data for R as input.

(c) Change in potential energy ΔU obtained from Q_d , R and Y_{CM} at the jumping maxima (dots), and by invoking conservation of kinetic energy K_0 after each rebound. The solid vertical line, spanning (a–c), separates the qualitatively different initial and final stage, here labelled (I) and (II). The dotted lines serve to correlate the key features in the graphs.

Figure 3.6: Escape radius of the droplet (just before impact) in repeated experiments at various voltages ($\pm(2 - 5)$ kV) and temperatures ($120 - 300$ °C), normalized by the predicted critical radius R^* given by equation (3.6). For the dashed line the low dielectric constant of FC72 was taken into account.

following analytical expression for the amount of charge Q_d on each sphere:

$$Q_d(R) = -\frac{2\pi^3}{3} \frac{\epsilon_0 R^2 V_s}{d}, \quad (3.5)$$

where $\epsilon_0 \approx 8.85 \cdot 10^{-12}$ F/m is the vacuum permittivity and we approximated the external field as $-V_s/d$. This is about twice ($2\pi^2/9$) the displaced charge one would find for a single sphere of radius R in the same electric field. Taking R from the measurements, we compare equation (3.5) to the experimental data in figure 3.5(b). Both magnitude and trend are in good agreement, without any fitting parameters.

3.5 Transient bouncing behaviour

From equations (3.2) and (3.5) it is clear that the droplet will eventually jump to the top electrode. As the droplet shrinks, its surface charge and therefore the upward electric force scales as $\sim R^2$, which eventually overcomes the downward gravitational force $\sim R^3$. The critical radius R^* for which this occurs can be estimated by balancing $F_g = -mg$ with $F_e \approx Q_d V_s/d$, leading to

$$R^* = \frac{\pi^2}{2} \frac{\epsilon_0 V_s^2}{\rho g d^2}. \quad (3.6)$$

As shown in figure 3.6 this expression predicts the escape radius reasonably well (within about 50%) in a series of experiments done at various voltages and temperatures, and with different liquids. In the case of FC72 an additional prefactor

$f = (\epsilon_r - 1)/(\epsilon_r + 2) \approx 0.2$ is required (dashed line) to take into account the liquid's low dielectric constant $\epsilon_r \approx 1.7$ (as will be discussed in §3.8).

It remains to explain the details of the transient bouncing behaviour, such as the (sudden) increases and decreases in amplitude. To this end we look at the total change in potential energy ΔU during each jump. This energy can be calculated in two ways: One way is to assume that air drag is negligible and invoke conservation of energy, so that ΔU is equal to the kinetic energy K_0 with which the droplet leaves the surface. Another way is to use the inferred charge to directly calculate $U_m = mgY_m + U_e(Y_m)$ at the jumping maximums Y_m and to subtract the corresponding values U_0 of the droplet close to the surface. As shown in figure 3.5(c) these independent energy measures give practically the same result, confirming that air drag can safely be neglected and validating the charge extraction method. For most parts of the trajectory the energy decreases after each rebound. For these low impact velocities this is likely due to the dissipation associated with the oscillatory motion of the droplet after impact [22, 25]. Interestingly, there is occasionally a large increase in energy. Comparing figure 3.5(c) with 3.5(a) one can see that these boosts in energy correlate with the sudden increases in jumping amplitude during the initial stage (I). We speculate that an electro-capillary instability, such as described in the next section, may be at the root of these energy injections. In the final stage (II), when the discharge occurs in well defined steps, the droplet's energy decreases almost monotonically. At first sight this may seem at variance with the overall increasing jumping amplitude, but this is not the case. Both the gravitational and electric field contributions to the potential energy make that smaller droplets can jump higher with the same energy. In the final stage the dissipation rate is not high enough to counteract this effect. Here the amplitude drops at every discharge, because these events cause the potential energy to shift up for the same height.

It has been shown [22] that even without an external electric field, Leidenfrost droplets display a surprising (quasi) elastic bouncing behaviour. It was demonstrated that the droplet finds a jumping mode in which energy dissipation is least, occurring when its oscillation time $t_R \approx \pi \sqrt{\rho R^3 / 2\gamma}$ becomes similar to the free fall time $t_f \approx \sqrt{2h/g}$ [22]. Solving $t_R = t_f$ for the fall height h , gives $h = \pi^2 g^2 \rho R^3 / 4\gamma$. This can also be rewritten as a condition for the kinetic energy by requiring $mv^2/2 = mgh$, with v the velocity of the centre of mass. Introducing the dimensionless Weber-number, $We = \rho R v^2 / \gamma$, and Bond-number, $Bo = \rho g R^2 / \gamma$, one finds the condition

$$We \approx \frac{\pi^2}{2} Bo^2. \quad (3.7)$$

If we evaluate this expression for our ethanol droplet, for which $1 \text{ mm} > R > 0.5 \text{ mm}$, we find $0.8 > We > 0.05$ and kinetic energies of $30 \text{ nJ} > K_0 > 0.5 \text{ nJ}$, which is in-

deed of the same order of magnitude as those found in figure 3.5(c). Note that in the presence of charge on the droplet the oscillation frequency would change to $\omega^2 = [8\gamma - Q_d^2/(8\pi^2\epsilon_0 R^3)]/(\rho R^3)$ [2]. However, in the experiment considered here the amount of charge is still far (at about 10%) from the stability limit, for which the frequency becomes imaginary. We can therefore safely neglect the second term between the brackets. Another effect we need to consider is that the electric force will alter the free fall time. This could be incorporated by introducing an effective gravitational acceleration $g' \approx g - Q_d V_s/md$, which decreases from $g' \approx g$ just after deposition to $g' \approx 0$ when the droplet flies to the top electrode. However, in this final stage the free flight time is a lot longer than the time for the oscillations to damp out, so that the whole consideration above loses its validity. We can therefore interpret equation (3.7) as a kind of initial condition for the experiment, giving the typical kinetic energy before the electric forces take over.

3.6 Discharge mechanism

To understand why the droplet loses its charge in steps, it is insightful to estimate the electric field strength $\sim V_d/H$ in the vapour film during a rebound, where H is the film thickness. The droplet's potential can be expressed as $V_d = (Q_d - c_{ds}V_s)/c_{dd}$, with the coefficients evaluated at $Y_{CM} = R + H$. Since we will have $H \ll R$, we can approximate $c_{ds}(R + H, R) \approx c_{ds}(R, R)$, which can be directly read off from equation (3.5): $c_{ds}(R, R) = -2\pi^3\epsilon_0 R^2/3d$. To find the second coefficient, $c_{dd}(R + H, R)$, we use the geometry in figure 3.4(b), but neglect the top electrode, as it is relatively far away in this case. This classical electrostatics problem [23, 26] has the solution $c_{dd}(R + H, R) \approx 4\pi\epsilon_0 R(\gamma + \ln(\sqrt{2R/H}))$ in the limit $H \ll R$, where $\gamma \approx 0.577$ is the Euler-Mascheroni constant. With this, the potential of the droplet can be written as:

$$V_d \approx -\frac{\pi^2}{6} \frac{R_0^2 - R^2}{R[\gamma + \ln(\sqrt{2R/H})]} \frac{V_s}{d}. \quad (H \ll R) \quad (3.8)$$

Here we assumed that the droplet made its last electrical contact at some radius R_0 , obtaining a charge $Q_d(R_0)$ as given by (3.5). We see that the potential starts out close to zero after each contact, and becomes negative as R shrinks due to evaporation. The minimum height of the vapour film, appearing in the logarithm in equation (3.8), can be estimated by balancing the Laplace pressure $P_\gamma = 2\gamma/R$ exposed in the flattened bottom, with the lubrication pressure P_μ in the vapour flowing out through the small gap [27]. The details of this estimate can be found in appendix 3.C. For the ethanol droplet under study we find $H \approx 6R^{5/4}\Delta T^{1/4}\mu\text{m}$, with R given in mm and

$\Delta T = T - T_b$. To give an estimate of the maximum value of V_d reached before a discharge event, consider a droplet of initial radius $R_0 = 0.6 \text{ mm}$ that evaporates by a small amount ΔR to a final radius $R = R_0 - \Delta R$. With $\Delta T \approx 140 \text{ K}$, we find $H \approx 10 \mu\text{m}$, so that equation (3.8) can be written as $V_d \approx -1.1 V_s \Delta R/d$. The duration of a charge step is approximately 1 second. From figure 3.5 we see that the droplets shrinks by about $\Delta R = 0.02 \text{ mm}$ in this time, so we find $V_d = V_c \approx -6 \text{ V}$. Although this gives rise to a strong electric field in the gap, of about 600 kV/m , it is still far below the breakdown voltage of ethanol vapour $V_b \approx 500 \text{ V}$ for gap sizes of $10 \mu\text{m}$ at atmospheric pressure [28].

Another pathway for discharge would be an electro-capillary kind of instability in the vapour gap, akin to the classical cases that can occur for a charged droplet as a whole [2, 5]. To investigate this possibility, consider a perturbation $h(x)$ on the flattened bottom of the droplet during a rebound. The pressure distribution at the liquid-vapour interface will have two main contributions: the Laplace pressure $P_l = \gamma \kappa \approx \gamma \partial_x^2 h$ and an electrostatic pressure $P_e = -\frac{1}{2} \epsilon_0 E^2 \approx -\frac{1}{2} \epsilon_0 [V_d/(H + h(x))]^2 \approx -\frac{1}{2} \epsilon_0 V_d^2 [1 - 2h(x)/H]/H^2$, where in the approximations we used that $h(x) \ll H$. This situation is similar to the unstable configuration of a dense fluid atop a lighter fluid, for which the Rayleigh-Taylor (RT) instability can set in [27, 29, 30]. As for the RT-instability, the Laplace pressure stabilizes the interface, while the destabilizing role of the hydrostatic pressure $\rho g h(x)$ is here played by the electrostatic pressure $\epsilon_0 V_d^2 h(x)/H^3$. From this analogy we can immediately obtain an expression for the smallest unstable perturbation wavelength. For the RT-instability we have $\lambda_{\text{RT}} = 2\pi \sqrt{\gamma/(\rho g)}$. Taking $\rho g = \epsilon_0 V_d^2/H^3$ as suggested by the analogy, we obtain:

$$\lambda_m = 2\pi \sqrt{\frac{\gamma H^3}{\epsilon_0 V_d^2}}. \quad (3.9)$$

The largest wavelength that can be supported on the bottom of the droplet surface is approximately $\lambda_m \approx 4a$, where a is the radius of the flattened area (that is, half a wavelength over the diameter $2a$). Using this condition in equation (3.9) we find a minimum droplet voltage for the onset of the instability as

$$V_c = -\frac{\pi}{2} \sqrt{\frac{\gamma H^3}{\epsilon_0 a^2}} \quad (3.10)$$

In the side-view recordings of ethanol droplets we observed that $a \sim R$ during each impact. Using this in equation (3.10), we find $V_c \approx -4 \text{ V}$, which is indeed close to the value of -6 V inferred from the measurements. Note that λ_m depends on H . This may facilitate a steepening of the growing mode when the drop's surface is attracted

closer to the bottom plate and H locally decreases. On the other hand, the strong evaporation in the gap may limit the amplitude of the instability. With the spatial and temporal resolution in our setup we were unfortunately not able to directly capture the details of a discharge event, which will be a topic for further investigation.

3.7 Effect of the plate temperature

In sections 3.3–3.6 we built the analysis and modeling around a single typical example (ethanol, $T = 220^\circ\text{C}$, $V_s = 2\text{ kV}$). In this and the following sections we will apply the developed analysis to different circumstances: a lower plate temperature (§3.7), different liquids (§3.8), and an opposite polarity of the top electrode (§3.9). We will also give a short overview of observations at field strengths for which the droplet becomes unstable as a whole (§3.10).

Figure 3.7(a) shows the trajectory and radius of an ethanol droplet of the same initial radius and in the same electric field as before, but on a plate which is colder by 90 K. Qualitatively the behaviour is similar. Quantitatively there are some differences. Firstly, the droplet evaporates somewhat slower. Fitting equation (3.1) to $R(t)$ we find mass transfer coefficients of $h \approx 12\text{ mm/s}$ in the initial stage and $h \approx 6\text{ mm/s}$ in the final stage, compared to $h \approx 15\text{ mm/s}$ and $h \approx 7\text{ mm/s}$ on the hotter plate (cf. figure 3.3). Secondly, it takes longer (about 6 seconds) before the droplet starts escaping. Its final radius is therefore smaller. From equation (3.5) we expect $Q \propto R^2$, so that this size difference should also be reflected in the charge on the droplet. In figure 3.7(b) we see that this is indeed the case. Besides the smaller magnitude of the charge in the final stage, also the duration of the discharge steps is smaller. This can be understood from the electro-capillary instability picture outlined in section 3.6. Here we found (equation (3.10)) that the critical voltage scales as $V_c \propto H^{3/2}R^{-1}$. Taking $H \propto R^{5/4}\Delta T^{1/4}$ for the gap H between droplet and plate (see appendix 3.C), we get $V_c \propto R^{7/8}\Delta T^{3/8}$, so that critical discharge voltage indeed decreases with decreasing R and ΔT . Comparing the radii for $T = 220^\circ\text{C}$ and $T = 170^\circ\text{C}$ at the same times in figure 3.7(a) one finds that, according to the above analysis, the duration of a step should decrease by about 30%. In reality it is closer to 60%. However, our estimate for H is very rough for the dynamic impact situation considered here. The relation could be checked more accurately by directly measuring the thickness of the vapour gap, using for example an interferometric method. We did not pursue this in this study.

In figure 3.7(c) we have also plotted the energy of the droplet. Both the magnitude (1 – 6 nJ) and the trends are very close to those on the hotter plate (cf. figure 3.5(c)). However, the minimum energy reached before the droplet gets its final kick and starts

Figure 3.7: The same experiment as in figure 3.5, but at a lower plate temperature of $T = 170^\circ\text{C}$ ($V_s = 2\text{ kV}$). Again the vertical line distinguishes the initial and final stage. (a) Droplet radius (black) and trajectory (red). For comparison $R(t)$ at $T = 220^\circ\text{C}$ is also shown (dashed line). (b) Inferred and predicted droplet charge. The inset shows a magnification of the charge steps in the final stage. (c) Change in potential energy during each jump.

to escape is somewhat lower, which explains its smaller escape radius. This delay is probably not directly related to the lower temperature, as we observed similar variations in the final radius in repeated experiments at a single temperature.

3.8 Effect of the liquid properties: Water vs FC72

In the model for predicting the droplet charge (equation (3.5)) it was assumed that the droplet behaves as a perfect conductor. We expect this to work for liquids with a high relative permittivity $\epsilon_r \gg 1$. In this section we will discuss results for water, which has a high permittivity of $\epsilon_r \approx 55$, and perfluorohexane (FC72), which has an extremely low permittivity of $\epsilon_r \approx 1.7$. Ethanol lies in between with a permittivity of about $\epsilon_r \approx 19$. Water and FC72 also have a respectively lower and higher volatility than ethanol (see figure 3.3). This means that the Leidenfrost temperature changes correspondingly. In the experiments discussed here the plate temperature was set to $T = 270^\circ\text{C}$ for water and $T = 120^\circ\text{C}$ for FC72. As before we obtained the radius, trajectory, charge and energy of the droplets.

In figure 3.8 a typical result for a water droplet ($V_s = 3\text{ kV}$) is shown next to that for an FC72 droplet ($V_s = 2.5\text{ kV}$). It can be immediately seen that the behaviour of the drops is quite different. The water droplet mostly stays close to the surface and takes one big leap near the end, while the FC72 droplet at some point starts to jump progressively higher, as was also observed for the ethanol droplets.

The water droplet displays three clear charge steps, with each step starting on the line predicted by equation (3.5). The duration of these charge plateaus is about 6 seconds in this case. In this time the droplet shrinks by about $\Delta R = 0.06\text{ mm}$. Again taking $H \sim 10\text{ }\mu\text{m}$ (which also turns out to be a good estimate for the water droplets) we find that the droplet voltage decreases by about $V_d = 1.1V_s\Delta R/d \approx 28\text{ V}$ before each discharge. About 5 times more than in the case of the ethanol droplet. This can be understood from the fact that for the water droplet the radius a of the flattened area during rebound is significantly smaller than R (see figure 3.9). Because the droplet here bounces with a small amplitude and velocity, this flattening is dominated by gravity and can be estimated as $a/R \approx \sqrt{\text{Bo}} = R\sqrt{\rho g/\gamma} \approx 0.2$ [31, 32] (see also appendix 3.C). According to equation (3.10) we have $V_c \propto 1/a$, so that this indeed gives rise to a factor of 5 in the critical voltage compared to ethanol, for which $a \sim R$.

The FC72 droplet shows just a single charge plateau, starting about 2 seconds before impact. During this same period it also starts to escape. Although this behaviour is similar to what was found for ethanol droplets, the amount of charge is about two orders of magnitude lower. One order of magnitude can be explained by the smaller radius of the droplet. Equation (3.5) would predict a charge of about $8 \times 10^{-12}\text{ C}$

Figure 3.8: Influence of the liquid properties on the behaviour of Leidenfrost droplets in an electric field. The same analysis as for the ethanol droplets is here performed for a droplet of water (left) and a droplet of FC72 (right). For water, the inset on Y_{CM} shows that also this droplet finally makes it to the top electrode. The dashed lines for Q_d represent the charge predicted by equation (3.5). For FC72 we took into account its low permittivity by multiplying this prediction by $f = 0.2$. Note that for FC72 the amount of charge is about two orders of magnitude lower than that for water and ethanol. This turned out to make it impossible to obtain reliable results for $U_m - U_0$, and this analysis is therefore omitted.

Figure 3.9: Maximal deformations during rebound of the three tested liquids. The water droplet deforms significantly less than the ethanol and FC72 droplets.

for the droplet radius at the start of the plateau. To understand why the charge is even smaller, we have to take into account the extremely low dielectric permittivity of FC72. As explained in section 3.4, equation (3.5) was derived by calculating the polarization of a bi-sphere in an external electric field. This polarization was found to be about twice as large as that of a single sphere in the same electric field. In this sense the bi-sphere behaves as a single sphere with radius $\sqrt{2}R$. The polarization of a *dielectric* sphere can be obtained directly from that of a conducting sphere by multiplying the latter with a factor $f = (\epsilon_r - 1)/(\epsilon_r + 2)$ [33]. Approximately the same factor will apply to the bi-sphere case. For ethanol and water this factor leads to a negligible correction, but for FC72, with $\epsilon_r \approx 1.7$, one finds $f \approx 0.2$, explaining the low amount of charge observed. In figure 3.8 we took this factor into account in the comparison between the inferred charge (dots) and the model (dashed line). Had we not done this, then the line would lie outside the field of view. Similarly, this factor is necessary to understand the escape radii plotted in figure 3.6.

The above considerations imply that, for FC72, also the formulas used for inferring the charge and potential energy (equations (3.3) and (3.4)) are inaccurate, because the coefficients c_{ij} were calculated for perfect conductors. This error will occur mainly through the estimation of second order forces due to image charges, and may explain for example why the charge plateau does not seem to be perfectly horizontal (this would also happen for water and ethanol in the simple point charge approximation).

Figure 3.10: Evolution of the charge on (a) ethanol droplets and (b) FC72 droplets, trapped under either a negatively (top panels) or a positively charged electrode (bottom panels). While for ethanol the behaviour is more or less symmetric, FC72 does not obtain any positive charge, even for electrode voltages as low as -5 kV.

3.9 Charging under a negative electrode

In the experiments described so far the top electrode was set to a positive voltage with respect to the grounded plate, so that the droplet attained a net negative charge. Figure 3.10 shows the results of two experiments, one with ethanol and one with FC72, in which the voltage on the top electrode was set to a negative value (so that the droplets should get a positive charge). For a direct comparison, similar experiments for which the voltage was positive are also plotted.

While ethanol droplets behave practically the same for positive and negative voltage (as does water), FC72 droplets show an interesting asymmetric behaviour under polarity reversal. The FC72 droplet seems to be unable to obtain any net positive charge. To trap the droplet under these neutral conditions we had to increase the magnitude of the voltage to at least $|V_s| = 5$ kV, and even then the droplet often rolled off the plate. This asymmetric charging behaviour of FC72 is likely related to the chemically inert nature of this fluor-rich fluid. Similar to a Teflon-rod that is charged by rubbing, FC72 prefers to hold a negative charge.

Figure 3.11: Instabilities observed for ethanol (a-b) and water droplets (b-c) at voltage differences above 4 kV. In (a) the ethanol droplet developed a sharp cone from which small droplets are ejected. A few bounces later (b) it temporarily formed a vertical bridge between the top electrode and the hot bottom plate, still hovering on a vapour film. Also the water droplet (c) first developed a cone, but in this case (d) the electrical tension is released by a violent discharge that ruptures the drop.

3.10 Approaching the charging limit

To observe the progressive increase in jumping amplitude, the voltage on the top electrode has to be high enough to overcome the loss in height due to energy dissipation (see §3.5). However, if the voltage is too high, the spherical shape of the droplet becomes unstable with respect to a conical shape [5]. For ethanol and water this happens around $V_s \gtrsim 4\text{ kV}$.

Figure 3.11 shows some snapshots of these instabilities. Initially, both the water and ethanol droplet developed a Taylor cone at their upper surfaces. For the ethanol droplet this cone quickly destabilized and started to eject small droplets. In the same recording the ethanol droplet occasionally stretched into a thin filament bridging the whole gap. This filament remained stable for a while, and then broke up into several smaller droplets, leading to a very irregular behaviour. For the water droplet no ejection was observed, instead the tension was released by a violent electrical discharge striking the drop's sharp tip.

3.11 Conclusion and outlook

Small Leidenfrost droplets in a vertical electric field of strengths between 2 and 5 kV/cm display a surprising regular and repeatable dribbling motion, in which they escape from the hot surface by jumping progressively higher. We have related this behaviour to the electrical and gravitational forces acting respectively on the charge and mass of the droplet. As the droplet evaporates, the gravitational force scales with R^3 while the charge decreases in a step like manner to remain proportional to R^2 , so that the electrical forces eventually dominate. The discrete discharge events were attributed to an electro-capillary instability in the vapour gap, occurring each time the electrical potential of the droplet reaches a critical value. From an analysis of the potential and kinetic energies of the droplets we have found that for most parts these energies are slowly decreasing in time. However, the droplet occasionally receives a boost, helping it to escape. In the final stage, the decrease in potential energy due to evaporation is by itself enough to allow the jumping amplitude to increase.

The analytical approach employed in this work, using capacitance and force coefficients to calculate potentials, forces and energies, can be extended to any geometry. This opens up the possibility to design electrical circuitry to trap and steer these hyper-mobile droplets. Furthermore, the method of inferring the charge from the droplet's trajectory can be used to study the basic charging properties of a liquid (such as the asymmetric behaviour of FC72), or the insulation properties of its vapour.

Appendix

3.A Horizontal trapping potential

The easiest configuration for a theoretical treatment of the electrical forces in the vertical direction would be that of two parallel plates. However, practically it is more convenient to let one of the electrodes have a slight curvature. First, there is then no need to align the electrodes. Second, it ensures that a charged droplet experiences a slight trapping force, keeping it in the field of view. The electrical potential between a sphere of radius R_s with its centre a distance d_c above a plate can be calculated numerically through a summation over image charges. The positions y_n and magnitudes q_n of these virtual point charges in the top electrode are given by the recursive relation:

$$\begin{aligned} y_1 &= d_c \\ y_n &= d_c - \frac{R_s^2}{d_c + y_{n-1}} \\ q_1 &= R_s V_s \\ q_n &= \frac{R}{d_c + y_{n-1}} q_{n-1} \quad (n = 2, 3, \dots) \end{aligned} \quad (3.11)$$

Another set of charges with the same magnitude but of opposite sign, are to be placed below the plate, mirrored with respect to the plate surface. The potential field $\phi(x, y)$ is then simply given by summing over the potentials $\phi_n(x, y) = \pm q_n / r_n(x, y)$, with r_n the distance to the point charge. Figure 3.12(a) shows a contour plot of the potential calculated in this way, with $V_s = 2$ kV. To extract the trapping potential (at a certain height Y_{CM}) we take a horizontal slice $\phi(x, Y_{CM})$, as shown in figure 3.12(b). The potential energy is given by $U(x) = Q_d \phi(x)$. For small motions about the centre this potential is approximately harmonic and we can define a spring constant as

$$k(y) \equiv Q_d \frac{\partial^2 \phi}{\partial x^2}. \quad (3.12)$$

Figure 3.12: Electrical potential ϕ between a conducting sphere of $V_s = 2\text{ kV}$ (black) and a grounded plate (white). Figure (b) shows a horizontal slice to clearly show the weak trapping potential close to the plate.

A droplet with mass m and charge Q_d will then oscillate with angular frequency

$$\omega^2 = \frac{k}{m} = \frac{Q_d}{m} \frac{\partial^2 \phi}{\partial x^2}. \quad (3.13)$$

In each experiment all quantities except Q_d are known, providing an independent method to extract the charge on the droplet. The result of such an analysis is shown in figure 3.13. Although the inferred charge is consistent with that found from the vertical motion, the horizontal motion is less regular, resulting in a large scatter.

3.B Capacitance and force coefficients

In first approximation the force acting on a charged droplet is given by $F_e = Q_d V_s / d$, which assumes that the droplet can be treated as a point in an external electrical field of strength V_s / d . The corresponding force coefficients would be $f_{dd} = f_{ss} = 0$, and $f_{ds} = 1/d$. Although this approximation gives already quite a good estimate of the amount of charge on the droplet, it fails when the droplet is very close to the plate. Furthermore, the charge plateaus are not horizontal in this approximation, giving the wrong impression that the charge here slowly increases or decreases. To circumvent these errors and to check the analytical expressions used in the main text, we used the

Figure 3.13: (a) Horizontal motion of the centre of mass of a charged ethanol droplet and (b) the charge inferred from this motion.

Figure 3.14: Geometry and mesh used to calculate the force and capacitance coefficients with COMSOL. Figure (b) shows a magnification of the gap between the top electrode and the plate, with the droplet in between. The surfaces of the droplet and the top electrode have a fine mesh. The simulations were axisymmetric.

electrostatics module of COMSOL (version 5.0) to directly calculate both the capacitance and force coefficients in our setup. Figure 3.14 shows the typical geometry and mesh used in these calculations. To calculate for example the capacitance coefficient c_{ds} , the voltage of the top electrode was set to 1V, while the droplet was grounded (cf. figure 3.4). c_{ds} is then given by the total amount of surface charge accumulated on the conductor that represents the droplet. To obtain sufficient accuracy for performing these integrals, the mesh was extra refined on the surfaces of the conductors.

These calculations were repeated for a range of droplet heights H and radii R , to obtain a fine grid of coefficients $c_{ij}(H, R)$ covering all the radii and heights found in the experiments. Values in between the grid points were obtained through interpolation. To give an idea of their behaviour, figure 3.15 shows the coefficients as a function of H , and a fixed radius of $R = 0.6\text{mm}$. In equation (3.8) we used approximations for c_{dd} and c_{ds} to calculate the electrical potential of the drop when it is close to the surface ($H \ll R$). In figure 3.15 these approximations are shown as dashed lines. They indeed approach the correct values in the limit $H \rightarrow 0$.

As explained in section §3.4, the force coefficients can in principle be obtained from the variation of capacitance coefficients with H by taking the appropriate combinations and then taking the derivative. However, it turns out that doing this numerically leads to some errors, especially for f_{ss} which is calculated as $f_{ss} = \partial_H(c_{ss} - c_{ds}^2/c_{dd})/2$. To circumvent this numerical differentiation, we also directly calculated the force coefficients by treating the droplet as a floating potential with a fixed charge $Q = 1\text{C}$ or 0C (and, as before, with the top electrode set to 1V or 0V) and directly calculating the net force exerted by the field on the surface charges. The plots in figure 3.15 show both the coefficients obtained through differentiation (black dots) and through direct calculation (grey lines). For f_{dd} and f_{ds} the two methods practically overlap, but for f_{ss} the direct method performs significantly better.

3.C Vapour film thickness

Our prediction for the critical discharge voltage of the droplet, equation (3.10), relies on an estimation of the minimum height of the vapour gap below the droplet during a rebound. For this estimation we will follow a similar procedure as outlined in [27] for droplets in a gravitational field. We then extend this approach to droplets impacting with a finite velocity to see whether it is the impact force or the gravitational force which dominates in our case. The situation is sketched in figure 3.16.

When a small droplet sits on a solid surface, with or without vapour in between,

Figure 3.15: Capacitance coefficients c_{ij} and force coefficients f_{ij} as a function of the gap between the droplet and the plate H , for a fixed radius of $R = 0.6$ mm. The black dots are the calculated coefficients (it is hard to see separate dots because of the fine grid of points). For c_{dd} and c_{ds} also analytical asymptotic solutions for $H/R \rightarrow 0$ are shown. The force coefficients were calculated both from the capacitance coefficients (black dots) and directly by integrating the force in the simulation (grey lines).

Figure 3.16: Sketch of a small droplet that deforms upon impact with a solid surface.

the bottom of the droplets gets indented by a small amount (see e.g. [31])

$$\delta_g \sim \frac{\rho g R^3}{\gamma} = RBo, \quad (3.14)$$

so that the decrease in potential energy due to the lowering of the centre of mass is balanced by an increase in the surface energy. From the spherical geometry of the droplet it follows that the radius of the flattened area is

$$a \sim \sqrt{R\delta_g} = RBo^{1/2} \quad (3.15)$$

The flattening of the bottom locally exposes the Laplace pressure of the droplet. In the solid this pressure is supplied by a small elastic deformation. When there is a vapour film between the solid and the droplet, the same pressure has to be built up in the vapour. This is possible when the gap becomes so small that viscous forces in the vapour become important. The flow in the gap can then be shown to be equivalent to the classical lubrication problem of a squeezing flow below a flat disk of radius a moving down with the velocity of the generated vapour:

$$v_v \sim \frac{k_v \Delta T}{L \rho_v H}, \quad (3.16)$$

where k_v is the thermal conductivity of the vapour and L the latent heat of evaporation. The maximum lubrication pressure for the squeezing flow scales as

$$p_\mu \sim \frac{\mu_v v_r a}{H^2} \sim \frac{\mu_v v_v a^2}{H^3}, \quad (3.17)$$

Figure 3.17: Minimum height of the vapour gap when gravity dominates inertia. Dots show experiments from [27] and the lines represent different scaling expressions, equation (3.18) (solid line) and equation (8) from [27] (dashed line). For both lines the pre-factor was adjusted to make the lines go through the first data point, with values of 0.75 and 2.5, respectively.

where $v_r \sim v_v a/H$ is the radial flow velocity and μ_v is the dynamic viscosity of the vapour. This pressure has to balance the Laplace pressure $p_\gamma \sim \gamma/R$. Setting $p_\mu \sim p_\gamma$, and using equations (3.14)–(3.17) we find

$$\frac{H}{R} \sim \left(\frac{k_v \Delta T R \mu_v \rho g}{L \rho_v \gamma^2} \right)^{1/4}. \quad (3.18)$$

This expression is similar to equation (8) in [27], except that we here find an exponent of 1/4 instead of 1/3 on the dimensionless term between brackets. The difference is that in the former work, it was assumed that heat transfer to the whole droplet surface contributes to the vapour flow in the gap. In figure 3.17 we reproduced the experimental data and equation (8) (dashed line) from [27], and also plot equation (3.18) derived above (solid line). The pre-factors were adjusted so that both lines go through the first experimental point, we find a pre-factors of 2.5 for the former and 0.75 for the latter, which seems to favour equation (3.18). However, given these pre-factors the correct slope cannot be inferred from the measurements, and for the radii we are interested in here, $R \sim 1$ mm, both lines predict a similar film thickness of about $H \approx 20 \mu\text{m}$. For droplets larger than about $R = 3$ mm the deformations are no longer small and the droplets cannot be assumed spherical, so that the models do not work in this regime.

When the droplet has a finite impact velocity v , its momentum will provide an additional force that pushes the droplet down. If we suppose that the droplet decelerates over a distance δ , we can interpret this in the frame of reference of the droplet

as an effective gravitational acceleration

$$g' \sim \frac{v^2}{\delta}. \quad (3.19)$$

Using this in equation (3.14), and solving for δ , we find

$$\delta_v \sim \sqrt{\frac{\rho v^2 R^3}{\gamma}} = RWe^{1/2} \quad (3.20)$$

Note that the same result is found by comparing the kinetic energy $\sim \rho R^3 v^2$ to the energy associated with the small deformation of the surface $\sim \gamma \delta^2$. Comparing equations (3.14) and (3.20) we see that the transition from a gravity to an inertia dominated regime occurs for

$$We \sim Bo^2. \quad (3.21)$$

Coincidentally this condition corresponds precisely to that for the natural jumping mode of small Leidenfrost droplets (cf. equation (3.7)). This means that in our experiment the droplets are always found in this transitional regime, and it does not matter much which scale we use to estimate H .

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4

Universal dissipation in inelastic droplet impact?*

Droplets colliding with a solid surface or another (similar) droplet with high inertia are always found to spread out significantly less than one would expect from a naive balance between the initial kinetic energy and an increase in surface energy. On the other hand, recent models which apply momentum and mass conservation without explicitly including any viscous damping, are quite successful in predicting the spreading. These observations hint at an universal dissipative loss in the droplet, which, reminiscent of the Taylor-Culick problem, is independent of the viscosity and surface tension of the liquid.

Building on direct numerical simulations and a detailed analysis of the energy budget in the flow, we work out the main sources of dissipation. It is shown that at high enough velocities the final amount turns out to be always roughly the same and equal to $1/2$ of the initial kinetic energy. We also demonstrate how this seemingly universal loss of ‘plastic deformation’ can be applied to accurately estimate the maximum spreading from a simple energy balance, without any fitting parameters.

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4.1 Introduction

The common event of a drop of liquid impacting onto a solid surface is a very rich phenomenon: droplets can splash, spread or bounce [1–4], often entrapping air in the process [5, 6]. But despite the great experimental progress on the impact problem [7] consensus has yet to be reached on many of its basic laws. One of the very basic questions (see figure 4.1) is to find out the final spreading diameter D_m of the droplet, given its initial diameter D_0 , its impact velocity V_0 , the properties of the liquid (density ρ , surface tension γ , and viscosity μ), and the conditions at the solid surface: the slip length λ [8] and the (dynamic) liquid-solid contact angle θ [9, 10]. The influence of the surrounding air is often negligible in the overall spreading dynamics [11]. Using dimensional analysis, the problem can be reduced to finding $D_m/D_0 = f(\text{We}, \text{Re}, \lambda/D_0, \theta)$, where

$$\text{We} \equiv \frac{\rho D_0 V_0^2}{\gamma} \quad \text{and} \quad \text{Re} \equiv \frac{\rho D_0 V_0}{\mu}$$

are the so called impact Weber- and Reynolds-number, which signify, respectively, the importance of the surface tension and viscosity with respect to the inertia of the drop. Because D_m sets the final surface area covered by the impacting droplet, knowing its value is of great importance in a wide variety of applications: from inkjet printing [12], spray cooling [13] and self-cleaning surfaces [14], to blood spatter analysis in crime scenes [15] and anti-icing of aircraft wings [16]. All these applications deal with high inertia impacts ($\text{We} \gg 1$, $\text{Re} \gg 1$) in which the droplet greatly deforms. This regime of *plastic* deformation is the focus of this chapter. For an in-depth discussion of the elastic regime ($\text{We} < 1$, $\text{Re} \gg 1$) the reader is referred to chapter 3.

When a droplet with a high inertia hits a solid surface, a thin lamella spreads out radially from the impact zone (see figure 4.1). Initially, the top of the droplet $H_c(t)$ moves on almost undisturbed, but after some time the droplet starts to slow down and reaches a maximum extension. At this point the droplet has the shape of a pizza: a flat central part, bordered by a thick rim. The maximum spreading diameter D_m and the time at which it is reached, t_m , strongly depend on the amount of friction between the drop and the solid surface. In figure 4.1 the extreme case of a *free-slip* (slippery) surface is shown next to that of a *no-slip* (dry) surface. As can be expected, on the free-slip surface the droplet spreads significantly longer and further than on the no-slip surface. This is also clearly seen in figure 4.2, where we have plotted the spreading diameter of the lamella $D_l(\tilde{t})$ and the central height $H_c(\tilde{t})$ as a function of the dimensionless simulation time $\tilde{t} = (V_0/D_0)t$.

Figure 4.1: The canonical problem in droplet impact: A droplet hits a solid surface (with or without slip) with initial velocity V_0 and diameter D_0 . What will be its maximum spreading diameter D_m ? The figure shows an example for impact parameters $We = 300$, $Re = 500$, and $\theta = 180^\circ$. During the impact, a thin lamella is squeezed out radially as the central height $H_c(t)$ of the droplet decreases. The insets show the radial velocity v_r in the lamella. In the no-slip case a velocity boundary layer with an approximately uniform thickness $H_b(t)$ develops near the surface. Such a boundary layer is absent in the free-slip case.

Figure 4.2: (a) Outer diameter of the spreading lamella D_l/D_0 as a function of the dimensionless time $\tilde{t} = (V_0/D_0)\tau$. $\tilde{t} = 0$ corresponds to first contact. The symbols indicate the spreading maximums D_m/D_0 occurring at times $\tilde{t}_m$. (b) Central height $H_c(\tilde{t})/D_0$ of the impacting droplet. The black line shows how the height would change without impact. The logarithmic scale reveals an exponent of -2 during the spreading phase. For no-slip impacts (red) the height saturates to a plateau value of $0.7 \text{Re}^{-2/5}$. The height of the free-slip droplets (green) keeps decreasing until it finally recoils

The main difference between the two cases lies in the nature of the viscous boundary layers that develop inside the droplet. In general, boundary layers occur wherever there is a mismatch between the (irrotational) velocity profile in the bulk of the liquid and the boundary conditions at the free or solid surfaces [17]. For example, for impact on a no-slip solid, the spreading of the lamella is hindered by dissipation in a velocity boundary layer that diffuses in from the solid. This layer develops because of a mismatch between the finite flow velocity in the drop and the zero velocity condition at the wall (see $H_b(t)$ in figure 4.1). In this case the maximum spreading diameter at large We-numbers, i.e. when inertia dominates over surface tension, is determined only by the viscosity of the liquid and is known to scale as $D_m/D_0 \sim \text{Re}^{1/5}$ [18, 19].

On a free-slip surface which is *flat*, no velocity mismatch occurs and a boundary layer will be absent. Boundary layers do develop where the liquid flows around *curved* sections of a free-slip interface [17]. But although the vorticity generated in such boundary layers can greatly influence the shape and dynamics of a free surface [20, 21], they often do not contribute much to the total dissipation in the flow [17]. For example, the terminal velocity of a bubble rising in a (clean) liquid at moderated Re-numbers can be estimated from the potential flow solution in the bulk alone [17]. Another textbook example is the viscous damping of gravity waves [17]. In both of these examples the total dissipation explicitly depends on the viscosity of the liquid. However, there are special cases in which it does not.

In 1959 Taylor worked out the problem of a retracting free edge on a thin liquid sheet [22]. This situation occurs for example when a soap film is punctured. Using momentum and mass conservation he found that, after some start-up period [23, 24], a thick cylindrical rim forms that consumes the sheet at a constant retraction velocity $V_c = \sqrt{2\gamma/h\rho}$, where h is the thickness of the sheet. One year later, Culick, seemingly unaware of Taylor's result, wrote a short comment [25] on the same problem, finding the same steady state velocity. Moreover, he emphasizes that this velocity is lower by a factor of $\sqrt{2}$ than one would get from an energy balance between the kinetic energy of the rim and the surface energy consumed by it. In other words, 1/2 of the available surface energy never makes it into kinetic energy. The rest must be dissipated somewhere, somehow. Although viscous friction does not enter explicitly in the momentum balance, Culick argued *a posteriori* that it must be concentrated near the rim entrance, where fluid from the stationary film is accelerated to match the velocity in the rim. The volume over which the associated dissipation occurs must then scale in such a way with viscosity, as to make the final answer independent of it.

Interestingly, a similar situation seems to be at hand for droplet impact. At high Re-numbers and on free-slip surfaces, the spreading of these droplets seems to be well described by models which do not explicitly incorporate viscosity in the momentum

balance [8, 18, 19], so that D_m/D_0 only depends on the We-number (and θ). On the other hand it has been often noted that the droplets generally spread significantly less than predicted by an energy balance [6, 19, 26]. As for the Taylor-Culick problem these observations hint at an universal scaling for the total dissipation, i.e. one which is independent of the impact parameters We and Re.

In this chapter we follow in Culick's footsteps and set out to identify the main sources of energy dissipation during inertial droplet spreading. Subsequently, we investigate whether, taken together, these contributions lead to the universal behavior alluded to above.

4.2 Method and validation

To calculate and visualize the local dissipation rates in an impacting droplet, detailed information on the flow field is required. To this end, we used the open source volume of fluid solver Gerris [27] to simulate axisymmetric water droplets surrounded by air, moving towards a solid surface. This numerical approach also makes it relatively straightforward to impose different slip conditions and liquid-solid contact angles. Gerris employs the volume of fluid method to solve the full Navier-Stokes equation on a dynamic adaptive grid [28]. Together with its thoroughly tested and physically sound treatment of free interfaces dynamics [27], Gerris is well suited for simulating two-phase flows with a multitude of length scales, such as droplet impact in air [11, 20, 21].

Figure 4.3 shows an example in which profiles obtained with the simulation method described above are directly compared to the experiments on high-velocity micro-drop impacts performed by Visser *et al.* [11]. The small size of these droplet allows one to use interferometry (fig. 4.3e) to extract accurate experimental profiles during the spreading phase (fig. 4.3f). An excellent match between simulation and experiments is found in all cases [11]. Additionally, in figure 4.2(b) it is shown that we recover the theoretically predicted [18, 29] and experimentally observed [8, 30] scalings for the droplet height: $H_c(\tilde{t})/D_0 \sim 1/\tilde{t}^2$ in the spreading phase and, for no-slip impacts, a final plateau at $H_c/D_0 \sim \text{Re}^{-2/5}$.

With the axisymmetry assumed in the simulations we obviously cannot capture non-axisymmetric effects like azimuthal rim destabilization and break-up [31]. However, this idealization does allow us to investigate scaling behaviors in the very high (> 1000) We-number regime, which is difficult to access experimentally.

For maximal contrast, we study the limiting cases of no-slip ($\lambda \rightarrow 0$, radial velocity $v_r = 0$ at $z = 0$) and free-slip impacts ($\lambda \rightarrow \infty$, $\partial v_r / \partial z = 0$ at $z = 0$). In the no-slip simulations the interface of the impacting droplet did not coalesce with the surface,

Figure 4.3: Validation of the simulations against experiment on fast micro-droplet impact on glass substrates [11]. In (a-c) simulation profiles (yellow) are shown to overlap with side views showing the impact of a droplet with $D_0 = 49.5 \mu\text{m}$ and $V_0 = 16.9 \text{ m/s}$, corresponding to $\text{Re} = 836$ and $\text{We} = 196$ in the simulations. The total time from (a) to (c) is $t = 1.1 \mu\text{s}$, or $\tilde{t} = 0.38$. In the spreading phase (d, $t = 3.4 \mu\text{s}$), bottom view interferometry (e) can be used to obtain accurate height profiles (f, red line). A good match with the simulations (black line) is found.

so that a thin layer of air remained between the surface and the liquid. During the spreading phase the effective slip length introduced by this air layer was always small compared to the thickness of the velocity boundary layer in the liquid, so that it did not noticeably change the overall dynamics as compared to true no-slip (we checked this for a few cases by forcing the droplet to coalesce at initialization). This non-coalescence behavior fixed the contact angle for the no-slip droplets to $\theta = 180^\circ$. For the free-slip case we used both $\theta = 180^\circ$ and $\theta = 90^\circ$. As the latter case is relevant to symmetric droplet-droplet collisions [29].

4.3 Local dissipation rates

Figure 4.4(a) shows two simulation snapshots (free-slip on the left, no-slip on the right) at $\tilde{t} = 1$ in which the red shading indicates the local dissipation rate ϵ_d in cylindrical coordinates (r, z) , given by:

$$\epsilon_d(r, z, t) = 2\mu \left[\left(\frac{\partial v_r}{\partial r} \right)^2 + \frac{v_r^2}{r^2} + \left(\frac{\partial v_z}{\partial z} \right)^2 \right] + \mu \left[\frac{\partial v_r}{\partial z} + \frac{\partial v_z}{\partial r} \right]^2, \quad (4.1)$$

where v_r and v_z are the radial and vertical velocity, respectively. In the no-slip case the $(\partial v_r / \partial z)^2$ term in the boundary layer is seen to cause a high dissipation near the surface, concealing any other contributions. Almost nothing is dissipated in the rim, which is slightly lifted from the surface so that the no-slip condition here has no effect.

In the free-slip droplet the boundary layer near the surface is absent, and we can start to see other sources of dissipation. A strong peak appears for example where liquid from the lamella enters the rim (see inset figure 4.4(a)). This is reminiscent of the dissipation behavior in the Taylor-Culick problem described in the introduction. To see how this peak develops in time, and how it contributes to the overall dissipation rate $\dot{E}_d(\tilde{t})$, we look at cumulative plots of the dissipation rate along the r -axis,

$$C_d(r, \tilde{t}) = 2\pi \int_0^r \int_0^{H_c} r' \epsilon_d(r', z', \tilde{t}) dz' dr', \quad (4.2)$$

so that at $r = D_l(\tilde{t})/2$ we have $C_d(D_l/2, \tilde{t}) = \dot{E}_d(\tilde{t})$. The resulting curves for times $\tilde{t} = 0.1, 0.2, \dots, \tilde{t}_m$ are shown in figure 4.4(b).

In the free-slip case two dissipation phases can be distinguished. For dimensionless times $\tilde{t} < 1$ most of the dissipation happens in the bulk, where liquid from the center flows around the corner into the lamella. For $\tilde{t} > 1$ the dissipation peak near the rim becomes dominant. While the contribution from the bulk diminishes in time,

Figure 4.4: Visualization of viscous dissipation inside an impacting droplet ($We = 300$, $Re = 500$, $\theta = 180^\circ$). Free-slip on the left, and no-slip on the right. (a) Simulation snapshot at $\tilde{t} = 1$, in which regions of high local dissipation rate ϵ_d are colored red. For clarity, the intensity was clipped at $\epsilon_d = 10\rho V_0^3/D_0$. For the free-slip droplet a close-up of the transition between the lamella (L) and rim (R) region is shown. (b) Spatio-temporal evolution of the energy dissipation. The solid lines represent, for different times $\tilde{t} = 0.1, 0.2, \dots, \tilde{t}_m$, the cumulative dissipation rate, eq. (4.2). For each solid curve the final value corresponds to the total dissipation rate $\dot{E}_d$ at time $\tilde{t}$, i.e. $\dot{E}_d(\tilde{t}) = C_d(D_m/2, \tilde{t})$. Mind the different scale on the y-axis for the two slip cases. The vertical dotted lines relate the features seen in figure (a) and (b).

the contribution from the peak first increases and then approaches a constant value, corresponding to that of a retracting rim on a stationary sheet. For the impact parameters taken here both phases contribute about the same amount to the total dissipation: $E_d = \int dt \dot{E}_d(t)$ (see also figure 4.5(a)).

During the no-slip impact the overall dissipation rate $\dot{E}_d$ is initially roughly twice as high as compared to the free-slip impact (mind the different scales on the axes). As the drop spreads out, this high rate then quickly drops to about the same final value as observed for the free-slip case. For all times, $C_d(r)$ increases steadily towards the rim of the droplet, as it is overwhelmed by the contribution from the no-slip condition. The lack of dissipation in the rim mentioned before, appears here as a flat region just before the outer edges of the cumulative plots.

4.4 Overall energy budget

As demonstrated above, the detailed dissipation behavior during impact and subsequent spreading is far from trivial. However, an interesting picture emerges when we look at the *final* energy distribution for free-slip impacts, shown in figure 4.5(a). For two orders of magnitude in We-number (between 30 and 3000), the part of the initial kinetic energy that makes it into surface energy at $\tilde{t}_m$, amounts to roughly 1/2, virtually independent of We and Re. At We = 30, the remaining 1/2 is distributed approximately equally among kinetic energy and dissipation, while at the higher We-numbers it is mainly dissipated. The latter can be contrasted with the no-slip case (see figure 4.5(b)), for which practically *all* of the energy is lost to dissipation at high We-numbers.

For $We \lesssim 30$ the maximum spreading and the dissipation behavior become largely independent of the slip conditions. This is because for these low We-numbers (and the studied range of Re-numbers) the no-slip boundary layer has no time to grow appreciatively before the edge of the drop retracts by surface tension. At We = 3, significantly more than 1/2 of the energy is stored in the surface. Here it approaches the elastic regime ($We \lesssim 1$) in which the droplet undergoes only slight deformations [32, 33].

4.5 Maximum spreading from an energy balance

The maximum spreading D_m/D_0 is by far the most reported parameter in experimental studies on droplet impact. Therefore, we now return to the basic impact problem formulated in the introduction, to see whether the observed ‘1/2-rule’ can be applied

Figure 4.5: Evolution of the energy budget for (a) free-slip impacts, and (b) no-slip impacts, normalized by the initial kinetic energy. The left graphs show for our reference cases ($We = 300$, $Re = 500$, $\theta = 180^\circ$) how the kinetic energy E_k is transformed into an increase ΔE_s of the surface energy and into heat E_d . The bar plots on the right show the final energy distribution for all simulations (with $\theta = 180^\circ$) at the time of maximum deformation $\tilde{t}_m$. The dashed line indicates the $1/2$ level.

Figure 4.6: Maximum droplet deformations D_m/D_0 as a function of the impact We-number found in simulations ran for Re-numbers of 100 ($\blacktriangledown$), 500 ($\blacktriangle$, $\square$) and 1000 ($\bullet$), and contact angles of $\theta = 180^\circ$ ($\blacktriangledown$, $\blacktriangle$, $\bullet$), and 90° ($\square$). Green symbols are used for impacts on a free-slip surface, and red symbols for impacts on a no-slip surface. The black curves show the predictions by equation (4.3), without any fitting parameters. Shown are $\theta = 180^\circ$ (solid line), and $\theta = 90^\circ$ (dashed line). The horizontal dotted lines represent the plateau value of $Re^{1/5}$ expected at high We-numbers for no-slip impacts. The insets show the typical shape of the droplets at low (puddle-shaped), and high We-numbers (pizza-shaped). The vertical line at $We = 30$ roughly indicates the point between the transition to the elastic regime (left) and the fully plastic regime (right).

Figure 4.7: For combinations of a low Re-number and a high We-number, a thin sheet is ejected from the edge of the droplet (arrow), which is not hindered by the no-slip conditions at the solid surface.

to estimate this ratio. This will allow for a direct comparison to a large set of experimental data.

For free-slip, the 1/2-rule is that the initial surface energy $E_{s0} = \pi\gamma D_0^2$ and about half of the initial kinetic energy $E_{k0}/2 = \pi\rho D_0^3 V_0^2/24$ are transformed into the final surface energy $E_s = \pi\gamma D_m^2(1 - \cos\theta)/4$, where $\gamma\cos\theta$ accounts for the work done in expanding the wetted area with a dynamic contact angle θ [10]. Equating these energies as $E_{s0} + E_{k0}/2 = E_s$ and solving for D_m/D_0 , leads to:

$$\frac{D_m}{D_0} = \sqrt{\frac{1}{1 - \cos\theta} \left(\frac{\text{We}}{6} + 4 \right)} \quad (4.3)$$

This expression is fundamentally different from previous analytical models of similar form [6, 34–36] as we here for the first time included the *plastic deformation loss* $E_p \approx E_{k0}/2$. Hence, the pre-factors are very different.

In figure 4.6 we plotted equation (4.3) for $\theta = 90^\circ$ and $\theta = 180^\circ$, together with the maximum spreading diameters found in our simulations. For the free-slip cases with $\text{Re} = 500$ and $\text{Re} = 1000$ we find an excellent agreement, without any fitting parameters. For $\text{Re} = 100$ the spreading is somewhat lower than predicted, as could be expected from the larger deviation from the 1/2-rule for this low Re-number case (see figure 4.5(a)).

As anticipated, the no-slip simulations show a large deviation from equation (4.3) at high We-numbers. Here the spreading is hindered by the growing boundary layer which limits the diameter to $D_m/D_0 \sim \text{Re}^{1/5}$ [18, 19, 37]. With a pre-factor ≈ 1 , this scaling gives a good estimate of the maximum spreading found in our simulations for $\text{Re} = (500, 1000)$ at $\text{We} = 3000$. A more robust way to define the spreading limit on no-slip surfaces is to look at the minimum droplet height H_m/D_0 reached. This

quantity only depends on the Re-number and, as shown before in figure 4.2(b), is well described by $H_m/D_0 \approx 0.7 \text{Re}^{-2/5}$. In the absence of a thick rim (i.e. $\text{We} \rightarrow \infty$) the final droplet shape will approximate that of a disk. Using mass conservation, $\frac{2}{3}D_0^3 = D_m^2 H_m$, we again obtain the upper bound $D_m/D_0 \approx \text{Re}^{1/5}$ (at $\text{We} = 3000$ a thick rim is indeed practically absent).

Surprisingly, the $\text{Re} = 100$ case somewhat exceeds the above limit. As it turns out, the combination of this low Re-number with a high We-number, makes that a thin sheet is ejected from the edge of the droplet during impact (see figure 4.7). This sheet is lifted from the surface, so that the no-slip condition has no effect on this part of the droplet, leading to the larger than expected spreading in this special case. One could say that this droplet experiences a mix of no-slip and free-slip conditions.

In figure 4.8 we compare our models and simulations with available experimental data on (a) free-slip and (b) no-slip impacts. Following [8] we expect the free-slip condition to hold for impacts of Leidenfrost droplets [38], which hover on a vapor film, and for symmetric droplet-droplet collisions [26, 39], where the mirror symmetry is equivalent to a free-slip condition and a contact angle of 90° [29]. In figure 4.8(a) we see that there is a good agreement between the free-slip data and equation (4.3), especially if one takes into account that the Re-number reached in the experiments is one order of magnitude higher than that in our simulations, providing strong evidence that for free-slip impacts the 1/2-rule for plastic deformation is indeed independent of Re, for large Re.

The droplet collision data for the highest viscosity (30 cSt) lay somewhat below the $\theta = 90^\circ$ line, and come closer to the prediction for $\theta = 180^\circ$. This could either be a manifestation of the Re-number dependence we observed also in our simulations at low Re-numbers, or an indication that the droplets did not immediately coalesce. However, the latter possibility is very unlikely, as these experiments were performed under vacuum conditions.

The no-slip condition generally holds for impacts on surfaces at room temperature, for which data [11, 19, 40] are shown in figure 4.8(b). The data overlap with the free-slip model at low We-numbers, but clearly start to deviate at larger We-numbers. Here the points are expected to bend towards the limit $D_m/D_0 \approx \text{Re}^{1/5}$, as was the case in our simulations. However, whereas in the simulations we kept Re fixed as We was varied, in experiments it is usually more convenient to vary the impact velocity V_0 , while keeping the droplet diameter and liquid properties fixed. For the free-slip prediction this is of no consequence, as it only depends on We, but for experiments on no-slip surfaces it means that the spreading limit effectively keeps shifting up as We is increased. For a given droplet diameter and liquid, we can predict this shift by expressing the Re-number in terms of We, as follows: $\text{Re}_{\text{We}} = (\rho\gamma D_0 \text{We})^{1/2}/\mu$, so

(a) free-slip

(b) no-slip

Figure 4.8: Comparison between the derived spreading models (lines) and (a) free- and (b) no-slip experiments (closed symbols). The color of the symbols indicates the Re -number, which in experiments with a single liquid cannot be varied independently of the We -number. Again the black curves represent the model for free-slip impacts (equation (4.3), dashed for $\theta = 90^\circ$, solid for $\theta = 180^\circ$). In (a) the simulation results for free-slip are overlapped (open symbols). In (b) the colored dotted lines also show the no-slip spreading limit $Re_{We}^{1/5} = Oh^{-1/5} We^{1/10}$ for two different droplet diameters ($D_0 = 3$ mm and $D_0 = 40$ μ m). The no-slip experiments should stay below both the free-slip curve and the dotted line corresponding to their diameter and liquid properties (water in this case).

that one expects the droplet diameters to stay below $D_m/D_0 \approx \text{Re}_{\text{We}}^{1/5} = \text{Oh}^{-1/5} \text{We}^{1/10}$, with the Ohnesorge-number $\text{Oh} \equiv \mu / \sqrt{\rho\gamma D_0}$. In figure 4.8(b) we have plotted this relation for water droplets of $D_0 = 3 \text{ mm}$ and $D_0 = 40 \mu\text{m}$, corresponding to the liquid and diameters used in the shown experiments. The no-slip data points indeed stay below both the free-slip line and the appropriate $\text{Re}_{\text{We}}^{1/5}$ line.

4.6 Universal dissipation?

To conclude, inelastic droplet impact seems to fall into a special class of fluid problems (which also includes the Taylor-Culick problem) in which the energy loss associated with the “plastic deformation” does not explicitly depend on the viscosity (nor surface tension) of the liquid. This energy loss is significant, as it always amounts to about 1/2 of the initial kinetic energy, even when all other sources of dissipation are negligible. Interestingly, it depends on the We-number which loss mechanisms are at work on a detailed level. For large We-numbers ($\gtrsim 300$) the loss rate is first dominated by viscous dissipation in the flow into the spreading lamella and later by viscous dissipation near the rim entrance. At moderate We-numbers ($30 \lesssim \text{We} \lesssim 300$) a part of the lost energy is to be attributed to internal motions. Whether it is a coincident or a fundamental law that at the time of maximal deformation the total loss is always roughly 1/2 of the energy that was available, remains an open question for now. Nevertheless, it can be used as a practical rule.

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5

Bursting of water droplets freezing from the outside-in *

Supercooled water droplets, freezing radially inward, were filmed at frame rates of up to 15000 fps. Three subsequent events are observed: (1) at a droplet temperature of about -15°C an ice front spontaneously nucleates at the drop's surface and completely encapsulates in about 50 ms, (2) the droplet freezes inward as it is further cooled by sublimation from the ice shell (3) after some time $\tau(R)$, which increases quadratically with the drop radius R , the thick ice shell bursts into a few large pieces accompanied by some smaller shards.

We show that the pressure build up in the fluid inclusion due to the expansion of the inward freezing water, leads to a perpetual fracturing of the surrounding ice shell. Only if the elastic energy released in such an event is sufficient to tear apart (cavitate) the liquid in the inclusion, can the ice fragments fly apart completely. Otherwise the cracks slowly heal, and the cycle repeats itself. We develop basic models for the radial ice growth and the build up and release of stresses, which allow one to predict when the droplet bursts and with what energy. Interestingly, these models also predict a minimum droplet radius of about $R = 50\mu\text{m}$ below which the ice droplets cannot explode at all.

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5.1 Introduction

Supercooled water droplets are a common phenomenon in high altitude clouds. In the absence of suitable nuclei these cloud droplets can become as cold as -40°C , while retaining their liquid form [1–3]. Besides air pollution [4, 5], one of the most effective nuclei for turning these droplets into ice are other ice particles [1]. Observations of supercooled droplets in natural clouds and under laboratory conditions unequivocally show that secondary ice particles or splinters can be ejected during the freezing of these droplets [6–11]. This implies that once a few droplets in a cloud freeze by other means, a kind of freezing avalanche can occur if the density of ice particles is high enough [7, 12, 13]. This idea is supported by the surprisingly high ratios (often orders of magnitude) of ice-particles to other types of nuclei observed in high altitude clouds [1, 13, 14].

In this chapter we study a mechanism that could greatly enhance the probability for a nucleated water droplet to induce nucleation of several other ones. We will show that the internal stresses that are built up when the droplet freezes radially inward can cause the ice shell to fracture and fly apart into several fragments. Although such a mechanism has been proposed before [6, 15], a direct visualization of this fast process and a detailed physical description seem to have been lacking so far.

To facilitate a theoretical treatment, our experiment is designed to approximate the ideal situation of an isolated spherical droplet. However, as shown in figure 5.1 in practice the phenomenon can also occur, for example, at extremities pushed out of a supercooled droplet that freezes after impact.

5.2 Setup and method

A surprisingly effective way to cool a water droplet below its freezing temperature is by letting it evaporate in a low pressure environment [16]. To cool down a water droplet by 1 K one needs to evaporate only $c_p/L_e \approx 0.2\%$ of its total mass, where $c_p \approx 4.2\text{ kJ}/(\text{kg K})$ is the specific heat of water and $L_e \approx 2270\text{ kJ}/\text{kg}$ is the latent heat of evaporation.

A schematic drawing of our setup is shown in figure 5.2. In each experiment a millimetric droplet of degassed demi-water was placed on a glass substrate in the center of a vacuum chamber with a volume of 7 L. To render the substrate superhydrophobic, we covered it with a fresh layer of soot by moving it through a candle flame [17]. A rotary vane pump (Edwards E2M2) was then used to evacuate the chamber. To increase the pumping efficiency for water vapor we cooled the bottom plate down to -10°C . The background pressure in the chamber was constantly mon-

Figure 5.1: Observation of a bursting ice droplet after riming of an impacted droplet. (a) Impact of a millimetric water droplet in a vacuum environment. (b) Due to evaporative cooling, the resulting puddle freezes over and some liquid is squeezed out, forming a hollow rod of ice. (c) After about 0.3 seconds, the small spherical droplet hanging from the end of this extremity bursts into pieces. The times between the two frames in (a–c) are 3 ms, 150 ms, and 3 ms, respectively.

Figure 5.2: Schematics of the setup used to supercool water droplets deposited on a superhydrophobic layer of candle soot. A vacuum pump and a cold bottom plate reduce the vapor pressure in the chamber, leading to a rapid evaporative cooling of the droplet. We can monitor the gas pressure P in the chamber and a thermocouple can be inserted into the droplet to roughly measure its temperature T .

itored with a digital vacuum gauge and a thermocouple could optionally be inserted into the droplet to record its temperature. The freezing and bursting events were captured with a high-speed camera using frame rates of up to 15000 frames per second.

5.3 Nucleation and freezing over

A typical freezing event is shown in figure 5.3. At a droplet temperature of about $T \approx -10^\circ\text{C}$ and a chamber pressure of 10 mbar, a freezing front nucleates at the liquid-gas interface of the droplet and completely encapsulates it in about 50 ms. Often some liquid is initially squeezed out at places where the ice fronts meet, which then freezes on the outside (see arrows in figure 5.3(a)).

Because of the latent heat of melting $L_m \approx 330\text{ kJ/kg}$ released during the freezing process, the temperature on the inside of the ice shell quickly rises to near the melting temperature $T_m = 0^\circ\text{C}$ (see figure 5.3(b)). Note that the amount of energy that could be transferred to the inside of the cold droplet is by far not enough to make it completely freeze upon nucleation. Equating the heat deficit, $(4/3)\pi R^3 \rho c_p (T_m - T)$, to the latent heat released in freezing a shell of thickness ΔR , $4\pi R^2 \Delta R L_m$, we find $\Delta R/R = \rho c_p (T_m - T)/3L_m \approx 3\%$. After freezing over, the droplet continues to cool by sublimation of the ice (with an associated latent heat of $L_s \approx 2800\text{ kJ/kg}$).

In figure 5.3(c) we see that the pressure in the chamber at the point of freezing has reached a value of about 1000 Pa. The vapor pressure P_v of water at -10°C is $P_v \approx 300\text{ Pa}$ (and similar for ice), that is, about 70% of the gas in the chamber still consists of the initially trapped air. In the experiments presented here we could not precisely control the temperature at which the droplets froze, but it generally occurred

Figure 5.3: Spontaneous nucleation and freezing over of a supercooled water droplet. (a) Snapshots before, during and after freezing over. Some water is initially squeezed out at the locations indicated by the arrows. (b) Rough temperature trace of a droplet during the evacuation of the chamber, obtained by inserting a thermocouple into the droplet. (c) Gas pressure in the chamber.

somewhere in between -8°C and -18°C , with a mean value of $\langle T \rangle = -15^\circ\text{C}$ and a standard deviation of 2°C .

5.4 Time from nucleation to bursting

After the droplet has frozen over, at first sight nothing seems to happen for some time, until the ice droplet suddenly bursts. It usually breaks up in two approximately equal halves which fly apart at velocities of a few m/s. Often these larger pieces are accompanied by some smaller shards. An example of such an event is shown in figure 5.4(b). The *bursting time* τ from freeze-over to bursting depends on the initial radius of the droplet (see figure 5.4(c)). Although there is some variation in the bursting time, the clear trend is that large droplets take longer to burst than small droplets.

That the droplet breaks in two approximately equal halves, implies that the ultimate crack nucleates close to the core of the droplet. In §5.6 we will show that the droplet indeed needs to freeze inward to a large extent before a crack can lead to an explosion. For now, we will assume that the droplet bursts once it is completely frozen. We can then estimate τ by solving the heat transfer problem of a sphere that freezes radially inward. For this, consider a droplet of outer radius R which at time t has a frozen shell of thickness $R - R_i(t)$, where $R_i(t)$ is the radius of the liquid inclusion as sketched in figure 5.5(a). As argued in §5.3, we assume that the inner shell surface is at the melting temperature T_m , while the temperature T at the outer surface is determined by the conditions for ice-vapor coexistence, set by the partial pressure of water vapor in the chamber. The quasi-steady heat flow through a spherical shell held at a temperature difference of $\Delta T = T_m - T$ is given by [18]

$$q_s = 4\pi k \Delta T \frac{R R_i(t)}{R - R_i(t)}, \quad (5.1)$$

where $k \approx 2 \text{ W/(m K)}$ is the thermal conductivity of the ice shell. This heat flow must match the rate at which heat is generated by the freezing front advancing inward ($dR_i/dt < 0$):

$$q_f = -4\pi \rho L_m R_i^2 \frac{dR_i}{dt} > 0 \quad (5.2)$$

where $\rho \approx 1000 \text{ kg/m}^3$ is the density of water. For simplicity we neglected the 9% decrease in density associated with the liquid to ice phase transition. Setting $q_s = q_f$ we find the following differential equation for $R_i(t)$:

$$R_i \frac{dR_i}{dt} = -\frac{k \Delta T}{\rho L_m} \frac{R}{R - R_i}. \quad (5.3)$$

Figure 5.4: Events before and after bursting of a millimetric ice droplet. (a) After freezing over, nothing seems to happen for some time τ . (b) Suddenly the droplet splits in two halves which (c) fly apart at velocities of a few m/s. (d) Observed bursting times as a function of the (maximum) droplet radius R . The open symbol at small R represents the (coincidental) observation in figure 5.1. The red line is equation (5.6) with $\Delta T = 15^\circ\text{C}$ and the dashed line indicates the capillary length, below which the model is expected to be most accurate. (e) Same data in a log-log plot, to highlight the expected scaling behavior.

Figure 5.5: Model for a droplet freezing from the outside-in. (a) Definition of the geometry and boundary conditions. (b) Solution in dimensionless form, with $R_i = \tilde{R}_i R$ and $t = \tilde{t} \rho L_m R^2 / k \Delta T$.

By introducing $R_i = \tilde{R}_i R$ and $t = \tilde{t} \rho L_m R^2 / k \Delta T$ this expression can be recast in dimensionless form as:

$$\tilde{R}_i \frac{d\tilde{R}_i}{d\tilde{t}} = -\frac{1}{1 - \tilde{R}_i}. \quad (5.4)$$

Note that the freezing rate diverges in both the initial and the final stage. Using separation of variables and integrating once the (implicit) solution to equation (5.4) is readily obtained as:

$$\frac{1}{3} \tilde{R}_i^3 - \frac{1}{2} \tilde{R}_i^2 + \frac{1}{6} = \tilde{t}. \quad (5.5)$$

It is clear from this relation and its graphical representation in figure 5.5(b), that the droplet will be completely frozen ($\tilde{R}_i = 0$) at $\tilde{t} = 1/6$, or in dimensional form:

$$\tau_f(R) = \frac{1}{6} \frac{\rho L_m R^2}{k \Delta T}. \quad (5.6)$$

In figure 5.4(c) this model is compared to the observed bursting times, taking for T the observed mean nucleation temperature $\langle T \rangle = -15^\circ \text{C}$. Because of the assumed spherical symmetry, the model most accurately describes droplets with radii smaller than the capillary length $R_c \approx 2.7 \text{ mm}$. For larger sizes the droplets are flattened by gravity and the bursting times are shorter as compared to the model.

From the agreement between the freezing model and the observed bursting times, we can conclude that the droplets indeed freeze inward to a large extent before they explode. However, note that the pre-factor in equation (5.6) is not very sensitive to changes in the final inclusion radius, as the freezing front accelerates near the end, when the inclusion radius becomes small (cf. figure 5.5).

Figure 5.6: High resolution photographs from the side (a) and top (b) of the two halves of a burst droplet.

5.5 Fracturing mechanism

Figure 5.6 shows photographs of the two halves of a droplet that has just shattered. Like the growth rings in a tree, the cross sections reveal many details about the freezing history of the droplet. For example, in the top view of the first halve we see how an irregular finite size inclusion is surrounded by a thick, smoothly cleaved ice shell. What is also clear from the images is that the ice droplet has already fractured multiple times before finally flying apart. Both side- and top-view images show partially healed cracks emerging from the center of the droplet. We envision the basic mechanism behind these patterns to consist of the following steps:

When a completely closed ice shell freezes inward, the expansion of the water upon freezing results in a build-up of pressure in the fluid inclusion. This change in pressure can be expressed in terms of the elastic bulk modulus of water $K \approx 2.2$ GPa and the expansion coefficient $\beta \approx 0.09$ associated with the phase transition:

$$dP_i = -K\beta \frac{dV_i}{V_i} \approx -3K\beta \frac{dR_i}{R_i}. \quad (5.7)$$

For example, if the radius of the inclusion decreases by 1%, an increase in the internal pressure of $dP_i \approx 6$ MPa will result. As depicted in figure 5.7(a), this internal pressure

Figure 5.7: Model to describe fracturing of the ice shell. (a) The radially inward freezing and expanding water leads to a high pressure P_i inside the liquid inclusion. (b) When the resulting tensile stress $\sigma_{\theta\theta}$ exceeds a critical value σ_c , the ice shell cracks open and the fragments are pushed apart.

P_i in turn leads to a tensile stress in the ice shell. This stress is maximal at the inner shell surface where it is given by [19]:

$$\sigma_{\theta\theta} = \frac{P_i}{2} \frac{2\tilde{R}_i^3 + 1}{1 - \tilde{R}_i^3}. \quad (5.8)$$

For thin shells of thickness $\Delta R \ll R$ this stress can be approximated as $\sigma_{\theta\theta} \approx P_i R / 2\Delta R$, while for thick shells we have $\sigma_{\theta\theta} \approx P_i / 2$.

Once the internal pressure and the resulting tensile stress become too high ($\sigma_{\theta\theta} > \sigma_c$) the brittle ice shell will crack open. Although the tensile strength σ_c of ice does not seem to be so widely investigated, values between 0.7 and 3.1 MPa are reported [20]. The geometric amplification factor $R/\Delta R$ for thin shells explains why in the initial freezing stage liquid is so easily squeezed out (cf. figure 5.3(a)). When this pushed out liquid freezes, the pressure inside can build up again and the cycle can repeat itself, until the droplet finally bursts.

5.6 Conditions for bursting

What remains to be explained is why the droplet does not burst immediately when the first cracks appear. Under what conditions will the two halves completely separate and fly apart? To answer this question we must investigate the dynamics of the droplet just after a crack has formed.

Consider the ideal situation in which a crack instantaneously completely splits the rigid shell in two equal halves, as illustrated in figure 5.7(b). Initially, the liquid in

the inclusion will still be pressurized, exerting a force $\pi R_i^2 P_i$ on each halve acting to separate them. If the halves move apart some distance $x(t)$, the volume of the liquid inclusion increases by $dV_i(t) \approx \pi R_i^2 x(t)$ and the pressure decreases accordingly:

$$dP_i(t) = -K \frac{dV_i(t)}{V_i} = -K \frac{3}{4} \frac{x(t)}{R_i}. \quad (5.9)$$

With this, Newton's equation of motion for the droplet halves, each moving over a distance $x(t)/2$, becomes:

$$\frac{\pi}{3} \rho R^3 \frac{d^2 x}{dt^2} = \pi R_i^2 \left(P_0 - K \frac{3}{4} \frac{x}{R_i} \right), \quad (5.10)$$

where P_0 is the initial pressure. This equation is equivalent to that of a freely oscillating mass-spring system with a natural frequency of

$$\omega = \frac{3}{2} \sqrt{\frac{K R_i}{\rho R^3}}, \quad (5.11)$$

and an initial compression of

$$x_e = \frac{4}{3} \frac{P_0}{K} R_i. \quad (5.12)$$

The initial pressure P_0 can be directly related to the tensile strength σ_c through equation (5.8), using that $\sigma_{\sigma\sigma} = \sigma_c$ at the moment of breaking. For example, for a droplet of outer radius $R = 1$ mm and inner radius $R_i = 0.5$ mm that breaks at $\sigma_c = 3$ MPa, we find values $P_0 = 4.2$ MPa, $\omega = 1.6$ MHz and $x_e = 1.3$ μ m. The maximum velocity reached by each halve in an oscillation cycle is $v_m = \omega x_e / 2 \approx 1$ m/s, which turns out to be close to the velocities at which the halves typically were observed to fly apart (cf. figures 5.1(c) and 5.4(b)). In general we can write

$$v_m(\tilde{R}_i) = 2 \sqrt{\frac{\sigma_c^2}{K \rho} \frac{(1 - \tilde{R}_i^3) \tilde{R}_i^{3/2}}{2 \tilde{R}_i^3 + 1}}, \quad (5.13)$$

which has a maximum at $\tilde{R}_i \approx 0.57$ for which $v_m \approx 0.5 \sqrt{\sigma_c^2 / K \rho}$. Interestingly, the velocity is independent of the size of the droplet and only depends on material properties and the ratio $\tilde{R}_i = R_i / R$.

After reaching the maximum velocity the droplet halves will overshoot their equilibrium position and the sign of the pressure in the inclusion reverses, putting the

Figure 5.8: Two factors that determine whether the droplet can burst upon fracturing: (a) the pressure in the inclusion must become low enough so that the liquid can cavitate and (b) there must be enough stored elastic energy to create the required new surface areas. The minimum pressure and the stored elastic energy density e only depend on the ratio $\tilde{R}_i = R_i/R$ (solid lines), while the surface energy (per unit volume) also depends on R (dashed lines).

liquid under tension. If the motion is undamped this pressure can reach $P_i = -P_0$ before the halves are stopped and are pulled back again. In figure 5.8(a) we have plotted $P_i(t)/\sigma_c$ for different ratios $\tilde{R}_i$. The maximum tension in the liquid is close to zero for a thin shell and increases as the inclusion gets smaller. This puts a first constraint on the conditions for which the droplet can burst: $\tilde{R}_i$ has to be small enough to make the pressure drop below the cavitation threshold of the liquid, which for clean, degassed water can easily be a few MPa into the negative [21, 22].

A second constraint is obtained by comparing the maximum kinetic energy of the droplet

$$E_k = \frac{1}{2}mv_m^2 = \frac{2\pi}{3}\frac{P_0^2}{K}R_i^3 = \frac{1}{2}\frac{P_0^2}{K}V_i \quad (5.14)$$

to the energy required to form two new liquid-vapor interfaces in the inclusion: $E_\gamma = 2\pi\gamma R_i^2$. As shown in figure 5.8(b) this puts again an upper limit on the inclusion size. In this case the limit also depends on the size R of the droplet. For droplets with radii below about $50\mu\text{m}$ the energy required to create the new surface area is always higher than the released elastic energy and the droplet might not be able to burst at all. In this study we did not explore the micrometer size range, but there are some indications [8, 10] that such a transition indeed exists in this regime.

Figure 5.9: Controlling the freezing conditions through an ice-vapor buffer on the cold bottom plate. Both the pressure in the chamber (a) and the temperature of the droplet (b) reach a constant value corresponding to the partial vapor pressure in the chamber, set by the temperature of the bottom plate (here -6.5°C). To nucleate the droplet under these conditions one can simply touch it with an ice-tip (c).

In the above calculations we did not consider the elastic energy stored in the ice shell, under the assumption that it does not contribute significantly to the motion separating the halves, but is only spent on crack propagation and internal vibrations. In any case, this energy will be similar in magnitude to the energy stored in the water inclusion [23] and it will therefore not change the overall picture.

5.7 Conclusion and outlook

We have shown that millimetric supercooled droplets of water freeze radially inward, leading to extreme internal elastic stresses due to the water's expansion. These stresses are periodically released by the fracturing of the brittle ice shell. Initially, the cracked ice shell is kept together by the liquid water on the inside, but once the

inclusion becomes small enough, the released energy can be enough to tear apart the liquid in the inclusion. If at the same time the stored elastic energy is sufficient to create the required new surfaces, the droplet will burst open. In theory the latter condition constrains the minimum droplet radius to about $50\mu\text{m}$. Smaller droplets are expected not to burst at all. Previous experiments done in this droplet size range seem to confirm the existence of such a threshold [8, 10]. It will be insightful to pinpoint this limit also in the current setup.

Outlook

For future experiments it will be advantageous to have a better control over the nucleation conditions. To this end we performed some preliminary experiments in which the cold bottom plate was covered with a layer of ice in the hope that it would act as a kind of vapor buffer, keeping the vapor pressure in the chamber constant at the value corresponding to the temperature of the bottom plate. As can be seen in figure 5.9 this indeed works very well. In this experiment the temperature of the bottom plate was set to -6.5°C . After about 100 seconds the pressure in the chamber reaches the corresponding ice-vapor pressure and the droplet temperature saturates to a value close to that of the bottom plate. In general, the supercooling will not be sufficient to make the droplet freeze over spontaneously. This can be resolved by gently touching it with an ice-tip as shown in figure 5.9(c). This technique has the additional advantage of having full control over both the nucleation moment and location.

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6

Conclusion

The ability of liquids (and solids) to withstand large tensions leads to a rich variety of phenomena. Once this tension is released the liquid undergoes a rapid partial phase transition to a gas, a solid or a void. Because of the energy stored in the liquid (or solid) when the tension is built up, this phase transition is always sudden and ‘explosive’ as compared to the same transition taking place under milder conditions in which the tension is already released in an early stage. This explosive behavior gives the surrounding medium not much time to respond, leading to interesting and surprising interactions, especially if this medium is under tension as well. In this thesis three such cases were visualized and studied in-depth (chapters 2, 3 and 5).

6.1 Summary

Chapter 2 treated a seemingly forgotten phenomenon, dubbed ‘tribonucleation’. It was shown that the rapid, brittle fracturing of small asperities on solids can lead to cavitation in a surrounding metastable liquid. By gently rubbing over a heated substrate of rough aluminum or silicon, one can write a trail of slowly growing mixed gas-vapor bubbles in a volatile, low viscosity liquid. When two bubbles in the trail coalesced, an intriguing hopping motion was observed in which the resulting bubble first hops up from the hot surface and then slowly settles down again (instead of rising, like free bubbles usually do).

Chapter 3 dealt with a playful dribbling of small Leidenfrost droplets in a strong vertical electric field. The droplets jumped higher and higher, until they finally collided with the top electrode. Despite the vapor film which electrically insulated these droplets from the grounded bottom plate, they were shown to regularly make short electrical contact. Evidence was presented that this occurs through a regular supercharging of the drop's surface, followed by a release of this electrical tension by an electrocapillary instability in the thin vapor gap.

Chapter 4 was not explicitly concerned with metastable liquids. However, the general ideas formulated in this chapter are directly applicable to Leidenfrost droplets impacting at high velocities. It was demonstrated that even though these droplets feel very little friction from the vapor-lubricated surface on which they spread, a significant amount (about one half) of the initial kinetic energy is always lost due to their strong deformation into a thin, pizza-shaped disk.

Finally, in chapter 5 supercooled water droplets were seen to burst into pieces after freezing radially inward. As for tribonucleation, also this phenomenon relies on a delicate interplay between a liquid and a brittle solid (ice). In tribonucleation a solid was surrounded by a metastable liquid. For the ice explosions, it was the other way around. In this case the static pressures that built up in the liquid inclusion as the freezing front proceeded inward, led to high tensions in the brittle ice shell. This tension was periodically released by a rapid fracturing of the shell. Once the elastic energies stored in the liquid and the shell were high enough, the liquid inclusion cavitated and the pieces of the fractured ice shell flew apart at velocities of a few m/s.

The four chapters dealt with a wide variety of metastable situations: superheating, supercooling, supersaturating and supercharging. Some of the transcending themes are highlighted below.

6.2 Interplay between fast and slow dynamics

Three stages can often be distinguished in the interaction between metastable systems. First, the tension in one of the systems is slowly built up. Second, this tension is released suddenly, giving the surrounding medium little time to respond. Third, the aftermath, which depends on whether the amount of released energy was enough to induce a further transition in the other medium.

These stages are most clearly seen for the bursting ice droplets, where they can be identified for multiple parts of the process. First, when the slow supercooling by evaporation is followed by a rapid, partial encapsulation by ice, and then in the cyclic build up and release of tension in this shell. The aftermath, in this case, is either a slow healing of the cracks or a violent explosion.

Something similar occurs in tribonucleation, where first tension is built up in an elastic solid asperity, which then suddenly breaks off. The resulting crack will initially be more easily filled with gas and vapor than with liquid. In the aftermath a trail of bubbles is observed, but only if the bubbles are large enough to grow in the surrounding hot liquid.

Finally, for the electrified Leidenfrost droplets the cycle occurs every time the surface charge density builds up due to the slow evaporation of the droplet. The sudden release of this electrical tension sometimes seemed to give the droplet an energy boost, helping it to jump higher.

6.3 Confined versus unconfined

As exemplified by the molten tin explosions in the introduction, the aftermath of a release of tension depends on whether the phase transition happens in a bounded or in an unbounded space. In the former case an explosive behavior can occur, while in the later case the phenomena will generally be less extreme.

This is again most clearly seen for the ice droplets, where the pressure build-up on the inside leads to a final bursting, while evaporation from the outside only lets it slowly cool down. In the case of the Leidenfrost droplets the phase transition (evaporation) is mainly unconfined. Only in the vapor flow in the thin gap between the solid and the liquid, some pressure is built up. This pressure is of course essential to keep the droplets from touching the hot wall.

Finally, in the tribonucleation experiments, an interplay between the collection of bubbles in the finite volume below the contact region, and the conditions in the unconfined liquid behind it, determined whether the bubbles could grow and form a trail.

6.4 Elastic or plastic response

A factor that determines whether tension can be built up at all, is whether the response of the involved materials is plastic or elastic. For example, tribonucleation was only observed on solids on which the asperities in the wear tracks showed a brittle behavior, implying a preceding build-up of elastic stress in them. On surfaces for which these roughness tips showed only plastic deformations, no bubbles could be nucleated.

Such a behavior was also observed in the case of the ice droplets. On the short fracturing time scale, when the response of the (confined) liquid was elastic, the

liquid could be put under tension and then cavitate. Whereas on a longer time-scale the liquid could flow (plastic behavior) and heal the cracks.

In the context of droplet impact, a kind of elastic behavior was observed for low impact velocities (chapter 3), while plastic deformation occurred for high impact velocities (chapter 4). In this case the elastic behavior did not originate from the molecular forces on the inside of the droplet, but instead from the small deformations of its interface.

6.5 Surface forces versus body forces

Another theme that stands out throughout the thesis is the competition between surface forces and body forces. Such a competition arises naturally in the context of metastable systems, as phase coexistence automatically implies that a separating interface is formed.

Since surface forces scale with the relevant length scale L as L^2 , and body forces scale as L^3 , the former overtakes when L decreases (or vice versa). At what physical scale the transition takes place, depends on the origin of the forces. For the bubble hopping in chapter 2 it was determined by a competition between buoyancy and the surface tension gradients near a hot surface, for the dribbling Leidenfrost drops it was electrical forces acting on surface charge versus the droplet's weight, and in chapter 5 a competition between surface tension and elastic body forces determined whether the ice balls could burst.

Sometimes surface effects become important even though from a scaling argument it is not to be expected. This happens for example for high inertia droplet impacts (chapter 4). In this case the ratio between kinetic energy and surface energy is very high, but as the thick droplets spread out into a thin lamella, the surface conditions at the solid strongly influenced their fate.

6.6 Outlook

While the different phases of matter are widely studied separately, the study of their coexistence and dynamical interaction is largely *terra incognita*. A part of it was explored in this thesis. Combining the four points of view outlined above proved to be very fruitful in analyzing a variety of dynamic situations in which high tensions are suddenly released: from the snapping tape measures in the introduction to the bursting ice droplets in chapter 5. The author thinks that these different angles can serve as a starting point for understanding (and controlling) metastable dynamics in many other situations. In natural phenomena like the sound generation in knuckle

cracks, and in industrial situations such as the molten metal explosions. And maybe even in the analysis of the tension that can arise between people and groups of people in a society. In the absence of plasticity and regular interaction, this tension often leads to explosive situations.

Samenvatting

Wanneer een vloeistof niet de bewegingsruimte of -tijd krijgt om te vloeien, dan kan deze, naast een drukkracht, tot op zekere hoogte ook een *trekkracht* opvangen. Tot op zekere hoogte, want zodra de interne spanning een kritieke waarde overschrijdt zal de vloeistof “breken” op het zwakste punt, waarbij er plotseling een bel ontstaat. Afhankelijk van de toestand in de omringende vloeistof, zoals de temperatuur en de hoeveelheid opgelost gas, wordt deze bel voor een deel gevuld met damp en/of gas. Hoe hoger de opgebouwde spanning, hoe explosiever de faseovergang zal zijn. De hoge snelheid van het proces geeft het omliggende medium weinig tijd om te reageren, wat vaak tot interessante interacties leidt. Vooral als ook dit medium onder interne spanning staat of wordt gezet.

Een populair voorbeeld wordt getoond in figuur 1.5 van de introductie. Hierin zorgt een stevige, korte klap op de *kop* van een met water gevuld bierflesje ervoor dat de *onderkant* van het glazen flesje er af valt. Dit verrassende verschijnsel neemt slechts een paar duizendste van seconden in beslag en bestaat grofweg uit de volgende stappen: (1) Door de klap ondergaat de bodem van het flesje een plotselinge neerwaartse versnelling. Omdat het ingesloten water op deze korte tijdschaal nauwelijks kan vloeien, trekt de onderkant van het flesje aan de nog stilstaande waterkolom. (2) Als deze spanning te hoog wordt, breekt het water los van het glas, waarbij grote bellen zichtbaar worden. Hoe schoner het water (ofwel hoe minder zwakke plekken), hoe harder de klap moet zijn en hoe explosiever de bellen groeien. (3) Wanneer het water vervolgens in beweging komt, ontstaan er, door een geometrische focussing in de bolvormige bellen, scherpe waterstralen richting het glas. (4) Bij de inslag van deze stralen wordt het glas lokaal onder grote spanning gezet wat resulteert in de catastrofale barsten.

Hoewel dit natuurlijk een speels voorbeeld is, komen dergelijke explosieve kettingreacties ook veelvuldig voor in industriële en natuurlijke processen. Een fundamenteel begrip is meestal van groot belang, maar de korte tijd- en vaak kleine lengteschalen van deze complexe (niet-lineaire) interacties bemoeilijken dit. In dit proefschrift zijn een aantal uiteenlopende gevallen in detail gevisualiseerd en gemoedelleerd om hieruit ten slotte een aantal generieke principes te distilleren.

Schrijven met bellen

Hoofdstuk 2 behandelt een in vergetelheid geraakt en bij toeval herontdekt verschijnsel: tribonucleatie van bellen. Dit verschijnsel treedt op wanneer twee ruwe, (lokaal) brosse materialen licht over elkaar gewreven worden in een vloeistof met een lage viscositeit (zoals water of ethanol). Bij het snelle breken van de ruwheidspunten ontstaat er waarschijnlijk tijdelijk een vacuüm in de vloeistof. Wanneer de vloeistof onder een interne spanning staat, bijvoorbeeld omdat deze tegelijkertijd wordt verhit of omdat deze is oververzadigd met gas, dan wordt dit gat gevuld met damp of gas voordat de vloeistof er in kan stromen. Ook kan er, afhankelijk van de materialen, gas gevormd worden door een chemische reactie tussen de vloeistof en de schone breukvlakken. Als de resulterende bel groot genoeg is, gegeven de mate van interne spanning in de vloeistof, dan groeit deze tot met het blote oog waarneembare proporties. Onder bepaalde omstandigheden vormt er zich een regelmatig spoor van bellen achter het wrijvingspunt en kan men dus ‘schrijven met bellen’.

Dribbelende druppels in een elektrisch veld

Dezelfde intermoleculaire krachten die ervoor zorgen dat een vloeistof een interne spanning aankan, maken dat het *oppervlak* van de vloeistof zich gedraagt als een soort elastisch membraan. Deze permanente oppervlaktespanning is er bijvoorbeeld verantwoordelijk voor dat kleine druppels en bellen altijd de vorm van een bol proberen aan te nemen.

Wanneer een kleine bolvormige druppel met een lage snelheid op schoon hard oppervlak valt, dan veert deze in veel gevallen terug als een stuiterbal. Normaal gesproken dempt een dergelijke stuiterbeweging langzaam uit totdat de druppel stil ligt, maar in hoofdstuk 3 wordt aangetoond dat deze in stand gehouden (en zelfs versterkt) kan worden door de druppel te laten stuiteren op een hete plaat in een sterk verticaal elektrisch veld. De hoge temperatuur van de plaat (ver boven het kookpunt) zorgt ervoor dat een dunne damp laag de druppel scheidt van de plaat, zodat de druppel nauwelijks wrijving ondervindt (het zogenaamde Leidenfrost-effect). Het elektrische veld maakt dat het oppervlak van de druppel geladen wordt en daarbij een opwaartse kracht ervaart. Doordat de druppel langzaam verdampt, wordt deze opwaartse kracht, die schaalt met het druppeloppervlak, steeds belangrijker ten opzichte van het gewicht van de druppel, dat schaalt met het volume. De druppel kan hierdoor steeds hoger opstuiten. De lading op de druppel kan accuraat worden voorspeld door middel van analytische modellen voor de capacitieve koppeling tussen de druppel en de elektroden en de stabiliteit van het geladen druppeloppervlak. Deze

mate van voorspelbaarheid zou in de toekomst gebruikt kunnen worden om de mobiele Leidenfrost-druppels te sturen en manipuleren met simpele elektronische schakelingen.

Plastische vervorming van inslaande druppels

In veel praktische toepassingen is men geïnteresseerd in de vervorming van druppels die met hoge snelheid inslaan op een vaste ondergrond. Denk hierbij bijvoorbeeld aan inkjetprinten of forensische bloedspatanalyse. In dergelijke gevallen vertonen de druppels geen elastisch gedrag (zoals in hoofdstuk 3) maar een plastisch gedrag. Tijdens de inslag vervormt de druppel van een bol naar een platte pizzavormige schijf.

In hoofdstuk 4 blijkt uit gedetailleerde numerieke simulaties dat, zelfs als het oppervlak vrijwel wrijvingsloos is (zoals bij Leidenfrost-druppels), een groot deel (ongeveer de helft) van de inslagenergie verloren gaat aan ‘vervormingsdissipatie’. Door dit verlies mee te nemen in een simpele energiebalans is kwantitatief te voorspellen hoe ver een druppel in de praktijk zal spreiden op gladde oppervlakken. Bovendien werpt deze studie de vraag op waarom *ongeacht de eigenschappen van de vloeistof* de vervormingsdissipatie altijd neerkomt op ongeveer de helft van de inslagenergie. Is dit toeval of een fundamentele wet?

Spontane ijsexplosies in onderkoelde wolken

In hoge wolken is de omgevingstemperatuur vaak ver onder de nul graden Celsius. Hoewel de meest stabiele toestand van water bij deze temperatuur ijs is, kunnen de wolkdruppels in deze schone lucht vaak vloeibaar blijven tot ver onder het vriespunt. De waterdruppels bevinden zich dan in een meta-stabiele, onderkoelde toestand. Bij de minste of geringste aanraking met een ijsdeeltje (of een vast deeltje met een soortgelijke structuur) zullen de druppels onmiddellijk voor een deel in ijs veranderen. Dit lijkt erg op het explosieve gedrag van vloeistoffen onder spanning, en op een hoger niveau (dat van de thermodynamica) zijn de principes inderdaad vrijwel hetzelfde.

Eén van de mysteries in het onderzoek naar onderkoelde wolken is dat er vaak veel meer ijsdeeltjes in deze wolken worden gevonden dan dat er geschikte vervuiliingsdeeltjes zijn om de druppels in ijs te veranderen. Dit wijst op een soort lawine-effect waarbij één bevroren druppel in staat is om meerdere andere aan te steken. In hoofdstuk 5 wordt een mogelijk mechanisme hiervoor blootgelegd: onderkoelde druppels kunnen spontaan exploderen nadat ze deels zijn bevroren.

Dit proces bestaat uit de volgende stappen: Eerst bevriest in enkele milliseconden de buitenkant van de druppel, waarbij vloeibaar water wordt ingesloten. Door de

warmte die vrijkomt bij de faseovergang van vloeibaar water naar ijs, kan de druppel nooit in één keer helemaal bevroren. Het water bevriest vervolgens langzaam verder naar binnen toe, terwijl de druppel de latente warmte via de steeds dikker wordende ijsschil kwijtraakt aan de omgeving. Water heeft de speciale eigenschap dat het uitzet wanneer het bevriest. Hierdoor wordt er al snel een hoge druk opgebouwd in het ingesloten water en komt de ijsschil onder grote spanning te staan. Elke keer als deze spanning te hoog wordt, breekt de schil en vloeit er wat water via de breuklijnen naar buiten. Wanneer dit water vervolgens bevriest kan de cyclus zich herhalen. Echter, zodra de elastische energie die vrijkomt bij het breken van de schil hoog genoeg is, caviteert de vloeistof en vliegt de bevroren druppel uit elkaar. Het model dat hiervoor is ontwikkeld, voorspelt dat een explosie alleen kan optreden bij druppels met een radius groter dan ongeveer 50 micrometer. Deze limiet moet nog getest worden, maar als deze inderdaad geldt, dan heeft dit belangrijke gevolgen voor de beschrijving van onderkoelde wolken, waarin druppels zowel grotere als kleinere afmetingen kunnen hebben.

Overkoepelende thema's

Op het eerste gezicht lopen de onderwerpen in dit proefschrift ver uiteen. Toch kunnen er een aantal overkoepelende thema's geïdentificeerd worden. Een belangrijk thema is bijvoorbeeld het spel tussen de gestage *opbouw* van spanning en haar (periodieke) *ontlading*. Tijdens de trage opbouw wordt er beetje bij beetje energie toegevoegd die vervolgens op een veel kortere tijdschaal vrijkomt, met alle gevolgen van dien.

Een daarmee samenhangend thema is *elastisch* versus *plastisch* gedrag. Spanning kan alleen opgebouwd worden (en breken) als de materialen zich elastisch gedragen. Vloeistoffen gedragen zich meestal plastisch (ze vloeien) maar op korte tijdschalen, bij totale insluiting, of wanneer de druk van binnenuit komt (bijvoorbeeld via opgelost gas), vertonen ze elastisch gedrag. Vaste stoffen kunnen daarentegen elastisch gedrag vertonen ongeacht de tijdschaal of de omgeving. Veel van de hierboven beschreven fenomenen vloeien voort uit een combinatie van deze materiaaleigenschappen.

Tot slot is er de interactie tussen *oppervlaktekrachten* en *volumekrachten*. Deze interactie bestaat van nature in de context van faseovergangen. Het naast elkaar bestaan van twee (of meer) fasen veronderstelt namelijk ook een scheidend oppervlak. Omdat het oppervlak schaalt met het kwadraat van de relevante lengteschaal (bijvoorbeeld de radius van een druppel), terwijl het volume schaalt met de derde macht, is er meestal een kritieke grootte waaronder oppervlaktekrachten domineren over volu-

mekrachten. Het hangt af van het type kracht waar deze grens precies ligt. In hoofdstuk 3 ging het bijvoorbeeld om een competitie tussen oppervlaktelading en massa en in hoofdstuk 5 tussen oppervlaktespanning en elastische energie. In sommige gevallen (zoals bij de druppelinslag in hoofdstuk 4) vervormt het volume dermate dat oppervlakte-effecten belangrijk worden terwijl dat niet uit een simpele schaalwet volgt.

Kortom: Er valt een hele wereld te ontdekken op het gebied van explosieve faseovergangen. Een aantal verkenningen zijn ondernomen in dit proefschrift. De thema's die hierbij naar voren kwamen, kunnen als leidraad dienen bij toekomstige ontdekkingstochten.

Dankwoord

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*“We live inside such people, and they live inside us” – Douglas Hofstadter in *I Am a Strange Loop*

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