Dynamics of dissolving surface droplets

Erik Dietrich

DYNAMICS OF DISSOLVING SURFACE DROPLETS

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1 | Introduction

Figure 1.1: When combined, oil (the yellow liquid inside the tank) will not mix with water (the clear liquid), but form a layer on top of it. We can use a thin needle to form an oil droplet in water (leftmost needle), or put the droplet on a substrate (bottom left), make a water droplet inside the oil (middle), or blow bubbles that rise upward through both water and oil (right).

There is no such thing as 100% truth, like there is no such thing as 100% pure alcohol

[Freud]

1.1 Introduction

Figure 1.1 shows a glass containing both oil and water. General knowledge tells us that oil and water do not mix, and therefore the oil and water will stay separated in two layers. Even if we take a needle and blow a droplet of water inside the oil, or vice-versa, water and oil will not mix. Like many things, the reality is not that simple and it will depend on the type of oil, the amount of oil, and many more other parameters if and how exactly the oil mixes with water. So even though Figure 1.1 represents an everyday and seemingly simple situation, it is a showcase for a complex system of intriguing physical phenomena: droplets, and droplet dissolution processes. The beauty of this topic lies in the fact that a droplet of one liquid inside another liquid (for example oil in water) is comparable to a droplet of water drying in air, or a bubble of gas in your fizzy drink. Therefore, if we understand the mixing of oil and water, we better understand the behavior of spilled coffee, we can predict how long it will take for paint to dry, for our glass of beer to loose its 'fizz', and we can understand why the olive oil and vinegar in our 'vinaigrette' indeed refuses to mix.

1.2 Droplets, bubbles, and surfaces

A droplet of rain sitting on a window is an example where a small pocket of one material (water) is enclosed by a second material (air), as illustrated in Figure 1.2. The phase of the material inside the pocket can either be liquid or gas, and determines if we refer to it as a *droplet* or *bubble*, respectively. The material surrounding the droplet or bubble is usually called the *bulk*. The bulk can also be gas or liquid, and with these choices, we can make three possible arrangements:

- Liquid droplet in a gaseous bulk, for example a rain droplet
- Gas bubble in a liquid bulk, for example bubbles in beer
- Liquid droplet in a liquid bulk, like the water-oil mixture shown in Figure 1.1

In each of these cases, the two materials are separated by a boundary, or *interface*, characterized by an interfacial tension. This interfacial tension γ is the result of cohesive forces between the molecules of a material. A nice example of this is the surface tension of the water-air interface, which allows some small insects (water striders, or 'schaatsenrijders') to walk on water. The absence of cohesive forces between gas molecules means that there is no such thing as a gas-gas interfacial tension, and therefore, gas bubbles in a gaseous bulk do not exist [1]. As will be explained in the course of this thesis, bubbles and droplets are in many cases similar, apart from some terminology. Because of this similarity we simplify matters, and continue the discussion in terms of the main topic, i.e., droplets in a liquid bulk.

Figure 1.2 shows two appearances of droplets. If a droplet is floating around in the bulk, we call it a *free droplet*. Although these free droplets will be mentioned every now and then, we will not discuss them in detail. Instead, we focus on droplets

Figure 1.2: Schematic representation of a free and a surface droplet. The surface droplet is characterized by its footprint radius R_{fp} , its height H , the contact angle θ , and the radius of curvature R . The red-shaded area around the surface droplet represents the distribution of dissolved droplet material in the bulk. The concentration of droplet material in the bulk at the droplet-bulk interface equals the saturation concentration c_s . A different concentration far away from the droplet c_∞ , results in a concentration gradient, and hence the diffusion of the droplet material at a rate characterized by the diffusion coefficient D .

which are attached to a surface (sometimes called a substrate), and use the term *surface droplets* to describe them. Surface droplets are also referred to as *sessile droplets*.

1.2.1 Surface droplets

The surface droplets in this thesis are in all cases small. Small is a relative term, and for droplets with density ρ_d in a bulk with density ρ_{bulk} , this means that they have sizes close to, or below the capillary length $\lambda_c = \sqrt{\gamma/(\rho_{bulk} - \rho_d)g}$ where g is the acceleration of gravity. Creating an interface between two materials of area A requires an input of an energy $E = \gamma A$. It is favorable to reduce this energy, which can be done by reducing the area of the interface. Of all different shapes (cubes, pyramids, etc), the sphere has the lowest interface area for a given volume, and it is because of this that small droplets are usually spherical. However, the influence

of gravity increases with droplet size, causing large droplets ($R > \lambda_c$) to spread and form a puddle, as illustrated by the rightmost droplet in Figure 1.3. λ_c indicates the cross over point above which the effect of gravity surpasses that of surface tension. The advantage of using droplets $< \lambda_c$ is that these droplets are spherical caps, i.e., parts of a sphere, and are easily described in terms of a footprint radius R_{fp} , height H , volume V , radius of curvature R , and contact angle θ , as drawn in Figure 1.2. In fact, any of these quantities can be calculated when only two of them are known.

Figure 1.3: Small droplets are dominated by surface tension, resulting in spherical shapes. The larger the droplet, the more gravity ‘flattens’ the droplet into a puddle. The transition is approximately given by the capillary length. For the water droplets shown here, $\lambda_c \approx 2$ mm, about twice the size of the ballpoint tip.

For surface droplets, the contact angle θ , sketched in Figure 1.2, is an important quantity in the description of the system as it reflects the mutual affinities of the droplet, bulk and substrate materials [2]. These affinities are reflected by the respective interfacial tensions of the droplet-bulk (γ_{DB}), solid-bulk (γ_{SB}), and the droplet-solid (γ_{DS}) interfaces. Combined, these interfacial tensions give Youngs contact angle θ_Y

$$\cos(\theta_Y) = \frac{\gamma_{SB} - \gamma_{SD}}{\gamma_{DB}}, \quad (1.1)$$

the angle at which all three forces balance, as illustrated in Figure 1.4. It is thus the specific combination of droplet, solid and bulk materials that determines the contact angle, where $\theta_Y < 90^\circ$ and $\theta_Y > 90^\circ$ are referred to as ‘wetting’ and ‘non-wetting’ situations, respectively. Although Equation 1.1 is simple and intuitive, much debate is still going on about its practical applicability [3, 4]. The reason for this is illustrated by the droplet drawn at the right hand side of Figure 1.4. A small roughness locally *pins* the contact line of the droplet, hindering free movement. This pinning introduces an additional force, resulting in a contact angle $\theta \neq \theta_Y$, and

contact angle hysteresis: the contact line stays pinned, until the contact angle has been increased or decreased by a certain amount with respect to θ_Y . The angles at which the contact line starts to move outward or inward are called the advancing (θ_A) and receding (θ_R) contact angles, respectively, as illustrated on the right in Figure 1.4. In practical situations, the measured contact angle θ can deviate from θ_Y , depending on pinning and the history of the droplet (e.g., how it has been deposited on the substrate) but will always lie between the advancing and receding contact angles, i.e., $\theta_R < \theta < \theta_A$.

Figure 1.4: Schematic representation of two droplets (red) on a surface (gray). The three interfaces, solid-droplet (SD), solid-bulk (SB) and droplet-bulk (DB), are characterized by their respective interfacial tensions γ , as indicated. The left droplet illustrates that when the contact line is free to move, the three tensions balance at a contact angle equal to Young's angle θ_Y , given by Equation 1.1. The right droplet shows that when the contact line is pinned by surface roughness, an additional pinning force is introduced, leading to contact angle hysteresis. This hysteresis is characterized by the advancing and receding contact angles, the angles at which the contact line starts to move outward or inward, respectively.

1.3 (In)solubility

Figure 1.5 shows a cup of tea with some sugar crystals at the bottom. We know from experience that within a few minutes, the sugar crystals will disappear from the bottom of the cup, adding their sweet taste to the tea. The sugar crystals have then gone through the mechanism of *dissolution*: its basic elements, the molecules, detached from the sugar crystals and found their place in between the water molecules, in other words, the sugar has *dissolved*. Figure 1.6 shows a sucrose molecule, the substance mostly used to sweeten our tea.

In the example of a mixture of vinegar and olive oil, known as vinaigrette, the oil will not dissolve in water (vinegar is mostly water), no matter how long we wait or how hard we stir. Apparently, there is a difference between olive oil and sugar,

Figure 1.5: The sugar at the bottom of the cup will dissolve in the tea because it has a high solubility in water.

Figure 1.6: Diagram of a sucrose (sugar) molecule, which consist of a carbon structure (gray spheres). The many oxygen atoms (red) and OH groups (hydrogen is shown in white) create local charges and possibilities to form hydrogen bonds.

influencing their ability to dissolve in water. This ability is called the *solubility*, which expresses the maximum amount of material that can be dissolved in another material. To get an idea about numbers: in one liter of water we can either dissolve 2 kg of sugar [5], or 1 tiny droplet of olive oil.* Materials that have a solubility (close to) zero are called *insoluble*.

1.3.1 The origin of (in)solubility

In general, the solubility of a particular material (the solute) in another material (the solvent) goes by the rule of 'like-dissolves-like', and we have to take a close look at the molecular structures of two materials to determine if they are alike. A likeness in materials means that they share properties which allows the molecules to interact. These interactions are called the intermolecular forces [7].

If we take a closer look at a water molecule (Figure 1.7) we see that it has an asymmetric shape. The oxygen atom has an electronegativity of 3.44 on the Pauling scale [8], larger than the electro-negativity of hydrogen (2.20). This means that the oxygen attracts the electrons from the hydrogen atoms, becoming negatively polarized and leaving the hydrogen with a partial positive charge. Because of the asymmetric shape and the charge distribution, the water molecule has a permanent net dipole moment. Therefore, water is a prime example of a *polar* material. This polarity gives a water molecule the possibility to orient its positive part towards

*Based on an estimated solubility of oleic acid in water of 10^{-6} mol kg⁻¹ [6].

the negative part of a neighboring dipole. This results in a so-called dipole-dipole interaction, the potential energy of which is given by the Keesom equation [8]

$$u = -\frac{2\mu_A^2\mu_B^2}{3(4\pi\epsilon_0)^2 r^6} \frac{1}{k_B T} \quad (1.2)$$

where the μ 's are the dipole moments of molecules A and B, ϵ_0 is the vacuum permittivity, r the distance between the molecules, and k_B and T are the Boltzmann constant and absolute temperature, respectively. The potential energy as calculated by Equation 1.2 is negative, as it represents the decrease in potential energy of the system upon the formation of a dipole-dipole bond between two molecules. This energy is then *released* by the system, usually in the form of heat. To break the bond again, an equal amount of energy must be invested and the potential energy of the system is increased. A dipole-dipole bond usually has an energy of 1-12 kJ mol⁻¹ [9]. A polar molecule can interact with another molecule that does not have a permanent dipole, by inducing a dipole in the non-polar molecule. This so called dipole-induced dipole, or Debye interaction is much like how a permanent magnet can induce magnetism in a non-magnetic material. Figure 1.7 illustrates how a water molecule induces a dipole moment in a non-polar oxygen molecule. The induced positive side of the oxygen molecule, aligns with the negative part of the water molecule. Something similar can even occur between two non-polar molecules, where a temporary dipole in one of the molecules (caused by fluctuations in the electron cloud) creates a dipole in the other molecule. While the latter two interactions are important, and in fact the reason while non-polar molecules stick together, there is another, much stronger interaction: the hydrogen bond. Hydrogen bonds are formed between the positively polarized hydrogen and an electronegative atom in another molecule, for example the oxygen in another water molecule as sketched by the dashed lines in Figure 1.7. The energy of such a hydrogen bond in water is about 23 kJ mol⁻¹ [10], generally stronger than (induced) dipole interactions.

With this in mind, we can turn our attention to the process of dissolution, which involves a few (simplified) steps. First, energy needs to be put into the system to break bonds between the solvent molecules, in order to form a 'cavity' in which the solute can be placed. Secondly, a solute molecule has to be removed from its neighbors, requiring more bonds to be broken. Finally, new bonds can be formed between the solute and solvent, a step which reduces the potential energy of the system. It seems logical to assume that if the energy released by forming the new bonds exceeds the energy required to break the bonds in the first place, the process is energetically favorable as it lowers the potential energy of the system. In this case, the change in enthalpy ΔH of the system is negative, and the excess energy is released in the form of heat, i.e., the process is exothermic. However, in some cases, dissolution can also take place if no energy is gained, or even when it costs energy to rearrange the bonds, i.e., $\Delta H > 0$ and the dissolution is endothermic. An example of this is the dissolution of potassium chloride in water, which causes the temperature of the water to decrease. In these cases, dissolution is not driven by enthalpy, but an increase in entropy ΔS . It turns out that dissolution only occurs

if the Gibbs free energy of dissolution

$$\Delta G = \Delta H - T\Delta S \quad (1.3)$$

is negative. If we now look at the example of sucrose (sugar) in Figure 1.6, we see that it has many O-H groups which allow for the formation of hydrogen bonds with water molecules, and that it has many oxygen atoms that create localized dipoles [11], making sucrose much 'like' water. The possibility to form dipole-dipole and hydrogen bonds with water molecules, combined with the gain in entropy when sugar and water mix, results in the high solubility of sucrose in water.

Oleic acid on the other hand, a component of olive oil, is a straight molecule, which mainly consists of CH₂ groups which are non-polar, as shown in Figure 1.7. C-H groups are generally not capable of forming hydrogen bonds [9], and are thus 'unlike' water. Introducing this molecule in water thus requires enthalpy, i.e., $\Delta H > 0$ [12], but more importantly, it has been shown [8] that when water molecules can not form proper bonds with a molecule, they form hydrogen bonds with neighboring water molecules, creating a 'cage' of water around the molecule. These molecules are immobilized, decreasing the entropy and hence resulting in $\Delta G > 0$, preventing dissolution. The formation of a water-cage is schematically drawn on the right hand side of Figure 1.7.

The oleic acid molecule, drawn in Figure 1.7, has an acid head (the O and OH part), capable of forming hydrogen bonds. Such a group, which can interact with water is sometimes called a 'hydrophilic head', however, the hydrophilic (literally, water-loving) properties of this small head are outweighed by the long, non-polar CH₂ tail, making the molecule overall hydrophobic (phobic=fearing). If we could make the hydrophobic tail shorter, we should be able to tune the hydrophobicity of the molecule, and hence the solubility. This is indeed possible, as shown by the examples of long-chain alcohols, which are drawn in Figure 1.8. Here, a hydrophilic OH group is combined with a hydrophobic tail which is between 5 (pentanol, penta=5) or 8 (octanol, octa=8) carbon atoms long, as shown in Figure 1.8. 1-pentanol and 1-octanol have solubilities of 22 g l⁻¹ and 0.5 g l⁻¹ respectively [13,14], and are thus more soluble than of olive oil. Both molecules combine the same hydrophilic OH head with a hydrophobic tail, the length of which tunes the solubility. The OH group in both molecules is usually referred to as an alcohol group, and the number in front of the alcohol name tells to which carbon atom in the chain the alcohol group is attached. It can be attached to the first (for example 1-heptanol), but also to any of the others (2- or 3-heptanol), as shown in Figure 1.8. Note that while the word *alcohol* is a popular word and commonly used, it usually refers to ethanol (C₂H₅OH), which is a particular member of the family of aliphatic alcohols, to which also the alcohols in Figure 1.8 belong. The fact that the carbon chain in the alcohols used in this thesis is relatively long (≥ 5 atoms) explains the name 'long-chain alcohol'.

Figure 1.7: A water molecule, consisting of an oxygen (red) and two hydrogen atoms (white), has a permanent dipole moment, as indicated in the left of the image. This can induce a dipole moment in non-polar molecules, like the oxygen (O_2). Hydrogen bonds can be formed between water molecules, as indicated by the dashed lines. The oleic acid molecule, drawn on the right hand side of the image, has a hydrophobic, non-polar carbon chain. Water can not bind to this tail, and the figure shows an impression (not to scale) of how a 'cage' of water molecules is formed.

Figure 1.8: Ball and stick models of the alcohols used in this thesis: A) 1-pentanol, B) 1-hexanol, C) 1-heptanol, D) 2-heptanol, E) 3-heptanol, and F) 1-octanol.

1.4 Surface droplet dissolution

Now that we have established the basic concepts of sessile droplets and the dissolution of long-chain alcohols, we can combine the two and discuss the basics of sessile droplet dissolution. A typical experiment, the results of which are presented throughout this thesis, involves a surface immersed in clean water, on which a droplet of a long-chain alcohol is placed. Depending on the type of substrate and type of alcohol, the droplet will adopt a certain contact angle θ , and the droplet will slowly dissolve. The top-left image in Figure 1.9 shows a typical image of such a droplet, in this particular case 1-heptanol, surrounded by clean water and placed on a shiny surface, which produces a mirror-image of the droplet. Over the course of more than 240 minutes (4 hours) the droplet dissolves until it eventually vanishes completely. A small picture of this measurement is also printed at the bottom of every odd page of this thesis. When the pages are flipped rapidly, the pictures will make a movie showing the dissolution of the droplets.

During the dissolution process, 1-heptanol from the droplet constantly dissolves into water, saturating the water at the interface up to a concentration of $c_s = 1.67 \text{ g l}^{-1}$ [13], the *saturation concentration*. Far away, the water is still pure, i.e., the concentration of alcohol is 0 g l^{-1} , which we denote as $c_\infty = 0$. The difference in concentration causes a *concentration gradient* in the water. This is schematically indicated by the 'cloud' around the surface droplet in Figure 1.2. The concentration gradient drives a movement of the dissolved heptanol through the water along the direction of the gradient, i.e., away from the droplet. This motion is called diffusion, and is characterized by the diffusion constant D . Usually, diffusion is slow, and the speed at which a droplet dissolves (called *dissolution rate*) is limited by the diffusion of alcohol away from the droplet. In this case, the dissolution process is said to be *diffusion limited*. The values for D of 1-heptanol in water, along with ρ , and c_s can be found in literature, and we can calculate the expected change in volume per second dV/dt by using the following equation [15]

$$\frac{dV}{dt} = -\frac{\pi R_{fp} D (c_s - c_\infty)}{\rho} f(\theta) \quad (1.4)$$

with

$$f(\theta) = \frac{\sin(\theta)}{1 + \cos(\theta)} + 4 \int_0^\infty \frac{1 + \cosh(2\theta\epsilon)}{\sinh(2\pi\epsilon)} \tanh[(\pi - \theta)\epsilon] d\epsilon \quad (1.5)$$

as a 'shape factor' that describes the influence of surface and the droplet contact angle. Equation 1.4 is an important one, since it allows us (in specific cases) to calculate the dissolution rate of any droplet, and from that, predict the time to complete dissolution.

1.5 Motivation

The previous paragraph gave a simplified description of droplet dissolution. However, there are numerous factors that, all together, make surface droplet dissolution

Figure 1.9: Time lapse of a dissolving 1-heptanol droplet at $t = 0, 80, 160$, and 240 minutes. The dotted line in each image shows the location of the solid surface. The shiny surface reflects part of the droplet, creating a mirror image.

a rich, complicated, and intriguing process. For example Equation 1.4 is only applicable when the bulk is stagnant. As soon as the bulk moves, dissolved alcohol 'goes with the flow', which increases the transport of alcohol away from the droplet, and one could ask how this accelerates the dissolution process. Another example is the droplet in Figure 1.9, which maintains the same shape during dissolution, and only becomes smaller. One could ask how the process would be influenced if the droplet changes its shape (becomes flatter, for example), or what would happen if another droplet is placed next to it, or a hundred droplets. Another relevant question could be what the process would look like if the droplet was not composed of pure heptanol, but mixed with, for example, olive oil? The answers to these questions are relevant for applications like inkjet printing, surface coating, distribution of medicines through the human body, or the dispersion of (harmful) substances in the environment [16–19]. In this thesis we describe efforts made to answer some of

these questions.

1.6 Guide through this thesis

The next chapter explains some of the experimental techniques that have been used throughout this thesis, including the surface preparation and the image recognition software. Chapter 3 describes the effort to measure the anticipated recirculation flow around surface nanobubbles, tiny gas filled bubbles. This flow could not be detected. However, at the end of chapter 3 we describe that our results should be interpreted carefully, since the possibility is high that our nanobubbles were not bubbles, but tiny droplets of contaminants. Chapter 4 describes how (the evolution of) the droplet shape influences the dissolution, and we describe the so called 'stick-jump' dissolution mode. In chapter 5 we use various experimental techniques to show that large surface droplets can create a flow (as opposed to what we present in chapter 3). We describe when, how, and why this flow occurs, and how it contributes to the dissolution of the droplet. Chapter 6 describes what happens to the dissolution process if we do not have a single droplet, but an ensemble of droplets placed close together. While chapters 4-6 deal with droplets that consist of only one type of liquid, chapter 7 extends the scope by making mixtures of different liquids, and describes how droplets of these mixtures dissolve. We conclude with a brief summary and general conclusions of the thesis, and give an outlook towards future work in chapter 8.

2 | Experimental techniques

Every chapter in this thesis contains a section which briefly explains the techniques that are used. However, a number of techniques and procedures are of key importance, and this chapter provides more specific and detailed information on these aspects.

Figure 2.1: Photograph of the experimental setup.

2.1 Optical microscopy and illumination

Optical microscopy has been used in every chapter. In chapters 4-7, small alcohol droplets are placed inside a water filled glass tank and imaged. In these chapters, an OCA 15 (Dataphysics, Germany) contact angle device is used as a basis for the setup. A photograph of this setup is shown in Figure 2.1. This machine is normally equipped with a diffusive halogen light source. While this works fine for large liquid droplets in air (which means a large difference in optical index between droplet and bulk), it provides insufficient contrast for our needs, i.e., imaging small droplets of liquids with optical indices close to that of the bulk. Therefore, the white light source is replaced by a monochromatic LED light source (Thorlabs) to eliminate chromatic aberration and enhance contrast. Furthermore, the light beam is collimated using a large, positive lens. This results in a parallel light beam which significantly improves the contrast, as shown in Figure 2.2. The LED and lens are shown in Figure 2.1, together with the adjustable mirror, which deflects the light through the tank, projecting the image of the droplet into the microscope, and finally on the CCD camera.

Figure 2.2: Comparison between the image obtained using the standard illumination (A) and the monochromatic, parallel light source (B). The enhanced contrast in panel (B) allows for a more accurate detection, especially for small droplets.

To accurately measure both tiny (radius $< 100\ \mu\text{m}$), and big droplets (radius $\approx 1\ \text{mm}$), the magnification of the microscope is adjusted to obtain the highest magnification that still captures the entire droplet within the image frame. Droplets are deposited through a thin needle (diameter $210\ \mu\text{m}$), from a syringe mounted in a vertically positioned syringe pump. The pump is computer controlled and can dispense droplets of any desired volume $\geq 20\ \text{nl}$. Delivery of smaller droplets (down to $0.5\ \text{nl}$) is possible, but less reproducible in terms of volume. After deposition of the droplet, the syringe is removed from the tank, and the tank is closed with a lid. The glass tank could be placed on a computer controlled motorized platform (Thorlabs), which allows to accurately move the tank (and thus also the substrate) in the horizontal plane. This function was used in chapter 6 to produce patterns of

droplets.

2.2 Image analysis

An experiment typically results in a series of a few thousand images, from which results are extracted. An example of such an image is shown in Figure 2.2B. Since we are interested in the temporal behavior of the droplet, we measure the droplet dimensions in each consecutive frame and evaluate how they vary from image to image. Figure 2.3 illustrates the necessary steps.

1. An edge detection algorithm [20] scans the original image (Figure 2.2B) to find where the gradient of the intensity exceeds a pre-defined threshold. These points (drawn in green in Figure 2.3A) roughly indicate the droplet shape, but also the surface, the reflection of the droplet in the surface, and occasionally dust particles.
2. From all points in the previous step, only the points detected above the substrate (indicated by the red-dotted line) are considered. The position of the substrate can be set manually at the beginning of the evaluation algorithm, or can be detected automatically in each frame. From the remaining points, only the leftmost and rightmost points at each horizontal cross section through the image points are kept to eliminate the points detected inside the droplet. The remaining points are plotted in blue in Figure 2.3B.
3. A circle, fitted through the detected points, gives a rough first approximation of the droplet shape (red line in Figure 2.3B), however, the example shows that a small dust particle is still detected and disturbs the measurement.
4. Image intensity profiles are then obtained along this circle, perpendicular to the droplet interface, as drawn by the white line in Figure 2.3B. This results in typical intensity profiles as shown by the blue line in Figure 2.3C.
5. This profile is then compared (cross-convoluted) with an error-function (black curve in figure Figure 2.3C). The convolution signal, plotted in red, shows a minimum at the inflection point of the intensity profile. This minimum is fitted with a parabola, to obtain the interface position with sub-pixel accuracy [21].
6. The previous step is repeated to obtain typically 100 points along the outline of the droplet, as plotted in Figure 2.3D (in green).
7. A circle (plotted in red in Figure 2.3D) is fitted through all of these points, which is the definite droplet profile.
8. By assuming that the droplet is a spherical cap [22], we can use the position of the substrate in conjunction with the circle center point and radius of the fitted circle to calculate the volume, footprint radius, height, and contact angle of the droplet.

The above procedure proved to be accurate, reliable, and independent of the background luminosity.

Figure 2.3: The intensity gradient in the original image (A) is used to detect the droplet outline, but it also identifies reflections and a dust particle, as shown by the green dots. Panel B shows that by fitting a circle through the outermost points (blue dots) above the surface (red dotted line), a rough approximation of the droplet profile can be made. However, the dust particle is still detected, so an extra step is required. A line profile of the intensity (blue line in panel C) is taken perpendicular to the droplet interface and compared to an error function (black line in C). The minimum in the convolution signal (red line) is obtained with sub-pixel accuracy by fitting a parabola. This minimum corresponds to the droplet interface position. The thus obtained points (green dots in panel D) are fitted with a circle, which is used to calculate the droplet parameters using a spherical cap approximation.

2.3 Substrates and coating *

The contact angle of a droplet is influenced by the wettability and roughness of the substrate, as explained in the Introduction. The contact angle, in turn, plays an important role in the dissolution dynamics of the droplet. To show this, Figure 2.4 shows 3-heptanol droplets, on a hydrophilic (A) and a hydrophobic (B) substrate. The surrounding water preferably wets the hydrophilic substrate, reducing the footprint area of the 3-heptanol droplet and resulting in $\theta > 90^\circ$, indicative for non-wetting behavior. The opposite is true for the hydrophobic substrate. This illustrates that, while both droplets have comparable volumes, the wettability of the two substrates results in a difference in contact angle θ , footprint radius R_{fp} , radius of curvature R , and height H between the two droplets.

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It is therefore important to know and control the wettability and other properties of the substrates. This section discusses the surfaces that have been used and the preparation procedure of these surfaces.

Figure 2.4: 3-Heptanol droplets with comparable volumes, placed on hydrophilic silicon (A), and hydrophobic PFDTs-coated silicon (B), immersed in water. The location of the substrate is indicated by the dashed line. The different wettability of these substrates results in different droplet shapes in terms of θ , R_{fp} , and H .

2.3.1 Substrates

The majority of the experimental work in this thesis is conducted on coated silicon substrates. These substrates are small pieces, typically $1 \times 1 \text{ cm}^2$, cut from a larger silicon wafer (P/Boron/(100), Okmetic). Silicon wafers are polished, providing an almost atomically smooth substrate and ensuring that the roughness of the surface shows little variation between individual pieces, allowing for reproducible results. Silicon is widely used, and as a consequence many (chemical) procedures are described to modify the surface (more on this later). An Atomic Force Microscope (AFM) image of a silicon substrate (Figure 2.5A) shows that untreated silicon has a smooth, feature free surface. In chapter 4 we describe that the droplet can be 'pinned' by small defects on the substrate. These defects can be of a chemical or a geometrical nature. A chemical defect is a localized area where the surface has a different wettability, e.g., a hydrophobic patch on an otherwise hydrophilic surface. An example of a substrate with many geometrical defects is shown in Figure 2.5B, where an AFM image shows that the surface of a glass microscopy slide is covered by an intriguing pattern of ridges and pits, most probably formed during the production. These glass microscopy slides are made from soda-lime glass; an amorphous material, and indeed reported to possess a roughness of a few nanometers [23].

2.3.2 Cleaning, coating, and cleaning

Both glass and silicon have a surface that consists of hydrophilic (polar) SiO_2 groups. When such a sample is immersed in water and an alcohol droplet is placed on the

Figure 2.5: AFM images of uncoated silicon (A) and glass substrates (B). Coating these surfaces with PFDTs slightly increases the roughness of the silicon substrate (C), whereas polymerization of the molecules around the crevices in glass leads to the formation of geometrical heterogeneities. The height scales amount to 1 nm (A), 10 nm (B), 5 nm (C), and 30 nm (D), respectively. Scan sizes are $5 \times 5 \mu\text{m}^2$. Panels A-C and B-D do not show the same surface area.

substrate, we observe non-wetting of the droplet, i.e., a droplet with $\theta > 90^\circ$, as shown in Figure 2.4A. It is beneficial to make the silicon substrates hydrophobic. Firstly because the alcohol droplets wet the hydrophobic substrate, i.e., $\theta < 90^\circ$ (see Figure 2.4B), which is handy from a practical point of view as droplets are more easily deposited. Secondly, hydrophilic substrates are easily contaminated by (airborne) contaminants, and are difficult to clean properly [24–27] while hydrophobic surfaces are easily cleaned.

Hydrophobization is achieved through vapor deposition of molecules. To this purpose, the substrates are first cut and cleaned to remove contaminants. The exact cleaning procedure 'evolved' somewhat throughout the chapters, but the multi-step procedure described in detail in chapter 4 proved to produce a reproducible res-

ult [28]. In the first step of the cleaning process, the substrate is soaked in hot piranha etch (a mix of sulfuric acid and hydrogen-peroxide) to remove organic materials. A subsequent bath in hot ammonium-hydroxide removed sulfur residue from the piranha step and small (silicon) particles. A final step in hot hydrochloric acid removes metallic contamination. Careful rinsing with hot ultra pure water after each step, and a drying step at the end of the cleaning procedure resulted in pristine surfaces which were then put in a glass vessel, together with a small container containing ≈ 300 μ l of chloro-silane. When the glass vessel is closed and vacuumized, the chloro-silane molecules evaporate and 'fly around' until they hit the substrate. There they bind to the substrate to form a so called 'self assembled monolayer' (SAM). The method of depositing molecules through the vapor phase is commonly known as chemical vapor deposition (CVD).

The SiO₂ surface of silicon and glass can be coated by chloro-silane molecules. A SAM of such silanes will result in a hydrophobic, chemically homogeneous surface [29]. The chloro-silane used mostly in this work (1H,1H,2H,2H-perfluorodecyltrichloro-silane, or PFDTS) consists of a fluorinated carbon tail (which is hydrophobic) and a silicon headgroup with three chlorine atoms. During the CVD process, which is illustrated in Figure 2.6, the head group reacts with water, replacing the chlorine by OH groups [30]. The OH groups on the silane molecule initially bind to the substrate via hydrogen bonds. Further polymerization produces water, and results in very strong covalent Si-O-Si bonds. Ideally, one of the three OH groups of the silane head binds to the substrate, while the other two silane groups bind with neighboring molecules, forming a dense and strong monolayer. In practice, it is observed that these molecules can polymerize into cross-linked superstructures [31], illustrated in the right part of Figure 2.6.

The growth of silane superstructures affects the substrate appearance. Figure 2.5 shows AFM images of the untreated silicon (A), and glass (B) surfaces. After coating, some small particles are visible on the the silicon substrate in Figure 2.5C, however, the roughness of the substrate has not been changed significantly by the coating. This is contrasted by the glass substrate in Figure 2.5D which features many large protrusions. We suggest that these protrusions are aggregates of polymerized PFDTS. Earlier work has shown that initial substrate roughness, enhances roughness after coating by causing PFDTS molecules to polymerize and form superstructures on their own [32]. The origin for this is reported to be due to the retention of water by hydrophilic crevices in the surface. This water accelerates polymerization of the silane molecules during the deposition process. The hypothesis that the observed features are polymerized PFDTS molecules is supported by the fact that the size and coverage of the protrusions are comparable to those of the crevices in the uncoated substrate. Cleaning the coated substrate in toluene or chloroform, which are solvents for unbound PFDTS, does not alter the surface appearance, indicating that the molecules inside the aggregates are chemically bonded to each other and to the surface.

Figure 2.6: PFDTs molecules consist of a hydrophobic tail (yellow), a silicon head (red) with three chlorine atoms. The chlorine reacts with water to form HCl, and the silicon head is hydroxylated. The middle three molecules illustrate the ideally desired situation, where the head groups are attached to the interface and their neighbors. However, the molecules can also polymerize and form superstructures, as indicated by the rightmost molecules.

3 Particle tracking around surface nanobubbles*

The exceptionally long lifetime of surface nanobubbles remains one of the biggest questions in the field. One of the proposed mechanisms for producing the stability is the *dynamic equilibrium* model, which describes a constant flux of gas in and out of the bubble. Here, we describe results from particle tracking experiments to measure this flow. The results are analysed by measuring the Voronoï cell size distribution, the diffusion, and speed of the tracer particles. We show that there is no detectable difference in the movement of particles above nanobubble-laden surfaces, as compared to nanobubble-free surfaces.

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3.1 Introduction

Surface nanobubbles are gaseous domains of nanoscopic size, found on immersed substrates. The first indication for their presence was discovered almost two decades ago [33, 34] and the topic has since then grown exponentially [35, 36]. One of the properties of surface nanobubbles which still puzzles the community is their extraordinary long lifetime, causing bubbles to remain stable [37]. According to classical expectations, the small radius of curvature (usually microns or less), combined with the high surface tension of the water-gas interface, gives rise to a high pressure inside the bubble, which should quickly drive the gas into solution. Different mechanisms have been considered to explain their stability, including diffusion limitation by surfactants [38], formation of water structures at the interface [39], and even the probability that nanobubbles are totally filled with contaminants of some kind [40]. Over the years, many experiments have been reported indicating that nanobubbles are indeed gas-filled, including different spectrographic methods such as Fourier transform infrared spectroscopy (FTIR) [34], and attenuated total reflectance infrared spectroscopy (ATR-IR) [37, 41], and the use of electrolysis to produce surface nanobubbles on HOPG [42–44].

In 2011, we argued that the peculiar contact angle and limited height of surface nanobubbles would mean that the gas inside must be of Knudsen type [45]. This observation supports the dynamic equilibrium mechanism, proposed three years earlier by Brenner and Lohse [46]: The fact that the gas is of Knudsen type means that the motion of the gas molecules is not random, but is directed mainly perpendicular to the substrate. Momentum transfer between the gas molecules and water at the bubble interface will result in a recirculation of liquid around the bubble. Gas that dissolves in the liquid would then recirculate around the bubble, allowing re-entry either directly through the three-phase line, or through adsorption at the substrate and surface diffusion.

Our previous paper [45], where indeed an upward flow is reported, has led to a new point of view for the field. In a recent paper, Chan and Ohl combined optical visualisation of surface nanobubbles with particle tracking [47]. Their motion analysis of 200 nm sized tracer particles did not show any recirculation of the liquid and particles near the nanobubbles. However, as the authors explain, their technique is only capable of visualising the largest nanobubbles, with diameters ≥ 230 nm. Taking this into account, one must consider the possibility that the motion of the particles is influenced by a few large nanobubbles, and many nanobubbles with sizes below the optical resolution limit. In this chapter, we present particle tracking measurements to analyse the motion of particles at hydrophobised silicon substrates. We compare results of particle tracking on identical substrates, differing only through the coverage of surface nanobubbles. We measure the Voronoï cell characteristics, diffusion coefficients, and particle tracks to address the question: Is there a recirculation near surface nanobubbles?

Like Chan and Ohl, we use microparticle tracking to try to detect recirculation. For this purpose, 1 μm diameter polystyrene particles are used (Fluoro-Max, Thermo

scientific, Fremont CA). These particles are almost neutrally buoyant (density ratio of ≈ 1.02) and small enough to follow the moving liquid (Stokes number $\approx 10^{-1}$, assuming a recirculation flow with characteristic size comparable to the bubble radius (microns), and circulation speeds in order of meters per second, as measured earlier [45]). Yet, they are large enough to be imaged with a microscope, and recorded by a CCD camera.

3.2 Samples and preparation

Silicon wafers with a native oxide layer (thickness ≈ 9 nm) were hydrophobized with PFDTs (perfluorodecyltrichlorosiloxane). Hydrophobized silicon is often used in nanobubble research, see for example [48–50]. Another substrate commonly used is Highly Oriented Pyrolytic Graphite (HOPG) [51,52] but since the silicon produced the best uniform illumination in the microscope, it became our substrate of choice. Nonetheless, a few experiments were conducted using HOPG, which produced results similar to those that will be presented below.

Vapour deposition of the PFDTs monolayer on the silicon wafer was done in an evacuated chamber. The chamber was successively opened to PFDTs and water reservoirs, to introduce the vapours and start the monolayer formation [53]. The advancing and receding contact angles for a water droplet on this substrate were found to be 116° and 97° , respectively, as measured by an OCA 15+ apparatus (Dataphysics, Germany).

The silicon substrates were cleaned in nitric acid prior to the vapour deposition of the PFDTs. The samples (wafers were cut to small pieces of about 2×2 cm²) were ultrasonically cleaned in isopropyl alcohol for 5 min, rinsed thoroughly with ultra pure water, and dried under a stream of nitrogen, prior to each measurement. The same cleaning procedure was used to clean the liquid cell, in which the sample was mounted. Two types of experiments were performed: (i) with bubbles (‘gassy’) and (ii) without bubbles (‘degassed’). In all gassy measurements, bubbles were nucleated using ethanol-water exchange. The substrate was initially wetted with ≈ 200 μ l ethanol (analysis grade, $\geq 99.9\%$, purchased from Merck, Germany) whilst fitted in an AFM liquid cell. Next, the ethanol was gently replaced with 2 ml of ultra pure water (Millipore Simplicity 185). This method is assumed to produce nanobubbles [54], and indeed features are observed by subsequent AFM imaging, as illustrated in Figure 3.1. However, more recent work has revealed that the use of disposable syringes and needles can introduce contaminants into the system [55]. These contaminants can form droplets with properties (in terms of sizes and deformability) comparable to those reported for gaseous nanobubbles. The last section of this chapter contains a more thorough description of the origin and nature of these contaminants, and how these relate to the ethanol-water exchange procedure.

For all ‘degassed’ experiments we use degassed water. To this purpose, ultrapure water was degassed at a pressure of 1.5 kPa for 1.5 h, whilst being stirred continuously. The degassed water was then gently poured on the substrate using a syringe. An AFM image of the PFDTs surface under degassed water is shown in Figure 3.1B.

Figure 3.1: A) Result of an ethanol-water exchange on hydrophobised silicon, as measured by AFM. B) Hydrophobised silicon in degassed water, as measured by AFM. Both panels represent a $15 \times 15 \mu\text{m}^2$ area, with height scales of 100 nm.

After the preparation of the substrate and liquid, a small volume (100 μl) of a tracer liquid was added to the liquid cell. The original particle suspension, which contained 1% particles by weight was diluted by clean water in a ratio 1 : 100. This diluted suspension was insonicated for 5 minutes prior to each measurement.

After the particles were added, the sample was placed in the microscope (Olympus, type BX-FM, using a 40x/0.8 water-immersion objective), and the microscope was focussed on the substrate. To do this, a small surface defect was identified (usually a small scratch or dent in the silicon top layer) to set the focus position. In this way, only the particles that are within $\approx 3 \mu\text{m}$ of the substrate are resolved, resulting in a good surface sensitivity. All measurements are conducted in ambient conditions, at room temperature ($21^\circ\text{C} \pm 1^\circ\text{C}$). During the measurement, the sample is shielded from air convection by means of a ring. Once everything was set, the CCD camera (Lumenera LM615, 1.4 MPixel monochrome) mounted on top of the microscope recorded the images at a typical rate of 2 frames s^{-1} . The combination of the microscope and the camera resulted in a recorded field of view of $155 \times 115 \mu\text{m}^2$. These images were later processed using an in-house developed Matlab program to detect the position of the individual particles.

3.3 Results and discussion

We now proceed to describe the results of the various statistical analyses that we made to describe the particle positions and motion.

3.3.1 Analysis 1: Voronoï

If a strong flow exists around surface nanobubbles, one would expect particles to be 'pushed' away from the centre, and cluster in between the bubbles. Clustering and depletion of particles can be characterized by measuring the Voronoï cell size distribution, as was recently shown by Tagawa and coworkers [56]. From each recorded

frame, the centres of mass of the particles are measured and a Voronoï analysis is employed using these points. Using this routine, 2D cells are constructed around each centre of mass where each point inside the cell is closest to the corresponding centre. Each vertex of a Voronoï cell is constructed by drawing the perpendicular bisector from the line connecting two neighbouring points. After construction of the Voronoï cells, the area of each cell (A) is stored. We only considered fully-closed cells in our analysis. Some cells, especially near the edges of the frame were ill-defined and not considered in the results. Figure 3.2 shows a close-up of a single frame, and the resulting Voronoï distribution, with the centres of mass in red.

Figure 3.2: (Left) Snapshot showing tracer particles, visible as black dots. Particles that are out of focus appear as blurred dots, or even as rings and are ignored in the analysis. (Right) Voronoï cells as constructed after analysis of the original image. The centre of masses are shown in red, the blue lines are the cell vertices.

By calculating the normalized probability density function (PDF) of the Voronoï cell sizes, the probability to find cells with a certain size can be compared to a test case, being a reference measurement or theory. We deploy this method by calculating the cell size PDF in the presence of nanobubbles and compare this PDF to the findings in degassed water. We compare our measurements to a fitted distribution of a two-dimensional random distribution, as proposed by Ferenc and Néda [57], as a reference. When the probability density function of the normalized cell size is calculated, a high probability to find small cells is indicative for clustering (small particle-particle spacing) whilst a high probability for large cells signals depletion. Looking at the right hand side of Figure 3.3, we see that the data from the ‘degassed’ and the ‘bubbly’ experiments coincide nicely, both with respect to each other and with the proposed fit. The maxima of all measurements lie within ± 0.3 of the

Figure 3.3: Probability density function of the normalised Voronoï cell size. Stars indicate degassed experiments (no bubbles), circles indicate experiments with nanobubbles, the dashed line shows the 2D random distribution [57], and colours represent different measurements. When reading the graph, one must realize that the graph is based on a histogram with linear bin sizes, and plotted on a logarithmic scale.

maximum from the work of Ferenc and Neda [57]. On the left-hand side of the graph, a deviation from the dashed line is visible for both kinds of experiments whilst the degassed (stars) and gassy (circles) experiments deviate from one another. Remarkably, the degassed experiments show a higher probability for small A , which indicates clustering. It has been shown that dissolved gas influences the dispersion of hydrophobic objects in water [58]; it is however beyond the scope of this article to investigate the exact cause of the clustering. A possible explanation for the difference between the modelled random distribution and experimental data may be that it is due to the random distribution coming from a purely 2D simulation whilst the experimental images are quasi-2D, accounting for the finite thickness of the slab of liquid imaged by the microscope's small depth of field.

3.3.2 Analysis 2: Diffusion

If the movement of the particles is purely Brownian, they will display a random walk. If there is a flow near surface nanobubbles, this flow will alter the movement of the particles by either actively pushing them away (above the centre of the bubbles)

or trapping them in certain areas. One way to quantify this is by measuring the diffusion of the particles using the mean square displacement. Equation 3.1 is the 2D form of the Einstein-Smoluchowski relation, describing the diffusion speed for Brownian motion.

$$\langle (r(0) - r(t))^2 \rangle = 4Dt \quad (3.1)$$

with $r(0)$ being the position where the particle is first observed (the starting point), $r(t)$ the particle position at time t , and D the diffusion coefficient. The pre-factor 4 accounts for the 2D situation; in 3D, it will become 6. If the diffusion is altered by the nanobubbles, we expect to find different values for the diffusion coefficient for the two types of experiments. The positions $r(0)$ and $r(t)$ are calculated using the previously found centres of mass, and a tracking algorithm is used to link the positions in different frames to individual particles. By averaging over all particles, in both gassy and degassed measurements, the mean squared displacement can be plotted as a function of time, as shown in Figure 3.4.

Figure 3.4: Mean square displacement as a function of time for all degassed measurements, shown in red, and gassy experiments, shown in blue.

In Figure 3.4, only the first 20 seconds are shown; the number of particles that stay within the field of view for times larger than this decreases rapidly, resulting in larger errors and deviations. This is already becoming apparent in the degassed experiments for $t > 12$ s. Again, slight differences appear to emerge between the gassy and degassed experiments, especially at larger time scales. However, the error bar for these times increases steadily, and the discrepancy between the two classes

becomes less pronounced.

3.3.3 Analysis 3: Image correlation

Another common method in microscopy for determining the diffusion speed is by image correlation: an initial image, taken at $t = 0$, is correlated with a series of subsequent images. The correlation coefficient is a measure of how identical the two images are: if imaged particles have moved only slightly, the correlation is large (images are almost identical). The faster the particles move, the more quickly the coefficient approaches zero. In our experiment the correlation intervals are 75 s. All images in each interval are correlated to the first image of that interval, resulting in an exponential decay of the correlation in time. An example with the results for one measurement is shown in the inset in Figure 3.5. In Figure 3.5, the correlation for a series of measurements is plotted versus the logarithm of time, resulting in linear trends.

Figure 3.5: Coefficient of correlation between an image taken at $t = 0$ and images taken in the subsequent 75 s. Stars indicate degassed experiments, circles gassy experiments. Inset is of one particular measurement, showing different series of correlations in time.

The diffusion coefficient is proportional to the slope of this line, so by analysing these slopes, we observe that once again, the spread is considerable. However, there is no clear trend that separates the degassed measurements from the gassy measurements.

3.3.4 Analysis 4: Local velocities

Our final statistical measure is of local particle velocities, following the work of Chan and Ohl [47]. We used the information from the particle tracking to construct paths and measure speeds of the particles. The particles did not show any deviation at specific locations; neither was there a noticeable mean velocity. In our efforts described previously [59], we employed the interference enhanced reflection microscopy to optically image the nanobubbles. Here as well, we added polystyrene particles and tracked their behaviour. We could not measure any trend in the velocity of particles when they were close to the bubbles. In Figure 3.6 the radial velocity of particles in the proximity of a nanobubble is plotted. It shows that our findings are similar to those reported by Chan and Ohl.

Figure 3.6: Radial velocity of particles in the proximity of nanobubbles, as a function of their distance from the nanobubbles. Lower graph shows the average value of the radial velocity.

3.3.5 A comment on the validity of the particle tracking technique

One could question whether it is appropriate to use particle tracking to measure phenomena in the first few microns near a substrate; electrostatic repulsion between the polystyrene particles and the substrate would result in a minimum spacing between them, below which the repulsion outweighs gravity and the Van der Waals potential.

A quick analysis based on the DLVO theory answers this question [60]. The three potentials, in the absence of convection in the liquid, are (i) gravity, (ii) the Van der Waals potential, and (iii) the electrostatic potential due to surface charge of the particle and the substrate. In this case, gravity is sufficiently small to be ignored, whilst the van der Waals potential is calculated with Equation 3.2:

$$F_{\text{vdW}} = \frac{-HR}{6d} \quad (3.2)$$

and the electrostatic potential can be calculated using Equation 3.3:

$$F_e = RZe^{-d\lambda_D^{-1}} \quad (3.3)$$

with H being the Hamaker constant (10^{-19} J), R is the radius of the particle (500 nm), and d the distance between the particle and substrate (measured in metres). λ_D is the Debye length, for which we assume a dissolved ion concentration of 10^{-7} M (pure water), and Z is the reduced surface potential, based on a surface charge of -80 mV for the particle and -56 mV for the substrate.

Figure 3.7: Potential energy of the particle, as a function of substrate-particle separation. The minimum separation will be around $50kT$. The red-dashed line shows calculations for an ion concentration of 10^{-6} M, and the black one for an ion concentration of 10^{-7} M.

We must consider the depth that particles can penetrate into the repulsive electric field and thus integrate the work needed to bring a particle closer to the wall. In Figure 3.7 the combined result of the attractive van der Waals potential and the repulsive electrostatics is shown. Assuming that the particle has a kinetic energy

around $50kT$, the minimum separation will be around $4\text{ }\mu\text{m}$. As stated above, we assumed an ion concentration of 10^{-7} M . In practice, small quantities of ions will be dissolved (for example dissolved CO_2 gas) which will increase the ionic concentration to $\approx 10^{-6}\text{ M}$. Then the tracer particles-wall minimum separation is reduced to $\approx 1\text{ }\mu\text{m}$: The tracer particles lie between the $\approx 1.4\text{ }\mu\text{m}$ minimum separation and the approximately $3\text{ }\mu\text{m}$ depth of field.

This shows that this method is indeed surface sensitive to within the first few microns near the substrate. Surface sensitivity can be further increased by using particles with a lower surface charge, or by adding salts to the liquid. However, the particle-particle repulsion becomes smaller and clustering of particles might occur.

3.4 Conclusion

In conclusion, our aim was to address the following questions: (i) is there a statistical variation in flow/diffusion of particles above a nanobubble laden substrate, and above a nanobubble-free substrate, and (ii) how can we understand the discrepancy between the particle tracking of Chan and Ohl and our recent uplift measurements? To address the first question: from the Voronoï analysis, as shown in Figure 3.3), one could argue that there is a tendency for particles in degassed experiments to cluster. This is counter-intuitive, since one would expect that a recirculation flow, if present, would cause clustering of particles in a wide perimeter around the bubble. As becomes apparent from Figure 3.3, the spread in the data is considerable, and additional experiments need to be carried out to draw a more solid conclusion. The same holds for the measurements on the diffusion coefficient. Although there is a spread in the data, as shown in Figure 3.4, with a slightly higher diffusion coefficient for the gassy experiments, the results do not indicate a clear difference between gassy and degassed experiments.

Since we measure (deviations of) the Brownian motion of the tracer particles, our method is highly susceptible to changes in temperature. Also, particles tend to sediment over time and thus increase the particle density at the solid-liquid interface. Thus although the particle density is measured and it is comparable between measurements, we cannot exclude the possible error due to changing particle numbers. Our particle tracking measurements endorse the conclusions of Chan and Ohl, so on the basis of all results, we too must conclude that, within experimental error, we cannot measure a recirculation flow around surface nanobubbles.

Regarding the second question, our conclusion seems to contradict findings reported in our earlier work. There, a considerable upflow was measured by moving an AFM tip over a large nanobubble, and a 2.7 ms^{-1} upflow was reported, which is in agreement with the proposed Knudsen gas model. One would expect that a flow of this magnitude would be detected easily, and clearly show up in our analysis. The fact that it does not calls for careful re-analysis of the measurements reported in [45]. There are a multitude of explanations for the measured deflection of the AFM tip above a nanobubble, including changing surface-tip interactions and drift in the vertical stage of the microscope. However, the Knudsen gas statement still

holds, since it only depends on the geometric properties of the nanobubble. As mentioned before, this results in a preferred direction of motion of the gas molecules and the water molecules at the interface. There is however a good possibility that the momentum transfer from the gas molecules to the water molecules is much smaller than previously anticipated. In 2002, de Gennes theoretically described liquid flow over a Knudsen gas film [61], and concluded that slip lengths on the order of microns can be achieved. This would result in liquid velocities at the interface which are much smaller than the predicted values. These small velocities might be undetectable by our method, so a more precise measurement and much larger data set is needed to test this smaller flow. The presence of a small outflux and diffusion of gas would be in agreement with earlier reports of preferred size distributions for nanobubbles [62, 63], which requires some sort of communication between nanobubbles. Recently, alternative mechanisms for nanobubble stability have been proposed by several researchers [64–66]. These new mechanisms still allow for gas exchange through the gas-liquid interface, but rely on pinning of the contact line and limitation of the gas outflux to explain the stability.

3.5 Post-scriptum

Recent work revealed that the use of disposable needles and syringes could potentially contaminate the system with PDMS (polydimethylsiloxane), and compromise the experiments [55, 67]. Liquid PDMS forms droplets with sizes and contact angles comparable to those of surface nanobubbles [38]. The work presented in this chapter did involve the concerned syringes and needles, and the conclusions should therefore be interpreted with caution. Subsequent attempts to repeat the experiments presented in this chapter proved to be difficult, as the well-known solvent exchange did not result in reliable formation of nanobubbles. A brief summary of these attempts and findings hereof will be given in this section.

3.5.1 Experimental details

The procedures and materials are identical to those described earlier in this section, with the exception of a few details. Solvents were obtained from freshly opened bottles to reduce the amount of contaminants that could accumulate over time in open bottles. Ethanol (Emsure, $\geq 99.9\%$ purity, Merck), isopropanol (Emsure, $\geq 99.8\%$ purity, Merck), or freshly double-distilled ethanol was used. To reduce PDMS contamination from needles or syringes, glass syringes fitted with stainless steel needles were used in combination with teflon or glass plungers. A teflon liquid cell was used in which a HOPG or hydrophobized silicon sample was kept in place using two teflon rods, see Figure 3.8A. HOPG was freshly cleaved on both sides by means of a piece of adhesive tape prior to each measurement. The silicon sample, the liquid cell, and the syringes were insonicated in acetone, isopropanol, and ethanol, rinsed with ultra pure water and blown dry in a stream of nitrogen, prior to each experiment.

Figure 3.8: Top and side view of the liquid cell with the sample (A). Panels B and C shows side views of exchange methods 1 and 2.

3.5.2 The exchange procedure

The solvent exchange [41, 48, 52, 68] is, in principle, a simple procedure: wet the substrate by a droplet of solvent and subsequently exchange it for water. The solvent has a high gas solubility, and the addition of water will create a gas oversaturation which is believed to be required for nanobubble formation [69]. While the usual cleaning and preparation procedures are elaborate, and often described in great detail, the exchange procedure is commonly described in a qualitative manner, e.g. the exchange rate is described as 'slow', or 'gentle'. Only very recently, the first quantitative investigations on this topic have been presented in the context of surface droplets [70, 71].

Two methods for conducting the solvent exchange were used in this section. These methods, illustrated in Figure 3.8 B and C, are based on discussions with coworkers in various laboratories and believed to be a fair representation of how the solvent exchange is commonly executed. In method 1, a small amount ($\approx 1 \mu\text{l}$) of solvent wetted only the upper surface of the substrate. Droplets of water were subsequently added to the solvent until the cell was filled and the water level was $\approx 5 \text{ mm}$ above the surface. In method 2, the entire liquid cell was initially filled with a large quantity ($\approx 2 \text{ ml}$) of solvent, completely covering the substrate and filling the cell. Water was then added slowly, while the excess liquid (water-solvent mixture) was removed.

3.5.3 Results

Method 1 resulted in vigorous mixing of solvent and water upon the addition of the first water droplets. The higher surface tension of water induced a Marangoni flow which made the droplet contract. This contraction reduced the droplet footprint diameter, causing the three phase contact line of the droplet to move over the substrate, exposing parts of the substrate temporarily to air. A sequence of images (Figure 3.9) illustrates the contraction of the droplet, and how it temporarily 'dewetted' parts

Figure 3.9: Top view photographs of a HOPG substrate during the solvent exchange following method 1. The top surface is initially fully covered with ethanol (A). The addition of a single droplet of water (B) to the ethanol induces strong mixing, causing parts of the substrate to dewet (B+C), indicated by the dotted lines which trace the three-phase contact line. After complete mixing, the droplet spreads again to re-wet the entire substrate (D).

of the substrate. The droplet spread again when the solute and water were mixed completely, re-wetting the entire substrate. This process was observed several times when more water droplets were added, each time dewetting different parts of the substrate. Water was added until the liquid cell was filled. In method 2, strong mixing and Marangoni flows were observed as well, but because the entire liquid cell was filled with solvent, it was ensured that the substrate was wetted throughout the procedure.

After completion of either of the two exchange methods, the liquid cell was mounted in the AFM and the solid-liquid interface was imaged. Method 1 was executed > 40 times, consistently producing nanobubble-like objects, such as those shown in Figure 3.10A-C. The majority of these objects had a spherical cap shaped geometry with a contact angle around 15° , footprint diameter ~ 100 nm, and heights of ~ 10 nm. The objects appear flatter when the tapping force is increased (Figure 3.10B), indicating that the objects are soft and deformable. This is supported by their bright appearance in the phase image (inset in Figure 3.10B). Occasionally, a sharp transition from a region with a high coverage to a feature-free region is observed, Figure 3.10C. Following the procedure described by Berkelaar et al [55], the (non)-gaseous nature of these objects is tested by exposing the sample to degassed water for 24 h. If the objects would be gaseous, they should have disappeared after this procedure. However subsequent AFM imaging revealed that the features persisted, thus confirming that they are not gaseous, but liquid droplets of some material. This is further confirmed by imaging (in air) the 'dewetted' parts of the substrate, the part where the solvent temporarily withdrew from. This reveals large, pancake-like regions as shown in Figure 3.10D. Figure 3.10E shows that these layers transform into small spherical caps upon the addition of water to the substrate. In addition, objects were found when double-distilled ethanol (Figure 3.10F) or isopropanol (Figure 3.10G) was used in the exchange. Notably the use of isopropanol often resulted in the formation of nanobubble-like objects on top of pancake-like structures which

Figure 3.10: AFM images of HOPG surfaces. A: Nanobubble-like objects formed after solvent exchange using method 1 (with dewetting). B: Same area as in A, scanned with a higher tapping force, which causes the objects to appear flatter. Inset: Phase image of B. C: A sharp transition between a region on the HOPG surface with high density of features and a feature-free region. D shows the surface after dewetting took place (measured in air). E shows the same area as D after re-wetting with water. F: Nanobubble-like objects formed after the exchange of double distilled ethanol with water using method 1. G: Nanobubble-like and micropancake-like objects are formed after the exchange of 2-propanol with water using method 1. H: A pristine surface is observed when no dewetting takes place during the exchange (method 2), although presence of macroscopic gas bubbles (inset in H) proves that gas enrichment was achieved. I) Surface covered with PDMS droplets after method 2 solvent exchange using ethanol pre-saturated with PDMS. The height scales (in nm) are 15, 6.5, 40, 3.2, 10, 47, 25, 10, and 105 for A-I, respectively.

Table 3.1: Surface composition of HOPG, a clean silicon surface, and a PFDTS-hydrophobized silicon surface before the exchange, after a droplet of ethanol is allowed to dry on the substrate (+ethanol), and after the complete solvent exchange (+exchange). Values are the averages over three measurements taken at different locations on each sample.

Sample	Element	C	N	O	F	Na	Si	Cl
HOPG		99.69		0.31				
HOPG + ethanol		92.57		6.73		0.25	0.46	
HOPG + exchange		98.63		1.16		0.12	0.09	
SiO ₂		8.33	0.22	41.84		0.11	49.50	
SiO ₂ + ethanol		8.99	0.88	40.73		0.22	49.19	
SiO ₂ + exchange		3.72	0.49	42.66			53.12	
PFDTS		12.41	0.13	32.37	13.79	0.01	40.19	1.10
PFDTS + ethanol		14.70	0.46	30.40	14.19	0.11	39.14	1.01
PFDTS + exchange		15.50	0.16	31.06	12.41	0.12	39.83	0.93

had typical thicknesses of 4 nm. As HOPG is known to quickly accumulate hydrophobic contaminants [27, 72], procedure 1 was repeated on PFDTS-coated silicon substrates, yielding similar results, which suggests that the contamination is not exclusive to HOPG.

Surprisingly, method 2 reproducibly resulted in droplet-free surfaces, as shown in Figure 3.10H. The formation of macroscopic gas bubbles at the interface (inset in Figure 3.10H) proves that the exchange did result in gas oversaturation. Method 2 was repeated on different substrates, different exchange rates, and a multitude of substrate and liquid temperature combinations [73], consistently producing feature-free surfaces, even when small amounts of contaminants (various types of water-insoluble oils and alkanes) were deliberately added to the solvent. Only when 2% by volume PDMS was added to ethanol, method 2 produced surface droplets, as shown in Figure 3.10I.

3.5.4 Identifying the nature of the contaminants by XPS

To get a clue on the composition of the found objects, X-ray Photoelectron Spectroscopy (XPS) was used. A Quantera SXM (Physical Electronics) is used with a 200 μm diameter beam at 1486.6 eV. Because HOPG will obscure signals from carbon based contaminants, and silicon those of silicon contaminants, both substrates were used to cross-check. Since XPS must be performed in vacuum, only dry samples were measured.

Three samples each, of freshly cleaved HOPG, silicon with a native oxide layer of ≈ 9 nm thickness (denoted as SiO₂), and PFDTS hydrophobized silicon (abbreviated as 'PFDTS' in Table 3.1) were tested. The first sample of each substrate was clean and

untreated to serve as a reference. A droplet of ethanol was placed on each second substrate and left to dry completely, resulting in a clear drying stain (We stress that this is *not* what we mean by 'dewetting'). A complete solvent exchange, following method 1 was conducted on the third substrate, after which the sample was removed from the liquid cell and dried in a nitrogen flow.

In Table 3.1 the composition of each of the substrate surfaces is shown. By comparing the various substrates and surface compositions, we deduce that the substrates accumulate carbon contamination, even without being wetted by either ethanol or water. All but one substrates are contaminated by sodium when brought in contact with ethanol and/or water. Note that both the coated and uncoated silicon 'clean' substrates are cleaned following the previously described procedure, and have thus been in contact with ethanol and water *before the experiment*. In addition to sodium, the HOPG surface reveals that some silicon is introduced with the liquids. Furthermore, nitrogen is observed on the silicon substrates only [26, 74, 75][†].

3.6 Discussion and conclusion

Marangoni flows during the mixing of ethanol and water in exchange method 1 caused the three-phase contact line to move over the substrate and expose parts of the substrate to air. Subsequent AFM imaging of the solid-liquid interface revealed that this dewetting produced features with similar mechanical and geometrical properties as have been previously reported for surface nanobubbles. The second exchange method did not result in dewetting of the substrate, and did not produce features on the substrate unless substantial amounts of contaminant were added to the solvent prior to the exchange.

XPS measurements detected carbon which could originate from a multitude of sources, including non-volatile contaminants in the solvents or from the air. Sodium and silicon were detected, which are constituents of borosilicate glass, the type of glass used for beakers, liquid storage, and syringes. It has been shown in many studies that small amounts of glass dissolve in water and other solvents [76–78], which could explain the sodium and silicon contaminants. A third component of borosilicate is boron, which is not observed in the XPS spectrum, possibly due to the low sensitivity of XPS to boron (only 10% of the sensitivity of sodium [79]). In the past, dissolved compounds such as carboxylic acids and silicates have caused misinterpretation of experimental data [80–82]. The fact that both the contaminant droplets and the gaseous nanobubbles reported in literature exhibit similar mechanical and geometrical properties, excludes the use of these properties as a proof of gaseous nature. Clearly, a degassing procedure such as proposed by Berkelaar et al. [55] could provide the touchstone needed to distinguish nanobubbles from (contaminant) droplets.

[†]The detections of fluoride, chloride, and increased amount of carbon on the coated silicon substrates originate from the fluoro-alkane hydrophobizing agent.

4 | Stick-jump mode in surface droplet dissolution*

The analogy between evaporating surface droplets in air to dissolving long-chain alcohol droplets in water is worked out. We show that next to the three known modi for surface droplet evaporation or dissolution (constant contact angle mode, constant contact radius mode, and stick-slide mode), a fourth mode exists for small droplets on supposedly smooth substrates, namely the stick-jump mode: intermittent contact line pinning causes the droplet to switch between sticking and jumping during the dissolution. We present experimental data and compare them to theory to predict the dissolution time in this stick-jump mode. We also explain why these jumps were easily observed for microscale droplets but not for larger droplets.

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4.1 Introduction

The evaporation of sessile droplets in air is of key importance for inkjet printing, surface coating, cleaning, and the deposition of small particles, see e.g. [15,17,83–85]. As a result, a great body of theoretical, numerical, and experimental work has been done in this research area, see e.g. [18,86,87]. A less studied, but completely analogous system is that of a liquid droplet surrounded by another liquid. Under certain conditions, namely when both processes are purely diffusion controlled, the two systems can be described by the same equations. In both cases, pinning drastically alters the evaporation or dissolution behavior of the droplet [88], changing the dissolution rates and the motion of the droplet [89,90].

Picknett and Bexon [91] described two basic modi in which surface droplets can evaporate. In the first mode, the contact line of the droplet is pinned to the substrate, and the droplet wets the very same area throughout the evaporation process. The base diameter L of the drop remains constant, hence the name of this mode: Constant Radius (CR). In the second process, the contact line is free to slide over the substrate so that the droplet can maintain the same contact angle θ during evaporation. This mode is called the Constant Contact Angle mode (CA). Recently, Stauber and coworkers [92] described a third mode which they called 'stick-slide' mode: droplets evaporated initially in the CR mode till a certain contact angle θ^* was reached. From this point on, the evaporation mode switched to the CA mode (with contact angle θ^*). The CA mode could last until the drop had disappeared, or could be followed by one or more subsequent stick-slide cycles. In the work of Stauber *et al.*, the duration of the 'stick' period was comparable to the 'slide' period.

In this paper we will study the 'stick-jump' mode in the context of droplet dissolution. In this mode, sketched in Figure 4.1, a droplet has an initial base diameter L_0 and initial contact angle θ_0 . During time interval τ_1 , the droplet is pinned and dissolves in the CR mode until the contact angle reaches θ^* . In the next time interval τ_2 , the droplet 'jumps' to a new geometry with contact angle θ_0 , and base diameter L_1 . This process continues with dissolution in the CR mode during another time interval τ_3 , and a jump during interval $\tau_4 \ll \tau_3$. This mode has been shown to occur in evaporating droplets containing substantial amounts of particles [84,93], on specially patterned substrates [94,95] and incidentally in other systems [16,96] where it also has been referred to as the 'stick-slip' mode. To avoid confusion between slip and slide, we will use the term "stick-jump" instead of "stick-slip" to describe the mode in which $\tau_4 \ll \tau_3$. We would like to emphasize that "jump" does not mean that the droplet detaches from the substrate, it merely reflects the droplets abrupt change in geometry, i.e., an increase in its height.

In this paper we will demonstrate that the stick-jump mode can occur for liquid droplets on un-patterned substrates. The paper will start with a description of the experiment and the experimental results. Subsequently, a theoretical model is developed, to which the experimental results are compared. This comparison will highlight the important parameters in the stick-jump dissolution mode.

Figure 4.1: Illustration (A) of the stick-jump dissolution mode. A water immersed 3-heptanol droplet on hydrophobized silicon with initial height H_0 , base diameter L_0 and contact angle θ_0 dissolves in the CR mode during time interval τ_1 . When $\theta = \theta^*$, the droplet jumps to retrieve θ_0 and a smaller base L_1 . This process is repeated with dissolution in the CR mode during time interval τ_3 , a jump during time interval $\tau_4 \ll \tau_3$, and dissolution during τ_5 and so on, until complete dissolution. Figure (B) shows snapshots of the initial droplet at $t = 0\text{ s}$, where the black line indicates the silicon surface. After a total time of $t = 220\text{ s}$ the droplet contact angle has decreased till θ^* . The red line indicates the initial shape of the droplet. At $t = 235\text{ s}$, the droplet has jumped to a new geometry and contact angle θ_0 . The outline of the droplet before the jump is added in green for comparison.

4.2 Experimental procedure

The droplet liquid in this study was 3-heptanol (Aldrich, 99% purity and used as received). This long-chain alcohol has a solubility in water between 4.0 kg m^{-3} at 25°C and 4.7 kg m^{-3} at 20°C [97,98], and a density of $\rho = 819\text{ kg m}^{-3}$. Since for 3-heptanol no experimental values could be found for the diffusion constant and interfacial tension with water, the values for 1-heptanol are adopted: $D \approx 0.8 \times 10^{-9}\text{ m}^2\text{s}^{-1}$ [99] and $\gamma = 7.7\text{ mN m}^{-1}$ [100]. Polished silicon wafers (P/Boron/(100), Okmetic) and glass microscope slides (Menzel Gläser) were cut into small pieces of about 1 cm^2 and cleaned in a hot Piranha bath followed by a SC-1 bath ($\text{H}_2\text{O}:\text{H}_2\text{O}_2:\text{NH}_4\text{OH}$ mixture) and a SC-2 bath ($\text{H}_2\text{O}:\text{H}_2\text{O}_2:\text{HCl}$ mixture) [28]. In between each step, the samples were rinsed with MilliQ water (obtained from a Reference A+ system, Merck Millipore, at $18.2\text{ M}\Omega\text{ cm}$) and insonicated in hot MilliQ water for 15 minutes. After cleaning, the samples were coated via chemical vapor deposition with PFDTs (1H,1H,2H,2H-Perfluorodecyltrichlorosilane 97%, ABCR GmbH, Karlsruhe Germany). The samples were then annealed for 1 hour in an oven at 100°C and son-

icated in chloroform for ≈ 10 minutes. The surfaces were characterized with atomic force microscopy (Agilent 5100) in tapping mode using NSC36 cantilevers (MikroMasch). The samples were cleaned in chloroform (Emsure $\geq 99\%$ purity, Merck) in an ultrasound bath for 10 minutes, prior to each measurement. The sample was placed in the center of a square acrylic container and 350 ml of MilliQ water was carefully added. This water was stored in a clean glass flask for a few hours prior to the experiment to reach room temperature. A small droplet, typically 10 – 30 nl of 3-heptanol, was subsequently placed on the substrate using a glass syringe mounted in a motorized syringe pump. Imaging of the droplet was done through two CCD-cameras, mounted with long distance microscopes. The first camera imaged the front view of the droplet, while the second camera recorded the side view (for silicon substrates) or, via a mirror, the bottom view of the droplet on the glass substrate. Using two axis imaging allowed us to track the position of the drop, and to confirm that the droplet maintained its spherical cap shape during dissolution. The acquired pictures were post-processed in a Matlab program, which traced the droplet shape with sub-pixel accuracy [101]. This shape was fitted with a spherical cap and the intersection of the circle with the base plane was measured to extract the contact angle and base diameter. Droplet height and radius of curvature could be extracted from these values using goniometric relations. Relevant parameters from both observation axes were compared and interpolated.

4.3 Experimental results

In Figure 4.2, the evolution of the parameters characterizing the droplet during dissolution is shown. At $t = 0$ s, directly after deposition, the droplet had a large contact angle θ_{00} which decreased as the droplet dissolved. The decrease in contact angle, at fixed base diameter, resulted in a decreasing height. When the contact angle has decreased to $\theta^* < \theta_{00}$, the contact line depinned and the droplet changed its geometry: the base diameter 'jumped' to a new and smaller base diameter, which yielded an increased contact angle and height. Note that the volume was conserved during the jump and that the original contact angle θ_{00} was not fully recovered: the droplet jumped back to a new contact angle θ_0 , where $\theta_{00} > \theta_0 > \theta^*$. Usually, one part of the contact line stayed pinned during the jump, causing the rest of the droplet to move towards this point. This is illustrated in Figure 4.2B, where the position of the droplet center is shown as it moved over the substrate.

From Figure 4.2C, it appears that the largest contact angle θ_{00} was observed at $t = 0$ s. This was caused by contact angle hysteresis during the deposition of the droplet [4]: A small droplet was put at the substrate and then inflated to the desired volume. For simplicity in description and notation we will omit the difference between θ_{00} and θ_0 . Unless explicitly stated otherwise, we will assume that the droplet starts at θ_0 , dissolves until θ^* and jumps to θ_0 , with a corresponding change in contact angle of $\delta\theta = \theta_0 - \theta^*$.

The exact values for θ^* and θ_0 differ from jump to jump as seen from Figure 4.2C and the base diameter shows a slow decay in between the jumps. This last observation

Figure 4.2: Dissolution of a water immersed 3-heptanol droplet on hydrophobized silicon: (A) Normalized volume (green), base diameter (red), droplet height (black) and contact angle (blue) in time. To allow for an easy comparison, all parameters have been normalized to their initial value: 26 nl, 680 μm , 138 μm and 44.2°, respectively. The graph is truncated after 2800 seconds, when only a small amount of residue was left on the substrate. (B) Location of the droplet center in the horizontal plane, during the dissolution process. The position of the droplet center shows little change during the pinned phases, and abruptly moves to a new position when the droplet depins. (C) Contact angle $\theta(t)$.

is consistent with the findings of Orejon *et al.* [93] for weakly pinned evaporating droplets. This is understandable, since the values for θ and the pinning depend on local heterogeneities which spatially vary. After a jump, the contact line will be pinned by numerous small pinning sites, each with an individual pinning strength. As the contact angle decreases, the contact line first depins from the 'weaker' sites, giving rise to a slow creep in the base radius. When the contact angle is reduced to θ^* , the drop is only pinned by the strongest pinning sites. A further decrease in θ will result in the next jump.

To verify the influence of surface roughness, we repeated the experiments on hydrophobized glass slides. The glass slides were coated using exactly the same procedure, but they exhibit a greater intrinsic roughness, as discusses in chapter 2. The rougher surface led to stronger pinning, which is reflected in significantly altered contact angles. For comparison, the main results on silicon and on glass are summarized in Table 4.1. The higher roughness on glass obviously increased the pinning strength, leading to higher initial contact angles θ_{00} and lower values for θ^* and θ_0 .

The observation of stick-jump behavior can therefore be related to a spatial variation in surface roughness and pinning. It is to be expected that a uniform roughness will result in stick-slide behavior: once the contact angle has reached θ^* and started to move, it only encounters pinning sites of equal strength, corresponding to θ^* . Dissolution will thus proceed in the CA mode. A local variation in pinning sites will result in temporary pinning of the contact line by the strongest sites, followed by the jump during which the contact line rides over all weaker sites. Consequently,

in the stick-slide mode the height H of the droplet is monotonous in time, whereas for the stick-jump mode it decreases during the pinning phase, but goes up at every jump.

Table 4.1: Average initial contact angles θ_{00} , contact angles just before (θ^*), and after (θ_0) the first observed jump, and the corresponding change in contact angle $\delta\theta = \theta_0 - \theta^*$. The excess free energy $\delta\tilde{G}$ per unit length (J m^{-1}) of the contact line at the first jump. Reported values represent averages of 6 and 2 measurements on hydrophobized silicon and glass substrates, respectively, which possess different roughnesses. The indicated deviations represent the observed variation of each value in different experiments. As a comparison, the contact angle θ_w of a sessile water droplet ($L \approx 1\text{mm}$) in air on both substrates is given.

Surface	θ_{00}	θ^*	θ_0	$\delta\theta$	rms	θ_w	$\delta\tilde{G}$
Silicon	$48^\circ \pm 4^\circ$	$41^\circ \pm 1^\circ$	$43^\circ \pm 2^\circ$	$2^\circ \pm 1^\circ$	1.3 nm	109°	7.9×10^{-9}
Glass	$55^\circ \pm 5^\circ$	$15^\circ \pm 5^\circ$	$18^\circ \pm 1^\circ$	$3^\circ \pm 2^\circ$	3.9 nm	107°	2.5×10^{-7}

4.4 Theory

4.4.1 Droplet dissolution

The dissolution or evaporation of a droplet is driven by a negative concentration gradient of the droplet's constituent(s) from the droplet interface towards the surrounding medium. The case of a free spherical air bubble in water was solved by Epstein and Plesset [102]. Their result has to be modified for sessile droplets, to reflect the modified geometry and the boundary conditions (i.e., no flux through the substrate). This was done for evaporating droplets in air by Popov [15] in 2005:

$$\frac{dV}{dt} = \frac{-\pi L D (c_s - c_\infty)}{2\rho} f(\theta) \quad (4.1)$$

with

$$f(\theta) = \frac{\sin(\theta)}{1 + \cos(\theta)} + 4 \int_0^\infty \frac{1 + \cosh(2\theta\epsilon)}{\sinh(2\pi\epsilon)} \tanh[(\pi - \theta)\epsilon] d\epsilon \quad (4.2)$$

and ρ the density of the droplet material, D the diffusion constant, and L the base diameter of the droplet. c_s is the concentration at the droplet-bulk interface, which equals the maximum solubility. Together with the concentration c_∞ far away from the droplet, the solubility determines the undersaturation of the system,

$$\zeta = 1 - \frac{c_\infty}{c_s} \quad (4.3)$$

In the current system, $c_\infty = 0$ and thus $\zeta = 1$, which means that we assume the water far away from the droplet to be pure. This assumption is justified since after

complete dissolution of our alcohol droplet, the concentration is only ≈ 10 ppm of the maximum concentration. Equation 4.1 demonstrates that two droplets of equal volume can have distinct life times, depending on their geometry. The droplet life time is defined as the time from the start of the experiment, when the droplet has initial volume V_0 , till complete dissolution. In the CA mode, where $\dot{\theta} = 0$, Equation 4.1 can be rewritten to find $\dot{L}$. Integrating $\dot{L}$ from L_0 till 0 then gives the life time. In the CR mode, where $\dot{L} = 0$, the life time can be obtained by rewriting Equation 4.1 to find $\dot{\theta}$ and integrating from θ_0 till 0. Stauber *et al.* [92] followed this route for evaporating droplets in air to obtain expressions for life times in the CA and CR modes, and combined the two for the stick-slide mode. They obtained the life time in the stick-slide mode as

$$\tilde{\tau}_{ss} = \left(\frac{2(1 + \cos \theta_0)^2}{\sin \theta_0 (2 + \cos \theta_0)} \right)^{\frac{2}{3}} \left[\int_{\theta^*}^{\theta_0} \frac{2d\theta}{f(\theta)(1 + \cos \theta)^2} + \frac{\sin \theta^* (2 + \cos \theta^*)}{f(\theta^*)(1 + \cos \theta^*)^2} \right] \quad (4.4)$$

where the time is non-dimensionalized by

$$T = \left(\frac{3V_0}{2\pi} \right)^{\frac{2}{3}} \frac{\rho}{2D(c_s - c_\infty)} \quad (4.5)$$

i.e., $\tilde{\tau} = \tau/T$. The first term inside the square brackets in Equation 4.4 is an integration over θ and reflects the evaporation in the CR mode. This mode is maintained until the contact angle has decreased to θ^* , after which evaporation continues with a fixed contact angle θ^* , reflected in the second term inside the brackets. By the choice of the timescale T , dimensionless life times $\tilde{\tau}_{ss}$ between 0 and 1 are obtained, regardless the initial droplet size or material properties. By using this scaling and the values for 3-heptanol in water, the above can be used to describe the present case.

In the stick-jump mode, the slide phase is replaced by a quick jump. As indicated in the introduction, the duration of the jump is very short. We can therefore neglect the mass loss during the jump and the dissolution solely takes place in the CR mode. Referring to Figure 4.1, the total life time will thus be $\tau_{\text{life}} = \tau_1 + \tau_3 + \tau_5 + \dots$. To find all individual contributions, we follow the same approach as in Equation 4.4 and integrate $\dot{\theta}$ between θ_0 and θ^* . In the stick-jump mode the base diameter changes during each jump, changing the dissolution rate. Therefore, $\tau_1 > \tau_2 > \tau_3$, and an additional term is required,

$$\tilde{\tau}_{\text{life}} = \left(\frac{2(1 + \cos \theta_0)^2}{\sin \theta_0 (2 + \cos \theta_0)} \right)^{\frac{2}{3}} \left[\left(\int_{\theta^*}^{\theta_0} \frac{2d\theta}{f(\theta)(1 + \cos \theta)^2} \right) \left(1 - \left(\frac{\sin \theta^* (2 + \cos \theta^*)}{(1 + \cos \theta^*)^2} \frac{(1 + \cos \theta_0)^2}{\sin \theta_0 (2 + \cos \theta_0)} \right)^{\frac{2}{3}} \right)^{-1} \right] \quad (4.6)$$

The first term inside the square brackets is again the integration over the contact angle. The second term is the summation over all intervals. A derivation of Equation 4.6 is given in appendix A.

In Figure 4.3, $\tilde{\tau}_{\text{life}}$ is plotted as a function of θ_0 for several values of θ^* . For comparison, the life times in the CR, the CA and the stick-slide mode are also shown. Figure 4.3 nicely illustrates that the life time in the stick-jump mode can exceed that in the stick-slide mode with as much as 10%. Only for $\theta_0 > 90^\circ$, the life time in the stick-slide mode can exceed that in the stick-jump mode, as shown in the inset in Figure 4.3.

Figure 4.3: Scaled life times for droplets dissolving in the stick-slide (green curves), stick-jump (red curves) and the CA and CR modes (solid black curves), as a function of the initial contact angle. The inset shows that for $\theta_0 > 90^\circ$, the stick-slide and stick-jump mode life times are not bound by the two principal modes. For some combinations for θ_0 and θ^* , the life time of the stick-slide mode exceeds that of the stick-jump mode.

4.4.2 Origin of the 'stick'

The CR, the stick-slide, and the stick-jump modes require the contact line to be stationary during (parts of) the dissolution process. Experimentally we observe that directly after formation of the droplet, it has a certain contact angle that we

refer to as θ_{00} . When θ_{00} is larger than the receding contact angle θ^* , the contact line does not move. Dissolution in the CR mode decreases the contact angle and when the contact angle reaches θ^* , the contact line will start to move and the first jump is observed. Contact angle hysteresis can be caused by heterogeneities at the interface [4] which can be of chemical nature, where 'patches' or islands with different hydrophobicity lead to local pinning of the contact line. Geometrical features can have a similar effect, for example when small pits, scratches, or bumps are present. Heterogeneities can originate from the droplet as well: The presence of micro- or nanoparticles inside the droplet will strongly alter the dissolution or evaporation dynamics. Convection inside the droplet will transport and deposit the particles near the contact line, giving rise to the well known coffee stain effect [85]. The deposited particles then act as pinning sites and many researchers have shown that addition of nanoparticles can affect the stick-slide or stick-jump process [83, 84, 93]. If the contact line is pinned during dissolution, the contact angle will increasingly deviate from the equilibrium value, resulting in an excess free energy. Shanahan [103] presented a theory in which he models the pinning of the contact line as an energy barrier U . In the ideal case where θ_0 is the equilibrium contact angle, and the droplet jumps between θ_0 and θ^* , the maximum excess free energy $\delta\tilde{G}$ was derived by Shanahan as

$$\delta\tilde{G} = \frac{\gamma L (\delta\theta)^2}{4(2 + \cos\theta_0)}, \quad (4.7)$$

with γ the interfacial tension of the droplet-bulk interface and $\delta\theta = \theta_0 - \theta^*$ (see Figure 4.1). The contact line stays pinned until $\delta\tilde{G}$ exceeds the pinning energy barrier. The droplet then jumps back to θ_0 , with an associated change δL in contact diameter. Equation 4.7 can be modified to express $\delta\tilde{G}$ in terms of δL instead of $\delta\theta$. By doing so, and assuming the potential barrier U to be fixed during dissolution or evaporation of the droplet, Shanahan showed that $\delta L \propto \sqrt{L}$. The feature of the small droplets as compared to larger ones becomes clear here: since $\delta L \propto \sqrt{L}$, we have $\delta L/L \propto 1/\sqrt{L}$ and thus the relative jumps in contact line diameter are larger when the droplet is small, making them easier to observe.

The work of Shanahan was recently commented on by Oksuz and Erbil [104]. They explained how to calculate $\delta\tilde{G}$ in experiments with an initial contact angle larger than the contact angle after the jump, e.g., when $\theta_{00} \neq \theta_0$, like in the present case. They argued that for the first observed jump, θ_{00} should be chosen as equilibrium angle, and $\theta_{00} - \theta^*$ should be taken as the deviation from equilibrium instead of $\delta\theta$. By following this and by using the value of L just before the jump, as Oksuz and Erbil did, we can calculate the excess free energy of the contact line $\delta\tilde{G}$ associated with the first jump for droplets on silicon and glass substrates. These values are listed in Table 4.1. The value of $\delta\tilde{G} = 2.5 \times 10^{-7}$ J/m on glass is comparable to the values found by others for evaporating droplets in air [93]. The weaker pinning on silicon ($\delta\tilde{G} \approx 8 \times 10^{-9}$ J/m) corresponds to small deviations from the equilibrium contact angle, and tiny jumps.

4.5 Comparison between experiment and theory

From Equation 4.1 we learn that the volume loss rate, and thus the life time, depends on the base diameter and contact angle. These values change during the experiment and from jump to jump. We therefore compare the expected volume loss per time unit, as calculated by Equation 4.1, to the actually measured volume change. This is done in Figure 4.4. The values for L and θ at each instance in time are not fixed, nor predicted, but taken from the actual measurement. The calculated value underestimates the actually measured volume loss by a factor of ≈ 2 . Keeping in mind that we used an estimated value for the diffusion coefficient, we use Figure 4.4 to estimate the actual diffusion constant in this system to be $D = 1.6 \times 10^{-9} \text{ m}^2\text{s}^{-1}$. The calculation using this value is shown as the dotted red line in the same figure. The inset in Figure 4.4 shows a zoom at the moment of a jump, which illustrates that the calculated dissolution rate before the jump is higher than after the jump. There are multiple explanations for the difference in the theoretical and observed rate of dissolution. Firstly, the theoretical diffusion constant of $D \approx 0.8 \times 10^{-9} \text{ m}^2\text{s}^{-1}$ is the value for 1-heptanol. The 3-heptanol molecule has a slightly different size, and its polar OH group is located at a different position, which might affect the diffusion constant. The exact influence is far from trivial, however, probably the difference will not be more than a few percent [99]. Furthermore, Equation 4.1 neglects convection, which in case of temperature differences or air flow in the laboratory may be an issue in evaporation experiments. The present work has been conducted in water which provides better thermal stability and dampens convection because of the higher viscosity. Still, the dissolving droplet itself could induce natural convection in the water, or water evaporation from the surface of the tank could induce a flow inside the bulk. Convection will bring clean water in to the vicinity of the droplet, increasing the dissolution rate [105]. Evidence for the existence of such a convection field, induced by the dissolving droplet itself, has recently been observed in preliminary experiments using particle image velocimetry.

In Table 4.2, the experimentally observed life times are compared to the theoretical values, as calculated using Equation 4.6. Using $D = 1.6 \times 10^{-9} \text{ m}^2\text{s}^{-1}$ and θ_0 and θ^* as observed in each individual measurement, all datapoints are close to, or within 20% of the expected value. Perfect agreement is not obtained, which is not surprising since our model assumes perfect pinning during the 'stick' phase, a contact angle that alternates between two fixed values, and in addition a round contact area, which is not exactly the case, due to the inhomogeneous pinning sites. Better agreement is likely to be obtained in systems in which the pinning is perfect and facilitates well defined contact angles, like for example the concentric circles used by Debuisson and coworkers [94, 95].

4.6 Conclusion

In addition to the three known modi that have been described earlier, we have shown that a fourth mode, called the 'stick-jump' mode, can occur. The stick-jump mode

Figure 4.4: Actual volume loss as calculated from the frame-to-frame change in volume (blue line) and the expected dissolution rate (red). $D = 0.8 \times 10^{-9} \text{ m}^2\text{s}^{-1}$ is used for the solid red line, the dashed line uses $D = 1.6 \times 10^{-9} \text{ m}^2\text{s}^{-1}$, which is estimated from our measurements. The experimentally measured base diameter and contact angle are used as input variables in Equation 4.1 to calculate the red curve.

could be studied in detail by using small dissolving droplets of 3-heptanol in water. We have shown that the dissolution of these droplets can be described by the same equations that apply to evaporating droplets.

Characteristic in the stick-jump mode is intermittent contact line pinning, which we related to surface roughness. Geometric heterogeneities provide anchoring points for the contact line, and by increasing the roughness of the substrate, pinning was enhanced drastically, resulting in more pronounced stick-jump behaviour. We also explained why the stick-jump behavior is more easily observed for the small droplets used in this study, as compared to large ones.

Experimentally observed life times of the droplets were in good agreement with the presented theoretical model. For initial droplet contact angles $\theta_0 < 90^\circ$, the life time in the stick-jump mode exceeds those in the constant radius mode or the stick-slide mode for initial contact angles. Even better agreement between measured and calculated life times might be obtained in future work, in which patterned substrates provide well-defined pinning sites.

Table 4.2: Non-dimensionalized experimentally observed ($\tilde{t}_{\text{exp}}$) and calculated ($\tilde{t}_{\text{life}}$) life times for droplets on hydrophobized silicon and glass substrates. We used $D = 1.6 \times 10^{-9} \text{ m}^2\text{s}^{-1}$, as found earlier.

Experiment	Surface	$\tilde{\tau}_{\text{exp}}$	$\tilde{\tau}_{\text{life}}$	$\tilde{\tau}_{\text{exp}}/\tilde{\tau}_{\text{life}}$
1	Silicon	0.91 ± 0.03	0.91 ± 0.01	1
2	Silicon	0.80 ± 0.03	0.91 ± 0.01	0.88
3	Silicon	0.90 ± 0.03	0.92 ± 0.01	0.98
4	Silicon	0.84 ± 0.03	0.92 ± 0.01	0.91
5	Silicon	0.90 ± 0.03	0.90 ± 0.01	1
6	Silicon	0.80 ± 0.03	0.90 ± 0.01	0.89
7	Glass	0.85 ± 0.03	0.70 ± 0.01	1.21
8	Glass	0.77 ± 0.03	0.74 ± 0.01	1.04

4.7 Appendix A: Life time in stick-jump mode

The rate of volume loss of a sessile droplet is given by Equation 4.1. The geometric relation

$$V = \frac{\pi L^3}{24} \frac{\sin \theta (2 + \cos \theta)}{(1 + \cos \theta)^2} \quad (4.8)$$

can be used together with Equation 4.1 to find an expression for $\frac{dL}{dt}$ to describe a droplet dissolving in the constant angle mode. In the constant radius mode, a similar approach can be used to find the change of θ in time:

$$\frac{d\theta}{dt} = \frac{-4D(c_s - c_\infty)}{\rho L^2} f(\theta) (\cos \theta + 1)^2 \quad (4.9)$$

Equation 4.9 can be integrated over θ from θ_0 till 0 to find the life time in the constant radius mode.

In the stick-jump mode, the contact line is pinned until the contact angle reaches the value θ^* , which is when the line depins and jumps. The time required for a droplet with base diameter L_0 to go from θ_0 to θ^* can be found by rewriting and integrating Equation 4.9:

$$\tau = \frac{\rho L_0^2}{4D(c_s - c_\infty)} \int_{\theta^*}^{\theta_0} \frac{d\theta}{f(\theta) (\cos \theta + 1)^2} \quad (4.10)$$

After this time the droplet jumps to $\theta = \theta_0$, a new base diameter L_1 , and the process starts over again. Assuming that the droplet always jumps from θ^* to θ_0 , the total life time of the droplet will consist of the combination of all intervals between the

jumps:

$$\tau_{\text{life}} = \frac{\rho}{4D(c_s - c_\infty)} \left(L_0^2 \int_{\theta^*}^{\theta_0} \frac{d\theta}{f(\theta) (\cos \theta + 1)^2} + L_1^2 \int_{\theta^*}^{\theta_0} \frac{d\theta}{f(\theta) (\cos \theta + 1)^2} + L_2^2 \int_{\theta^*}^{\theta_0} \frac{d\theta}{f(\theta) (\cos \theta + 1)^2} + \dots \right) \quad (4.11)$$

with L_0 the initial base diameter, L_1 the diameter after the first jump, L_2 after the second jump, etc.

The initial volume V_0 relates to the initial base diameter L_0 and the initial contact angle θ_0 via:

$$V_0 = \frac{\pi L_0^3 \sin \theta_0 (2 + \cos \theta_0)}{24 (1 + \cos \theta_0)^2} \quad (4.12)$$

Just before the first jump, when $\theta = \theta^*$ but still $L = L_0$, this volume has decreased to $V_{0,\text{end}}$:

$$V_{0,\text{end}} = \frac{\pi L_0^3 \sin \theta^* (2 + \cos \theta^*)}{24 (1 + \cos \theta^*)^2} \quad (4.13)$$

Since the volume is assumed to be conserved during the jump, $V_{0,\text{end}} = V_1$, which is equivalent to

$$V_1 = \frac{\pi L_1^3 \sin \theta_0 (2 + \cos \theta_0)}{24 (1 + \cos \theta_0)^2} = \frac{\pi L_0^3 \sin \theta^* (2 + \cos \theta^*)}{24 (1 + \cos \theta^*)^2}, \quad (4.14)$$

which can be re-arranged to find

$$L_1^3 = L_0^3 \frac{\sin \theta^* (2 + \cos \theta^*)}{(1 + \cos \theta^*)^2} \frac{(1 + \cos \theta_0)^2}{\sin \theta_0 (2 + \cos \theta_0)} \quad (4.15)$$

The same can be done around the second jump, when $V_{1,\text{end}} = V_2$:

$$V_{1,\text{end}} = \frac{\pi L_1^3 \sin \theta^* (2 + \cos \theta^*)}{24 (1 + \cos \theta^*)^2} = \frac{\pi L_2^3 \sin \theta_0 (2 + \cos \theta_0)}{24 (1 + \cos \theta_0)^2} \quad (4.16)$$

Substituting Equation 4.15 in to Equation 4.16 results in an expression for L_2 in terms of L_0 , θ_0 and θ^* :

$$L_2^3 = L_0^3 \left(\frac{\sin \theta^* (2 + \cos \theta^*)}{(1 + \cos \theta^*)^2} \right)^2 \left(\frac{(1 + \cos \theta_0)^2}{\sin \theta_0 (2 + \cos \theta_0)} \right)^2 \quad (4.17)$$

This procedure can be repeated to find a general expression for the base diameter of the droplet after the N-th jump:

$$L_N^3 = L_0^3 \left(\frac{\sin \theta^* (2 + \cos \theta^*)}{(1 + \cos \theta^*)^2} \right)^N \left(\frac{(1 + \cos \theta_0)^2}{\sin \theta_0 (2 + \cos \theta_0)} \right)^N \quad (4.18)$$

Equation 4.10 and Equation 4.18 can be combined to obtain the life time of a droplet dissolving in the stick-jump mode:

$$\tau_{\text{life}} = \frac{\rho L_0^2}{4D(c_s - c_\infty)} \left[\int_{\theta^*}^{\theta_0} \frac{d\theta}{f(\theta) (1 + \cos \theta)^2} \right] \sum_{N=0}^{\infty} \left(\frac{\sin \theta^* (2 + \cos \theta^*)}{(1 + \cos \theta^*)^2} \frac{(1 + \cos \theta_0)^2}{\sin \theta_0 (2 + \cos \theta_0)} \right)^{\frac{2N}{3}} \quad (4.19)$$

which can be simplified to

$$\tau_{\text{life}} = \frac{\rho L_0^2}{4D(c_s - c_\infty)} \left[\int_{\theta^*}^{\theta_0} \frac{d\theta}{f(\theta) (1 + \cos \theta)^2} \right] \left[1 - \left(\frac{\sin \theta^* (2 + \cos \theta^*)}{(1 + \cos \theta^*)^2} \frac{(1 + \cos \theta_0)^2}{\sin \theta_0 (2 + \cos \theta_0)} \right)^{\frac{2}{3}} \right]^{-1} \quad (4.20)$$

As derived by Picknett and Bexon [91] and Stauber *et al.* [92], the maximum life time that a droplet can achieve is in the constant angle mode with $\theta = 90^\circ$. Stauber *et al.* non-dimensionalized the life time τ_{life} in such a way that the scaled life time ($\tilde{\tau}_{\text{life}}$) in this situation equals 1 [92], i.e., with T as in Equation 4.5. Scaling in this way allows for easy comparison between the different modes. Adopting the same non-dimensionalization to our expression results in:

$$\tilde{\tau}_{\text{life}} = \left(\frac{2(1 + \cos \theta_0)^2}{\sin \theta_0 (2 + \cos \theta_0)} \right)^{\frac{2}{3}} \left[\int_{\theta^*}^{\theta_0} \frac{2d\theta}{f(\theta) (1 + \cos \theta)^2} \right] \left[1 - \left(\frac{\sin \theta^* (2 + \cos \theta^*)}{(1 + \cos \theta^*)^2} \frac{(1 + \cos \theta_0)^2}{\sin \theta_0 (2 + \cos \theta_0)} \right)^{\frac{2}{3}} \right]^{-1} \quad (4.21)$$

5 | Role of natural convection in the dissolution of sessile droplets*

The dissolution process of small sessile droplets in water is studied, disentangling diffusive and convective contributions. The latter can arise for high solubilities of the alcohol, as the density of the alcohol-water mixture is then considerably less than that of pure water, giving rise to buoyancy-driven convection. The convective flow around the droplets is measured, using micro-particle image velocimetry (μ PIV) and the schlieren technique. A universal scaling relation between the Rayleigh number and Sherwood number is found for all alcohols (of different solubilities) and all droplets in the convective regime. From this scaling, we find a relation between the droplet initial size and its convective dissolution time, which is found to agree with experimental data. Also, we show that the convective plume can be described in terms of the Rayleigh number by a scaling relation which is also found to agree with the μ PIV data. The convective dissolution regime is found to exist when the Rayleigh number $Ra > Ra_t$, where $Ra_t = 12$ is the transition Ra number as extracted from the data. For $Ra \leq Ra_t$ and smaller, convective transport is progressively overtaken by diffusion and the above scaling relations break down.

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5.1 Introduction

Conventional wisdom says that oil and water do not mix. However, some oily liquids, e.g. long-chain alcohols, are slightly soluble in water (see Table 5.1). When a droplet of such an alcohol is placed in a bath of water, it will slowly dissolve, analogous to the much studied topic of sessile droplet evaporation [17, 19, 87], or the dissolution of small gas bubbles [106]. Figure 5.1 shows an example of a sessile 1-hexanol droplet in water dissolving in the stick-jump mode [88, 107]: Unavoidable chemical and geometrical inhomogeneities in the substrate cause the contact line of the droplet to be pinned during dissolution, until the contact angle θ has decreased to a critical depinning value which was found to be $62^\circ \pm 2^\circ$. At this point, the contact line depins and the contact angle quickly increases to a value $\theta = 66 \pm 1^\circ$, resulting in a simultaneous decrease of the footprint radius R_{fp} . For the 1-hexanol droplet in figure 1, the dissolution time τ was approximately 3 hours. Considering this long dissolution time, it may seem plausible to assume that mass transport away from the droplet is governed by diffusion. Equivalent to the diffusion-driven mass transport from small gas bubbles [102] or small sessile droplets [15, 19, 88, 92], the relevant time scale would in this case then be given by

$$\tau_d = \frac{R_0^2 \rho_d}{2D\Delta c} \quad (5.1)$$

where R_0 is the initial equivalent radius of the droplet, D is the diffusion constant of the alcohol in water, ρ_d is the density of the droplet material, and Δc is the difference between the saturated concentration c_s at the droplet interface and the (undersaturated) concentration $c_\infty < c_s$ far away from the drop. However, for the 1-hexanol droplet with an initial radius $R_0 = 0.7$ mm, one finds $\tau_d \approx 11$ hours, which is much longer than the 3 h observed experimentally. In previous work [107], we hypothesized that this discrepancy is caused by the neglect of buoyancy-driven convection of the slightly lighter alcohol-water mixture near the droplet interface. The same idea has been put forward in the context of slowly growing CO_2 bubbles in small supersaturations [108] and evaporating droplets [109]. Also in these cases, the rate of mass transport in excess of the diffusion-limited prediction could be explained by assuming a contribution from buoyancy-driven convection. On the other hand, even for millimetre-sized droplets, there also seem to be circumstances under which the diffusive time scale is accurate [86, 91, 92, 110]. This reflects the existence of a threshold for convection. However, the details of this threshold remain unclear. The low velocities and small refractive index differences involved often inhibit direct observation of the buoyant flow in the surrounding medium. As far as we are aware, direct visualization attempts of the external flow have only been undertaken in the context of evaporating droplets, using either schlieren [111], infrared spectroscopy [112] or interferometry [113] techniques, and only very recently by tracing tiny oil droplets in air [114].

In this work we combine qualitative schlieren imaging with quantitative micro-particle image velocimetry (μPIV) to directly visualize the concentration field and flow around slowly dissolving droplets of various types of long-chain alcohols in clean

Figure 5.1: (A) Snapshot of a dissolving long-chain alcohol droplet (1-hexanol) in water. The dotted black line indicates the location of the silicon substrate, which mirrors part of the droplet. The footprint radius R_{fp} and the contact angle θ are indicated. A movie of the entire dissolution process is available online as supplementary material. (B) Evolution of the aforementioned parameters in time, along with the volume V of the droplet and the equivalent radius $R = (3V/(2\pi))^{1/3}$. All parameters have been normalised by their initial values: $V_0 = 750$ nL, $R_{fp,0} = 0.825$ mm, $R_0 = 0.708$ mm, and $\theta_0 = 72^\circ$.

water. We show that above a transition solutal Rayleigh number, which corresponds to the buoyancy of the alcohol-water mixture, which is lighter than the surrounding clean water, the solute is mainly transported away in a single steady plume above the droplet. Knowledge of the flow structure allows us to derive scaling laws for both the dissolution rate and the plume velocity in the convective regime, which are in good agreement with experiments. Finally, as the droplet shrinks and its Rayleigh number drops below the transition value, a transition occurs in which convection dies out and is overtaken by diffusion.

5.2 Experimental procedure

5.2.1 Materials and preparation

As shown in Table 5.1, the solubility of long-chain alcohols strongly depends on their length, while other properties, such as density and diffusion coefficient are relatively insensitive to this. By increasing the number of carbon atoms in the chain from five (pentanol) to eight (octanol), one decreases the solubility (and thereby the buoyant force of the water-alcohol mixture) by two orders of magnitude. This makes these alcohols very suitable to study the possible transition between diffusion and convection. Alcohols with purities of $\geq 98\%$ (Sigma-Aldrich) were used. The density of the alcohol-water mixture (Table 5.1) was calculated for a mixture at 100% saturation, using the molal volume ϕ_V^0 at infinite dilution [115, 116]. The molal volume ϕ_V gives the volume occupied by one mole of solute in the solvent.

The assumption is made that ϕ_V is independent of the solute concentration, which introduces a negligible error in $\Delta\rho$ of $< 1\%$ when compared to the direct density measurements given by [116].

A sketch of the experimental set-up is provided in Figure 5.2. All measurements were conducted in a cubical glass tank of $5\text{ cm} \times 5\text{ cm} \times 5\text{ cm}$. The container was cleaned using isopropyl alcohol and water, and then filled with 100 ml of clean water. This water was obtained from a Reference A+ system (Merck Millipore, at $18.2\text{ M}\Omega\text{ cm}$) several hours before the measurement and stored in a clean flask to equilibrate and thus reduce thermal convective currents. After the tank was filled, a single droplet was dispensed from a glass syringe with a Teflon plunger, fitted in a motorized syringe pump. The droplet was placed on a hydrophobized silicon wafer $\approx 1\text{ cm} \times 1\text{ cm}$ (P/Boron/(100), Okmetic), placed at the bottom of the tank. Hydrophobization was achieved by coating the wafer with a self-assembled monolayer of PFDTs (1H,1H,2H,2H-perfluorodecyltrichlorosilane 97%, ABCR GmbH, Karlsruhe Germany), following the procedure described earlier [28]. Prior to each experiment, the samples were cleaned by insonication in acetone for 10 min and dried under a stream of nitrogen. After the droplet was placed on the substrate, the needle was removed and the tank was closed.

5.2.2 Imaging

The droplet was illuminated from one side using a collimated light-emitting diode (LED) light source (Thorlabs, wavelength $\lambda = 625\text{ nm}$) and imaged onto a charge-coupled device (CCD) camera (Pixelfly USB, PCO Germany), with a long-distance microscope providing a magnification up to $16\times$. The images were recorded at a rate of one frame per second (f.p.s.), and post-processed using a Matlab code to extract the droplet profile with subpixel accuracy [101]. Since all droplets were smaller than the capillary length ($\sqrt{\gamma/(\rho_{H_2O} - \rho_{alcohol})g} \approx 2\text{ mm}$), the droplet profile could be accurately fitted to a spherical cap to obtain the radius of curvature and contact angle. With this method, droplets could be traced until $V < 0.05V_0$.

5.2.3 Schlieren

The concentration gradients developing around the dissolving droplets were qualitatively visualized using the schlieren technique [118]. For this, a positive lens and a knife edge were placed at the camera side of the tank, as shown in Figure 5.2. After passing through the tank, the parallel light from the LED source is focused onto the edge of a sharp knife placed perpendicular to the beam. To be sensitive to both horizontal and vertical concentration gradients, the knife edge was placed at an angle of 45° . In the resulting image, solute-rich regions are visible as local changes in light intensity.

Table 5.1: Properties of the alcohols used in this work, measured at 25°C: Chemical composition, density ρ of the pure alcohol, diffusion constant D of the alcohol in water, saturation solubility c_s of the alcohol in water, molal volume ϕ_V^0 of the alcohol in water at infinite dilution, density difference $\Delta\rho = \rho_{H_2O} - \rho_{H_2O, \text{sat}}$ between clean water and water saturated with the alcohol, interfacial tension γ of the water-alcohol interface. The diffusive timescale τ_d is calculated according to equation (5.1), for $R_0 = 0.7$ mm. No values for γ for 2-heptanol and 3-heptanol could be found. Data were obtained from [13][‡], [14]^{*}, [115][♣], [117][♢], [100][♣], [99][†], [116]^{*}, and [98][♦]. Diffusion constants for 2-heptanol and 3-heptanol were assumed to be equal to the 1-heptanol value, and the diffusion constant of 1-octanol was obtained by extrapolating data from [99].

Alcohol	Composition	ρ [kg m ⁻³]	D [10 ⁻⁹ m ² s ⁻¹]	c_s [kg m ⁻³]	ϕ_V^0 [cm ³ mol ⁻¹]	$\Delta\rho$ [kg m ⁻³]	γ [mN/m]	τ_d [10 ⁴ s]
1-Pentanol	C ₅ H ₁₁ OH	811	0.888 [†]	22 [‡] *	102.62 ^{*♣}	3.42	4.4 [♣]	1.0
1-Hexanol	C ₆ H ₁₃ OH	814	0.83 [†]	5.9 [‡] *	118.65 ^{*♣}	0.92	6.8 [♣]	4.0
1-Heptanol	C ₇ H ₁₅ OH	822	0.800 [†]	1.67 [*]	136.95 [*]	0.29	7.7 [♣]	14.5
2-Heptanol	C ₇ H ₁₅ OH	817	0.800	3.5 [♢]	134.39 [♣]	0.53	-	7.6
3-Heptanol	C ₇ H ₁₅ OH	818	0.800	4.0 [♦]	133.30 [♣]	0.57	-	5.8
1-Octanol	C ₈ H ₁₇ OH	827	0.780	0.5 [‡] *	148.41 [*]	0.07	8.52 [♣]	48.1

Figure 5.2: Experimental setup, showing the glass tank (1), with the substrate and the droplet in place (not to scale). The droplet was deposited under water using a syringe (2) fitted in a motorized syringe pump (not drawn). A dichroic mirror (3) was used to couple the laser beam (4) into the long distance microscope (5). A trigger-delay box (6) synchronized the laser pulses with the camera exposure. Parts (3), (4), and (6) were used in the μ PIV measurements only. The assembly used for schlieren, consists of a positive lens (7) and a knife edge (8), located in the focal point of the lens. The parallel LED light source (9) was used in all experiments, with the exception of the PIV measurements.

5.2.4 μ PIV measurements

For the μ PIV measurements the water in the tank was seeded with red fluorescent tracer particles (Fluoro-Max, Thermo Fisher Scientific, $3\ \mu\text{m}$ diameter). A pulsed green laser, (Nd:YAG, $\lambda = 532\ \text{nm}$) was coupled into the microscope by a dichroic mirror. The focal plane of the microscope was centred at the droplet. Therefore, only tracer particles in the $\approx 100\ \mu\text{m}$ thick focal plane were imaged, producing a two-dimensional velocity field around the symmetry axis of the droplet. The red light ($\lambda = 612\ \text{nm}$) emitted by the fluorescent particles was recorded by the CCD camera at 8 frames per second. A BNC 575 pulse/delay generator was used to synchronize the laser pulse and the camera exposure. The obtained images were then post-processed in ImageJ to remove static features and to enhance the contrast. Consecutive image pairs were analysed with JPIV, using an interrogation window of 32×32 pixels, corresponding to $\approx 70\ \mu\text{m} \times 70\ \mu\text{m}$. The concentration of tracer particles was kept low to avoid excessive absorption and blurring by out-of-focus particles. Because of this low particle density, the velocity fields from multiple image pairs were combined for improved accuracy [119].

5.3 Visualization results

Figure 3 shows snapshots of the μ PIV and schlieren measurements for 1-pentanol (left) and 1-heptanol droplets (right). The dissolving 1-pentanol droplet generates a clear plume originating from its apex, while fresh liquid is drawn in from the sides. The tip of the plume ends in a vortex ring. As this ring moves away from the droplet as the experiment proceeds, the effect of the transient flow generated by the vortex ring diminishes rapidly, leaving behind a single plume (see Figure 5.3C and Figure 5.11). For 1-heptanol, with its lower solubility, the plume is far less pronounced. The particle velocities are significantly lower and the contrast of the schlieren image had to be strongly enhanced to see the plume at all (see Figure 5.3D). The weak 1-heptanol plume seems to be affected by a small mean flow in the cell, possibly caused by thermal convection due to changes in room temperature or the illumination. As we will show later on, this mean flow seems to have little influence on the dissolution behaviour. Appendix A contains additional μ PIV results, including time-resolved velocity fields around a 1-pentanol droplet, the velocity field around an insoluble sessile droplet, and the flow around a dissolving sessile droplet placed on a vertical substrate.

The two different techniques used in Figure 5.3 reveal that the convective plume displays two different features, as illustrated in Figure 5.4. Firstly, the schlieren images visualize the plume-shaped region that contains dissolved alcohol. The concentration profile is characterized by a width $2\delta_c$, which increases as $\delta_c \propto \sqrt{Dz/v_p}$, with z the height above the droplet, and v_p the plume flow speed. Secondly, the buoyant force on the (lighter) water-alcohol mixture results in a flow, as visualized by the μ PIV. The velocity profile of this flow (also drawn in Figure 5.4) is characterized by a width $2\delta_v$. The liquid viscosity ν also causes the velocity profile to broaden for increasing height, namely with the same height dependence as the concentration profile, i.e. $\delta_v \sim \sqrt{\nu z/v_p}$. Therefore, the ratio ζ between the widths of the concentration and velocity profiles is fixed, $\zeta = \delta_v/\delta_c \sim \sqrt{\text{Sc}}$ [120], where Sc is the Schmidt number, $\text{Sc} \equiv \nu/D$. In the current system, $\text{Sc} \approx 1200$, so $\delta_v \approx 30\delta_c$ is expected.

To obtain a theoretical description for the velocity and concentration profiles at $\text{Sc} = 1200$, we solved equations (II.8) and (II.9) in the paper of Fujii [121], who described the analogous case of a thermal plume above a heat source. Here, we followed the numerical procedure described by Vázquez and Castellanos [122], and used equation (II.15) in Fujii's paper as a condition in the solving procedure, to obtain the velocity and concentration profiles at $\text{Sc} = 1200$, as shown in Figure 5.5A by the black and pink lines, respectively. The lateral coordinate $\tilde{X}$ in the theory is scaled by $\sqrt{Lz}$, with $L = \sqrt{2\pi\nu^3/(g\beta_c\dot{m}_d)}$, where g is the acceleration of gravity, $\beta_c \equiv \frac{\partial\rho}{\partial c}/\rho_b$ is the solutal expansion coefficient, and $\dot{m}_d$ is the mass loss rate of the droplet. The high Sc number in the current system results in distinct shapes for the velocity and concentration profiles. The measured value for ζ therefore depends on the definition of the plume width, as shown in Figure 5.5A. The anticipated $\zeta = 30$ is retrieved when evaluated at a relative amplitude of 0.1, corresponding to the 90% boundary layer definition.

Figure 5.3: Velocity fields (A&B) and solute concentration fields (C&D) surrounding droplets dissolving in water. A&C show droplets of 1-pentanol, B&D droplets of 1-heptanol. The contrast of the outlined area in D has been modified to increase the visibility of the plume. Note that panels A-C and B-D represent separate experiments. The dashed line in C indicates where the cross-sectional profiles, shown in Figure 5.5, are taken. The images were taken approximately 30 seconds (A), 2 minutes (C) or 4 minutes (B&D) after deposition of the droplet.

To compare our measurements to the theoretical profiles, a cross-sectional intensity profile was measured in the schlieren image (Figure 5.3C) at a height of $300\ \mu\text{m}$ above the apex of the droplet (as illustrated by the dashed line in Figure 5.3C). This intensity profile is plotted as the solid red line in Figure 5.5B, where we have to keep in mind that it represents the first derivative of the concentration profile, as it is the result from a schlieren measurement. To allow for an easy comparison, we plotted the theoretical concentration profile (pink solid line) from Figure 5.5A and its derivative (red dashed line) in Figure 5.5B, and fitted the derivative to match the experiment. From this fit, a conversion factor was obtained to translate the dimensionless lateral coordinate of the theory to the length scale of the experiment.

We executed the same procedure to obtain the velocity profile from the μ PIV data in Figure 5.3A, again at 300 μm above the droplet. This profile is plotted as the black circles in Figure 5.5C. The theoretical velocity profile (black solid line) is superimposed on the measurement, where the previously found conversion factor was used to match the lateral coordinate. Comparison of the experimental and theoretical profiles in Figure 5.5C reveals that while the central part of the plume shows fair agreement with the theoretical profile, the general shape of the plume is much narrower than expected from theory. The cause of this discrepancy is not understood as of yet. Possibly the vortex, substrate and the droplet influence the plume shape, and the expected profile can be recovered when measured at higher distance above the droplet.

As mentioned before, the plume changes over time. To visualize the evolution of the plume, cross-sections are taken in the μ PIV data at subsequent times, at 300 μm above the 1-pentanol droplet. These cross-sections are plotted in Figure 5.5D, and show that the plume properties are linked to the droplet size: both the width and the maximum velocity of the plume steadily decrease as the droplet shrinks. At $t = 3000$ s, the droplet has dissolved completely.

5.4 Dissolution rate and plume velocity

The μ PIV and schlieren images show that the convective flow around small droplets takes the form of a thin boundary layer over the droplet interface, culminating in a single plume rising from its apex. A schematic drawing of this flow and the concentration profile is shown in Figure 5.4. If we assume (1) that at the interface of the droplet the solute concentration is constant and equal to c_s and (2) that the droplet shrinks sufficiently slowly, then this situation is mathematically equivalent to the buoyant flow around a hot sphere of constant temperature T and fixed radius R . The second statement relies on a quasi-steady approximation, and is supported by the fact that, firstly, $\tau/(R_0^2/D) \gg 1$, reflecting that the time scale of the boundary layer effects is much smaller than the total dissolution time of the droplet. Secondly, due to dissolution, the droplet interface moves at a speed $\dot{R} < 1 \mu\text{m s}^{-1}$, from which we can calculate the Péclet number $\text{Pe} = \dot{R}R/D \ll 1$, indicating that advective mass transport due to the motion of the droplet interface is much smaller than the diffusive mass transport. This, combined with the fact that the measured bulk velocities are $> 10 \mu\text{m s}^{-1} \gg \dot{R}$, allows us to safely regard the droplet as quasi-steady. In the context of thermal convection, the flow structure in both the boundary layer and plume are well known (see e.g. [120, 121]). In this section we recapitulate the main findings in terms of the dissolution problem and compare them directly to our observations.

5.4.1 Dissolution rate

To study the droplet dissolution dynamics as a function of droplet liquid and size, individual droplets of varying initial volume and alcohol type were imaged throughout

Figure 5.4: Sketch of a sessile droplet dissolving at a rate $\dot{m}_d$, and convective plume. A concentration boundary layer of thickness δ_c develops over the droplet interface, since $Sc \gg 1$, the velocity boundary layer has a thickness $\delta_v > \delta_c$. The boundary layers merge into plumes with diameters $2\delta_c$ and $2\delta_v$, moving at a vertical velocity v_p . The boundary layer widths δ_c and δ_v will change as a function of height, but are linked via the relation $\delta_v/\delta_c \sim \sqrt{Sc}$ [120].

the dissolution process. Since the footprint radius R_{fp} shows steps due to the stick-jump mode dissolution [19,88,107], we define the equivalent radius $R \equiv (3V/(2\pi))^{1/3}$ to provide a continuously decreasing measure for the droplet size. Figure 5.6 shows $R(t)$ for 1-pentanol (Figure 5.6A) and 1-heptanol (Figure 5.6B) droplets. From this, the mass loss rate $\dot{m}_d$ was extracted and plotted as a function of R in Figure 5.7 for all six alcohols. Note that while $\dot{m} < 0$ for a shrinking droplet, we define the droplet mass loss rate as a positive amount, as it provides a more intuitive measure for the dissolution process. Using this, Figure 5.7 shows that the measured mass loss rates for the various droplet sizes and alcohol types span two orders of magnitude. To find a universal description for the dissolution dynamics, we continue by defining dimensionless numbers which take both the droplet size and liquid into account.

In (convective) heat exchange problems, the heat exchange is usually expressed in terms of the (dimensionless) Nusselt number, which is the ratio of the heat transfer rate and the rate for pure diffusion. The equivalent for solutal convection is the

Figure 5.5: A) Theoretical velocity profile (black) and concentration profile (pink) for a plume at $Sc = 1200$. The profiles are axi-symmetric around their plume centre at dimensionless lateral coordinate $\tilde{X} = 0$, as illustrated in the inset, which shows a zoom around $\tilde{X} = 0$. The observed ratio $\zeta = \delta_v / \delta_c$ depends on the definition of the plume width, as illustrated by the horizontal dashed lines. The anticipated $\zeta = 30$ is recovered when the plume width is evaluated at a relative amplitude of 0.1. B) The schlieren signal (red line), measured at a horizontal cross section $300 \mu\text{m}$ above a 1-pentanol droplet ($R_0 = 700 \mu\text{m}$), represents the derivative of the concentration profile. Therefore, both the theoretical concentration profile (pink solid curve) and its derivative (red-dashed curve) are plotted, and the derivative is fitted to match the schlieren measurement. Panel C shows the velocity profile (black circles), also measured at $300 \mu\text{m}$ above an equally sized 1-pentanol droplet, and the theoretical velocity profile (black solid line). Panel D shows the velocity profiles at subsequent times, revealing that both the plume width and velocity decrease. For clarity, the plots are vertically shifted, with the baselines $v_p = 0$ given as dashed lines. At $t = 3000 \text{ s}$, both droplet and plume have disappeared.

Sherwood number

$$Sh \equiv \frac{\langle \dot{m}_d \rangle_A R}{D \Delta c} \quad (5.2)$$

Figure 5.6: Equivalent radius $R = (3V/(2\pi))^{1/3}$ as a function of time for 1-pentanol droplets (A) and 1-heptanol droplets (B) dissolving in water. The inset in A illustrates how for each droplet with initial radius R_0 , the lifetime τ is estimated to lie between the lower estimate τ_l at the end of the experiment, and the upper estimate τ_u , found by extrapolation using Equation 5.16 (green dashed line). The lifetime τ is plotted as a function of R_0 in figures C and D for the 1-pentanol and 1-heptanol measurements, respectively. The lines in figures C and D illustrate the $\tau \sim R_0^2$ and $\tau \sim R_0^{5/4}$ relations, as expected for diffusion and convection, respectively. The vertical line in (D) indicates the transition Ray-number $Ra_t = 12$ which marks the transition between convection ($Ra > Ra_t$) and diffusion ($Ra < Ra_t$). For 1-pentanol, $Ra_t = 12$ corresponds to $R = 0.07$ mm.

where $\langle \dot{m}_d \rangle_A$ is the actual (measured) mass transfer flux (rate per area), averaged over the droplet surface area A . This mass flux is compared to $D\Delta c/R$, the mass flux of pure (steady) diffusion from an equally sized spherical droplet (or a sessile droplet with $\theta = 90^\circ$). In the case of pure diffusion from our sessile droplets ($45^\circ < \theta < 75^\circ$), we expect to find a diffusion-limited Sherwood number $0.9 < Sh_d < 1.3$, the exact value of which depends on the droplet contact angle, as discussed in appendix B. For the case of laminar flow at high Sc number, Bejan [120] provides a complete and insightful derivation of the momentum equation, showing that the flow can be described using the Boussinesq approximation of the Navier-Stokes equation. This approximation assumes a slender boundary layer (i.e. $\delta_c \ll R$, which is justified by Figure 5.3C and Figure 5.3D, which indeed show a thin boundary layer over the

Figure 5.7: Rate of mass loss as a function of R for droplets of different alcohols. The mass loss rates are ordered as a function of alcohol solubility, with 1-pentanol and 1-octanol being the best and least soluble alcohols, respectively.

droplet), a constant pressure over the width of the boundary layer and a limited density difference. For high Sc numbers, the buoyant force is balanced by viscosity and it can be shown that $\delta_c/R \sim Ra^{-1/4}$, independent of Sc [120]. Here Ra is the Rayleigh number which is the ratio of the buoyant force to the damping force,

$$Ra \equiv \frac{g\beta_c\Delta cR^3}{\nu D} \quad (5.3)$$

Taking δ_c as the typical length scale over which diffusion takes place in the presence of convection, we find $\langle \dot{m}_d \rangle_A \sim D\Delta c/\delta_c$, so that

$$Sh \sim R/\delta_c \sim Ra^{1/4}, \quad (5.4)$$

again independent of Sc . If we recast the data from Figure 5.7 in terms of the Ra and Sh numbers, all data sets from the six different alcohols collapse, as shown in Figure 5.8. This figure also reveals that, for large Ra , the data follow the anticipated $Sh \sim Ra^{1/4}$ scaling, which is plotted as the dashed line. For small Ra numbers, Sh converges to a plateau, as expected for diffusion. It is noteworthy that the $Sh(Ra)$ dependence from Enríquez *et al.* [108], who studied the growth of CO_2 gas bubbles in slightly supersaturated water, is almost identical to our Figure 5.8. This indicates that the flow structures around bubbles and droplets are very similar.

To better understand the transition between the convective and the diffusive behaviour, and to find the value of the transition Ra number Ra_t , we fitted a crossover function of the form

$$Sh(Ra) = Sh_d \left[1 + \left(\frac{Ra}{Ra_t} \right)^n \right]^{\frac{1}{4n}} \quad (5.5)$$

to the data. Here n is a fitting parameter that describes the sharpness of the transition. Equation 5.5 was fitted to the individual datasets of each alcohol, to obtain $Ra_t = 12.1 \pm 5.8$, $Sh_d = 1.2 \pm 0.2$ and $n = 1.0 \pm 0.5$. Equation 5.5 is plotted in Figure 5.8, using the mean values. The fitted curve confirms that, for $Ra > Ra_t \approx 12$, the data follow the $Sh \sim Ra^{1/4}$ scaling.

A transition exists around Ra_t , where the contribution of convective mass transport gradually decreases. When $Ra < Ra_t$, we obtain the diffusive limit $Sh \approx 1.2$, independent of Ra . A convective contribution to the evaporation of water droplets on mica has been claimed by Shahidzadeh-Bonn *et al.* [109], for droplets with radii of approximately 1 mm, corresponding to $Ra = 10$. However, they did not directly measure or visualize a convective flow, and their finding was rebutted by Guéna *et al.* [123], who studied the same system and excluded a convective contribution by flipping the system upside down. This hindered the development of a convective flow, and no difference in evaporation was reported whether the droplet was sessile or hanging, demonstrating that no convection developed around water droplets with radii up to 3 mm. The absence of convection around droplets with Rayleigh numbers well above the found value of Ra_t can be explained by Shahidzadeh-Bonn *et al.*'s choice of the droplet diameter as characteristic droplet size, leading to an overestimation of the Rayleigh number. Water droplets fully wet the hydrophilic mica substrate, resulting in a large difference between the droplet lateral size and its height, and thus to only a *seemingly* high value of Ra , when taking the diameter. For the convective problem it makes a great difference whether the solute-rich surface is parallel or perpendicular to the direction of gravity. This is highlighted by the fact that, in the case of a horizontal heated surface, there exists a critical value for the onset of convection, while this is not the case for a vertical heated surface, where a smooth transition is to be expected, as we find in the present case. We therefore believe that the length scale parallel to the direction of gravity is the more appropriate choice. As a final remark on this issue, we would like to encourage future work on droplet evaporation to be done in a humidity-controlled environment, as the density of air changes with humidity, which potentially could result in a different onset of convection and a different Rayleigh number.

5.4.2 Plume velocity

Similar to the concentration boundary layer around the droplet, the local velocity and structure of a convective plume are determined by a competition between buoyant and viscous stresses. For a thermal plume, this is described by the *local* thermal Rayleigh number $Ra(z)$, based on the local temperature difference between the centre of the plume and the surroundings (see e.g. [121] and [122]). The local

Figure 5.8: Sherwood number as a function of Rayleigh number. The plot shows the mean value and the spread for a total of 70 measurements on droplets with initial volumes $2 \text{ nl} \leq V_0 \leq 1200 \text{ nl}$. Since the Ra -number depends both on the droplet size and its material properties, large Ra -number droplets are easily made using large droplets of 1-pentanol, whereas low Ra droplets are best studied using small droplets of the poorly soluble 1-heptanol and 1-octanol. Equation 5.5 is plotted as the solid black line, using $Ra_t = 12.1$, $Sh_d = 1.2$, and $n = 1.0$.

solulal Rayleigh number can be written similarly, based on the local concentration difference $\Delta c(z)$,

$$Ra(z) \equiv \frac{g\beta_c \Delta c(z) z^3}{\nu D} \quad (5.6)$$

The plume can be linked to the dissolving droplet, as the transport of solutes inside the plume must equal the dissolution rate of the droplet,

$$\dot{m}_d \sim \delta_c^2 \Delta c v_p, \quad (5.7)$$

with v_p the central velocity of the plume. Similarly to the previous derivation of the flow over the droplet interface, where again a slender boundary is assumed (as verified by Figure 5.3C and Figure 5.3D), and R is replaced by the vertical coordinate z , it can be shown [120,121] that for $Sc \gg 1$ the plume width δ_c behaves as

$$\delta_c \sim z (Ra(z))^{-1/4} \propto z^{1/2}, \quad (5.8)$$

and the plume velocity as

$$v_p \sim \frac{D}{z} (Ra(z))^{1/2} = \left(\frac{g\beta_c \dot{m}_d}{\nu} \right)^{1/2}. \quad (5.9)$$

Substituting these relations into Equation 5.7, we find the relation between Δc and $\dot{m}_d$ as $\Delta c \sim \dot{m}_d / (Dz)$, so that Equation 5.6 can also be written as

$$\text{Ra}(z) \sim \frac{g\beta_c \dot{m}_d z^2}{D^2 \nu}. \quad (5.10)$$

Again by exploiting the analogy with the thermal case, one finds the following scaling behaviours for the width of the plume $\delta_c(z)$ and the central velocity v_p of a solutal plume with $\text{Sc} \gg 1$ [121]:

$$\delta_c \sim z (\text{Ra}(z))^{-1/4} \propto z^{1/2} \quad (5.11)$$

$$v_p \sim \frac{D}{z} (\text{Ra}(z))^{1/2} = \left(\frac{g\beta_c \dot{m}_d}{\nu} \right)^{1/2} \quad (5.12)$$

Note that v_p is independent of z . We use the droplet dimension R to non-dimensionalize the plume velocity, and define a plume Reynolds number

$$\text{Re}_p \equiv \frac{v_p R}{\nu} \quad (5.13)$$

By using the relation for v_p from Equation 5.12 we obtain

$$\text{Re}_p \sim \left(\frac{g\beta_c \dot{m}_d R^2}{\nu^3} \right)^{1/2}, \quad (5.14)$$

in which we can insert the previously found expression for $\dot{m}_d$ to obtain

$$\text{Re}_p \sim \text{Ra}^{5/8} \text{Sc}^{-1} \quad (5.15)$$

To test this scaling, we measure the maximum vertical velocity in the μPIV data at a height of 300 μm above the droplet, together with the size of the droplet, and use this to calculate $\text{Re}_p(\text{Ra})$. The result of this analysis is shown in Figure 5.9. For $\text{Ra} \gg \text{Ra}_t$, we find the anticipated $\text{Re}_p \sim \text{Ra}^{5/8}$. Note that this scaling breaks down already around $\text{Ra} \approx 400 \gg \text{Ra}_t$, reflecting the broad transitional regime also observed for the Sherwood number (Figure 5.8) and as quantified by the value of the fitting parameter $n = 1$ in Equation 5.5. For the measurements shown, there seems to be some dependence of the scaling prefactor on the initial size of the droplet. The smallest droplet displays a somewhat lower overall plume velocity than the two larger ones. We are not yet able to pinpoint the reason for this difference. One possible hypothesis might be that inertia of the bulk flow plays a role, and that the larger droplets create a stronger convection that persists throughout the dissolution. However, more work is required to confirm or rebut this hypothesis.

5.5 Dissolution time

The convective flow and the related increase in mass transport were described in the previous section. In this section we proceed by deriving an expression for the

Figure 5.9: The plume Reynolds number as a function of Ra-number for three individual 1-pentanol droplets with $V_0 = 700$ nl (red), $V_0 = 550$ nl (green), and $V_0 = 140$ nl (blue). The expected $Re \sim Ra^{5/8} Sc^{-1}$ scaling is indeed found when $Ra \gg Ra_t$, but breaks down when Ra approaches Ra_t . This marks the onset of the transition region (located around Ra_t), in which convective transport is gradually exceeded by diffusive transport. To obtain the fits to the two measurements, plotted in red and blue an additional prefactor of 0.25 (red/green) and 0.1 (blue) was required.

convective droplet dissolution rate and associated dissolution time τ_c . However, we start by briefly introducing diffusive dissolution, which we will use later on.

An expression for the diffusive volume loss rate dV/dt has been given by Popov [15] in the context of evaporating sessile water droplets. Popov's solution can be rewritten to find the rate of change of the droplet, expressed in terms of the previously introduced equivalent radius R

$$\frac{dR}{dt} = -\frac{D\Delta c}{2\rho R} f(\theta) \left[\frac{2}{2 - 3 \cos \theta + \cos^3 \theta} \right]^{1/3} \sin \theta \quad (5.16)$$

where

$$f(\theta) = \frac{\sin(\theta)}{1 + \cos(\theta)} + 4 \int_0^\infty \frac{1 + \cosh(2\theta\epsilon)}{\sinh(2\pi\epsilon)} \tanh[(\pi - \theta)\epsilon] d\epsilon \quad (5.17)$$

is a geometrical shape factor to describe the effect of the impenetrable substrate. Note that for simplicity we have neglected the intermittent contact line pinning which

was observed in the experiments [88, 107], and Equation 5.16 describes dissolution in the constant contact angle mode. Integration of Equation 5.16 results in the dissolution time, with the associated diffusive time scale given by Equation 5.1, i.e. in particular $\tau_d \propto R_0^2$.

We can perform a similar calculation for the convective mass exchange, again based on the cooling sphere analogy. An important difference between the cooling sphere and our dissolving droplet is that, in the latter case, the radius decreases in time. However, if the dissolution is slow, we can assume the process to be quasi-static and neglect this effect. We start by equating the rate of mass loss, $\dot{m}_d \sim -R^2 \rho (dR/dt) > 0$, to the rate at which mass is carried away in the convective plume, $\dot{m}_p = AD\Delta c Sh/R \sim AD\Delta c Ra^{1/4}/R$, with $A \propto R^2$ the area of the droplet-bulk interface. From this we obtain

$$\frac{dR}{dt} = -a \left(\frac{g\beta_c \Delta c_s^5 D^3}{\nu \rho_d^4 R} \right)^{1/4} \quad (5.18)$$

with a prefactor a of order 1. Separation of variables and integrating R from $R = R_0$ till $R = 0$, and time from $t = 0$ till $t = \tau_c$, gives the dissolution time with the associated convective time scale τ_c with

$$\tau_c = \frac{4}{5a} \left(\frac{\nu \rho_d^4 R_0^5}{g\beta_c \Delta c^5 D^3} \right)^{1/4}. \quad (5.19)$$

Therefore, for droplets dissolving in the convection-dominated regime, we expect a dissolution time $\tau_c \propto R_0^{5/4}$, with a material-dependent prefactor.

To test this scaling behaviour, we used the $R(t)$ curves in Figure 5.6A and B and extracted the dissolution time from each droplet. Since the droplets could not be measured until complete dissolution, the actual value of τ had to be estimated. Therefore, we assumed that the last stage of the dissolution process was diffusion-limited and extrapolated the droplet evolution by integrating Equation 5.16, using the smallest still measured droplet size of the experiment as initial value. This extrapolation (illustrated by the green dotted line in the inset of Figure 5.6A) provides the upper bound of τ , whereas the lower bound is given by the time at which the experiment was terminated. The values for τ thus obtained are plotted as a function of R_0 for 1-pentanol and 1-heptanol in Figure 5.6C and Figure 5.6D, respectively. For larger droplets we indeed find $\tau \propto R_0^{5/4}$ as expected from Equation 5.19, while for smaller 1-heptanol droplets $\tau \propto R_0^2$ is found, as expected for pure diffusion. The vertical line in Figure 5.6D indicates $Ra = 12$, showing that the transition from diffusive to convective dissolution occurs around Ra_t , consistent with our findings in section 4.

Now that we have confirmed the $\tau_c \propto R_0^{5/4}$ behaviour for large droplets, we finally test whether Equation 5.16 and Equation 5.18 provide accurate descriptions of the dissolution dynamics in the diffusive and convective regimes, respectively. Moreover, we can test whether the transition between these regimes indeed occurs around $Ra_t = 12$, as found before. To this purpose, the curves in Figure 5.6A and Figure 5.6B are replotted in Figure 5.10A and Figure 5.10B as a function of the

Table 5.2: Value of the dimensionless prefactor a in Equation 5.18 for all alcohol types as determined from a fit to the data, together with the observed contact angles of these droplets on the PFDTs-coated substrates in water.

	<i>1-pentanol</i>	<i>1-hexanol</i>	<i>1-heptanol</i>	<i>2-heptanol</i>	<i>3-heptanol</i>	<i>1-octanol</i>
a	0.65 ± 0.05	0.65 ± 0.05	0.55 ± 0.05	0.65 ± 0.05	0.7 ± 0.05	0.65 ± 0.05
θ	70°	70°	70°	52°	45°	70°

time $t - \tau$. Figure 5.10C and Figure 5.10D provide a close-up of the final stage of dissolution, the outlined parts of panels A and B, respectively. Along with the experimental data, we plotted the numerical integration of the convective dissolution model, Equation 5.18, which is the upper black line in all panels. We also plotted the diffusive dissolution model, Equation 5.16, represented by the lower black line in each panel. Figure 5.6 A-D shows that, for $Ra \gg Ra_t$, Equation 5.18 accurately captures the droplet dissolution process, reflecting convection-dominated dissolution. The value for the prefactor a in Equation 5.18 was adjusted for each alcohol to obtain a good fit in the convective regime. The values used are listed in Table 5.2, along with θ , for all alcohols. For $Ra \approx Ra_t$, the overlap between our convective model and the experiments becomes worse, consistent with the transition from convection-dominated to diffusion-dominated dissolution. The final stage of dissolution is best observed in Figure 5.10C and Figure 5.10D. When $Ra < Ra_t$, the dissolution is purely diffusive, reflected by the good overlap between Equation 5.16 and the measurements. The above findings confirm the applicability of our convective dissolution model when $Ra > Ra_t$, and validate $Ra_t \approx 12$ as the transitional Ra number for the transition from convective to diffusive dissolution dynamics.

5.6 Conclusion

Sessile droplets of long-chain alcohols immersed in water are ideally suited to experimentally study the basic laws of mass transfer around small objects. By choosing alcohols of different chain lengths, the alcohol's solubility in water can be varied by almost two orders of magnitude, while its other properties remain practically the same. This large range of solubilities allowed us to vary the convective driving parameter, the Rayleigh number, by over six orders of magnitude, while keeping the droplets large enough to visualize their shrinkage and the flow around them.

Using a combination of μ PIV and schlieren technique, we directly demonstrated that, above a transition Rayleigh number $Ra_t \approx 12$, a buoyant flow develops around a dissolving droplet, due to the density differences between the lighter alcohol-water mixture, as compared to the heavier clean water. By modelling the observed boundary layer structure at the droplet interface and in the plume, we derived a basic scaling relation $Sh \sim Ra^{1/4}$ for convective mass transport. Using this relation as a starting point, we derived expressions for the shrinkage rate of the droplet and the

Figure 5.10: Equivalent radius $R = (3V/(2\pi))^{1/3}$ as a function of time to complete dissolution $t - \tau$ for 1-pentanol droplets (A) and 1-heptanol droplets (B). Panels C and D provide a zoom of the outlined parts of A and B, respectively. The upper and lower black curves in each panels represents the integration of Equation 5.18 and Equation 5.16, respectively. When $Ra > Ra_t = 12$, Equation 5.18 accurately describes the dissolution dynamics. Around Ra_t , which is indicated by the horizontal line in each panel, a transition exists, in which convection is progressively overtaken by diffusion. In the final stage ($Ra < Ra_t$), the dissolution is well described by diffusion, i.e., Equation 5.16. The color coding for the individual measurements is the same as in Figure 5.6.

velocity of the plume. In the convective regime, these models are in good agreement with our data. However, once the droplet dissolves to a size close to Ra_t , diffusion gradually overtakes convective mass transport and the convective scaling relations break down.

The observed convection and associated increase in mass transport confirms earlier work on growing bubbles in supersaturated water [108] and evaporating droplets [111], indicating that it is a universal phenomenon. It should be noted that the considerations in this work assume that the plume is transported away from the substrate, against gravity. In the opposite case in which the surface is placed upside down, different effects such as the formation of a stable stratification layer near the surface will also play an important role. Also we expect that the prefactor a found in our experiments will be affected by parameters such as the geometry of the droplet,

confinements around the droplet and the inclination of the substrate.

The value for Ra_t presented in this work provides an important indication to determine the dominant transport mechanism in droplet dissolution. In conjunction with this, the convective dissolution model allows for more accurate predictions of droplet dissolution times. The demonstrated predictability of the dissolution behaviour of single sessile droplets on a horizontal substrate invites the testing of the derived scaling relations and fitting parameters in more complicated situations. For example, the applicability of the derived scaling relations and measured value for Ra_t could be tested in the context of bubble growth or droplet evaporation. Moreover, interesting changes in the flow profile can be expected, for example, when the orientation or the wettability of the substrate is changed. Other possible research directions include placing multiple droplets close together, to study their interaction, or making the droplets so large ($R > \lambda_c$) that they form a puddle.

5.7 Appendix A: Micro-particle image velocimetry data

The flow structure around the dissolving droplet has been measured using micro particle image velocimetry (μ PIV), utilizing the procedure and set-up described above. In Figure 5.11, the time evolution of the velocity field around a dissolving 1-pentanol droplet ($V_0 = 700$ nl) is shown. Shortly after deposition of the droplet (Figure 5.11A), the data reveal the presence of a toroidal vortex above the droplet, and a strong, narrow plume originating from the droplet apex. At 600 s into the dissolution process, shown in Figure 5.11B, the centre of the vortex is observed to have moved away from the droplet, causing the plume to slow down and broaden. Figure 5.11C shows the droplet at 2000 s after deposition: the droplet has shrunk considerably; however, a small plume is still visible, along with a small mean flow, from right to left. Close to the end of the experiment ($t = 2800$ s, Figure 5.11D), the droplet has almost disappeared, as has the plume. A small right-to-left mean flow is still observable.

To show that the plume is caused by solutal convection, and not simply by the presence of a spherical object at the interface, the experiment is repeated using an equally sized droplet of 1-decanol. This alcohol has negligible solubility, $c_s = 0.037$ g l⁻¹ [14]. For this droplet, $Ra \approx 10$, which means that solutal convection should be absent. The velocity field around this 1-decanol droplet is shown in Figure 5.12. From this figure, it is clear that the presence of the droplet does not cause the formation of a plume. A slight mean flow is present, which can be seen to flow *around* the droplet. Although not visible in Figure 5.2, it should be noted that, in this particular experiment, tracer particles adhered to the droplet interface, something that did not happen in all other experiments where soluble droplets were studied.

Hypothetically, the convection could be induced by surface tension gradients as well, developing over the droplet-water interface. These gradients would cause Marangoni convection over the alcohol-water interface [124]. If this were the case, the plume would always have the same shape and orientation with respect to the droplet and substrate, regardless of the direction of gravity. To check whether this is the case,

Figure 5.11: Velocity fields in water around a dissolving 1-pentanol droplet, 30 s after deposition of the droplet (A), and 600 s (B), 2000 s (C), and 2800 s (D) after deposition.

the substrate with a 1-pentanol droplet in place is mounted vertically in the centre of the tank. The resulting flow, shown in Figure 5.13, is found to be mainly parallel to the substrate. Liquid is replenished by inflow from the side and bottom, creating a large convection roll. The fact that the plume orients in a direction opposite to gravity, regardless of the orientation of the substrate, confirms that the convection is buoyancy-driven.

5.8 Appendix B: Derivation of the Sherwood number

The Sherwood number has been defined in Equation 5.2. In the diffusion-limited case, the mass loss rate $\dot{m}$ can be calculated from the droplet properties and its size.

Figure 5.12: Velocity fields in water around an in-soluble 1-decanol droplet.

For a spherical droplet with radius R , floating in an infinite bulk, the steady-state mass loss is [102]

$$\frac{dm}{dt} = -4\pi R D \Delta c, \quad (5.20)$$

resulting in a Sherwood number of $Sh_d = 1$.

For a sessile droplet, the presence of a substrate changes the dissolution, and a suitable correction factor has to be used [15]:

$$\frac{dm}{dt} = -\pi R_{fp} D \Delta c f(\theta) \quad (5.21)$$

with

$$f(\theta) = \frac{\sin(\theta)}{1 + \cos(\theta)} + 4 \int_0^\infty \frac{1 + \cosh(2\theta\epsilon)}{\sinh(2\pi\epsilon)} \tanh[(\pi - \theta)\epsilon] d\epsilon \quad (5.22)$$

and R_{fp} the footprint diameter of the droplet. Using goniometry, both R_{fp} and the droplet surface area A can be expressed in terms of the volume (and thus the equivalent radius $R = (3V/(2\pi))^{1/3}$) and the contact angle. From this, the Sherwood number for a sessile droplet with contact angle θ , dissolving purely via diffusion is found to be

$$Sh_d = \frac{f(\theta)}{\sin \theta \left(1 + \tan^2 \frac{\theta}{2}\right) \left(\frac{2}{2 - 3 \cos \theta + \cos^3 \theta}\right)^{1/3}}, \quad (5.23)$$

which indeed depends only on the droplet contact angle. Note that we defined the mass loss rate as a positive quantity, and dropped the minus sign from Equation 5.21, resulting in $\text{Sh}_d > 0$. By solving $f(\theta)$ numerically, $\text{Sh}_d(\theta)$ is plotted as the black line in Figure 5.14. When $\theta = 90^\circ$, the droplet has the shape of a hemisphere, and Sh_d is equal to that of a free sphere, $\text{Sh}_d = 1$. When $\theta > 90^\circ$, the mass transport is reduced (as compared to that from a free sphere) and hence $\text{Sh}_d < 1$.

When $\theta < 90^\circ$, Sh_d decreases towards zero, which is an implication of the choice of our characteristic length scale: For practical reasons, the equivalent radius R is chosen as the characteristic length scale. In the extreme case of dissolution from a flat disk, $\theta \rightarrow 0$, $V \rightarrow 0$, and thus $R \rightarrow 0$, resulting in $\text{Sh}_d = 0$. This does not provide a proper physical representation of the actual system, as it would result in zero mass exchange in the case of complete wetting.

Then an alternative characteristic length scale is the footprint radius R_{fp} , in which case Sh_d is given by the red curve in Figure 5.14. By using R_{fp} as the characteristic length scale, Sh_d for evaporation from a flat disk with radius R_{fp} , can be calculated exactly: $f(\theta = 0) = 4/\pi$ [92], which gives $\text{Sh}_d = \frac{4}{\pi}$. However, the drawback of using R_{fp} as the length scale appears for $\theta > 90^\circ$. Especially when $\theta \rightarrow 180^\circ$, $R_{\text{fp}} \rightarrow 0$, resulting once again in $\text{Sh}_d \rightarrow 0$.

So what experimental value for Sh_d is expected? The Sherwood number scales mass exchange with respect to a diffusive, free and spherical droplet. Hence $\text{Sh}_d = 1$ when $\theta = 90^\circ$. Owing to the substrate, the mass loss from a surface droplet with $\theta < 90^\circ$ is *larger* as compared to the mass exchange from the same segment of a free and spherical droplet [89]. The opposite is true when $\theta > 90^\circ$ [125]. Still, Sh_d is always of order 1 for practical droplets ($10^\circ < \theta < 160^\circ$) and independent of droplet size. The detailed dependence, as proposed in Figure 5.14, could be the subject of future work, where small droplets (ensuring $\text{Ra} < 10$) dissolve on substrates of various wettability.

Figure 5.13: Velocity fields in water around a dissolving 1-pentanol droplet, sitting on a vertical wall, measured 300 s after deposition.

Figure 5.14: Diffusion limited Sherwood number Sh_d , as a function of the droplet contact angle θ , calculated using the equivalent radius R (black line) or the footprint radius R_{fp} (red line), as characteristic length scale. Both curves cross at $\theta = 90^\circ$, corresponding to a hemisphere with $R_{fp} = R$ and $Sh_d = 1$. The dotted region indicates the range of contact angles and experimentally observed values for Sh_d .

6 | Collective effects in patterns of dissolving surface droplets^{*,†}

The effect of neighboring droplets on the dissolution of a sessile droplet, i.e. collective effects, are investigated both experimentally and numerically. On the experimental side small 20 nl approximately mono-disperse surface droplets arranged in an ordered pattern were dissolved and their size evolution is studied optically. The droplet dissolution time was studied for various droplet patterns. On the numerical side, Lattice-Boltzmann simulations were performed. Both simulations and experiments show that the dissolution time of a droplet placed in the center of a pattern can increase with as much as 60% as compared to a single, isolated droplet, due to the shielding effect of the neighboring droplets. However, the experiments also show that neighboring droplets enhance the buoyancy driven convective flow of the bulk, increasing the mass exchange and counteracting collective effects. We show that this enhanced convection can reduce the dissolution time of droplets at the edges of the pattern to values below that of a single, isolated droplet.

Figure 6.1: Schematic drawing of a pattern of surface droplets with footprint diameter L and contact angle θ , placed in a hexagonal pattern with center-to-center distances d .

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[†]Numerical work performed by Gianluca Laghezza.

6.1 Introduction

The evaporation or dissolution of a single surface droplet is a well-studied topic due to its high importance in various applications, for example in the field of coating, and the deposition of particles [17, 19, 87]. Even more relevant but far less studied is the evaporation or dissolution of surface droplets surrounded by other droplets. This situation for example occurs whenever a spray is applied to a surface, or in inkjet printing. The presence of neighboring droplets makes the analytical approach more challenging as compared to a single droplet, and in general no analytical solution for the collective dissolution problem (on which we will focus here) exists. The addition of neighboring droplets, like in the pattern sketched in Figure 6.1, is expected to change the concentration gradient by saturating the water in between the droplets, which in turn leads to a decrease in the mass loss rate [64]. This change in concentration gradient, caused by the presence of the neighboring droplets, explains the observed increased droplet dissolution time [88].

In this paper, we further investigate the collective effect in patterns of dissolving surface droplets. A diffuse interface numerical scheme is introduced and applied to simulate this system, and the numerical results are compared to experiments. Simulations and experiments on single droplets, finite, and infinite patterns are conducted. In particular, we will discuss the competition between on the one hand the slowed down dissolution due to the enhanced surrounding concentration thanks to the neighboring droplets and the resulting slower diffusion, and on the other hand enhanced convection due to collective convective effects.

6.2 Methods

6.2.1 Experimental procedure

A dissolving sessile droplet of long-chain alcohols in water is a versatile system to study various aspects of the dissolution process [107, 126]. In the current work, 1-heptanol (Sigma-Aldrich, $\geq 98\%$ purity) is used: a long-chain alcohol with an oily appearance, which has a saturation solubility $c_s = 1.67 \text{ g l}^{-1}$ in water [14], a diffusion constant $D = 0.8 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ [99], and a density of $\rho_d = 819 \text{ kg m}^{-3}$ [127].

$2 \times 2 \text{ cm}^2$ pieces of silicon wafers (P/Boron/(100), Okmetic), hydrophobized with PFDTs (1H,1H,2H,2H-Perfluorodecyltrichlorosilane 97%, ABCR GmbH, Karlsruhe Germany) [107] were used as substrates. These substrates were cleaned by insonication in acetone, and dried under a stream of nitrogen, prior to the experiment. The substrate was then placed at the bottom of a $5 \times 5 \times 5 \text{ cm}^3$ glass tank, as sketched in Figure 6.2. With the substrate in place, the cell was filled with 100 ml water, obtained from a millipore machine (Reference A+ system, Merck Millipore, at $18.2 \text{ M}\Omega \text{ cm}$). Subsequently, a glass-teflon syringe fitted with a thin needle ($210 \mu\text{m}$ outer diameter) and connected to a motorized syringe pump, was put into the water. $20 \text{ nl} \pm 4 \text{ nl}$ droplets of the 1-heptanol were dispensed through the needle of the syringe and gently placed on the substrate. A motorized, computer controlled X-Y stage

Figure 6.2: Sketch (not to scale) of the experimental setup, showing the glass tank with the substrate placed under water. The syringe is connected to a syringe pump (not drawn) to dispense droplets of 1-heptanol. Using the X-Y translation stage, the tank is moved with respect to the syringe. A LED illuminates the middle droplet of the pattern, and projects the side view image of this droplet onto a long-distance microscope and CCD-camera.

(Thorlabs) moved the cell and substrate with respect to the needle, and droplets were placed one by one to form patterns of $n = 5, 19, 41$, or 127 droplets, see for example Figure 6.3A-D. Droplets were placed in a hexagonal arrangement, as sketched in Figure 6.1, with the exception of the outermost droplets in the largest pattern. All droplets in the experiments dissolved in the stick-jump mode [19,88,107], causing the contact angle θ of the droplet to vary between 65° and 70° . The time to create the largest pattern (127 droplets) was ≈ 15 minutes, which should be compared to the total dissolution time of > 2.5 hours. The relatively large volume of water in the tank ensured that even after complete dissolution of the largest pattern, the bulk saturation level was $\leq 0.02c_s$.

A collimated light emitting diode light source (Thorlabs, $\lambda = 625$ nm) produced a beam parallel to the substrate and projected the side view image of the center droplet in the pattern onto a CCD camera (Pixelfly USB, PCO Germany) fitted with a long working distance microscope. Since other droplets would obscure the view of the center droplet, only this droplet was placed in the center row. The white arrow in Figure 6.3 indicates the center droplet, and the direction of view. Simultaneous measurements of the outermost droplets were unfortunately impossible, as their side view was obscured by the surrounding droplets, prohibiting the accurate contact angle determination required for volumetric measurements. The images obtained were post-processed in Matlab to extract the profile with sub-pixel accuracy [101]. Other experiments were carried out as well to provide a top view of the droplet pattern. To this purpose, a droplet pattern was deposited in the usual way after which the tank was placed under a Leica DM2500H microscope, operated in the

incident light mode, using a $5\times$ magnification objective.

Figure 6.3: A-D: Top view photographs of the water-immersed silicon substrate with the droplet patterns. The photographs show patterns with 5 (A), 19 (B), 41 (C), and 127 (D) 20 nl sized droplets of 1-heptanol. Panel E is a schematic side view of the numerical set-up showing the shell (E1), side (E2), top (E3) boundary condition used to simulate a single drop, multiple drops and an infinite array of drops respectively. The dashed lines in E indicate the surfaces, where the chemical potential is fixed at a non-equilibrium value to drive dissolution. The wavy dashed lines in panel (E3) represent periodic boundary conditions.

6.2.2 Numerical procedure

We performed three-dimensional simulations using a hydrodynamics model based on the Navier-Stokes equations and the Cahn-Hilliard model into which we have implemented evaporation following ref. [128]. The droplet-bulk system is considered as a binary liquid and by setting the chemical potential of the model at a value away

from equilibrium, one phase is favored over the other. This physically corresponds to the situation that dissolution takes place if the solute concentration is lower than its saturation value (which is the equilibrium value). Three-dimensional surface droplets were simulated. For numerical optimization reasons we adopted a droplet contact angle of $\theta = 90^\circ$ and the following boundary conditions (see Figure 6.3E):

1. For a single droplet, the chemical potential is fixed on a hemispherical shell surrounding the drop (referred to in the following as "shell BC");
2. For a finite pattern of droplets, the chemical potential is fixed at the top and the sides of the computational domain ("side BC");
3. For an infinite pattern of droplets, the chemical potential is fixed at a plane at the top of the computational domain and periodic boundary conditions are applied at the sides of it ("top BC").

More detailed information on the numerical procedure is provided in the appendix.

6.3 Results

6.3.1 Single droplet

To provide a simple test case and a basis to compare further measurements, we start with the dissolution of a single surface droplet, which has been well described in the context of the analogous processes of dissolving bubbles or evaporating droplets. In the case of steady-state, diffusion-limited dissolution, the dissolution rate of a droplet is given by [15, 19, 86, 91],

$$\frac{dV}{dt} = -\frac{\pi LD(c_s - c_\infty)}{2\rho_d} f(\theta), \quad (6.1)$$

where,

$$f(\theta) = \frac{\sin \theta}{1 + \cos \theta} + 4 \int_0^\infty \frac{1 + \cosh 2\theta\epsilon}{\sinh 2\pi\epsilon} \tanh[(\pi - \theta)\epsilon] d\epsilon \quad (6.2)$$

is a geometrical factor to describe the effect of the droplet contact angle and the impermeable substrate. By inserting the values for a 1-heptanol droplet with initial volume $V_0 = 20$ nl, and numerical integration of Equation 6.1, we obtain the black dashed line in Figure 6.4 which represents the droplet volume as function of the time to dissolution $t - \tau$, where τ is the dissolution time: the time needed to completely dissolve the droplet.

Comparison of the experiments on single droplets of different initial volumes (plotted as the colored solid lines in Figure 6.4) to the diffusion-limited model of a single droplet reveals a considerable discrepancy: the experiments are characterized by a higher rate of mass loss and therefore shorter dissolution time τ for a given initial volume. It has been shown [126] that the increased mass transport is caused by a convective contribution to the dissolution process, driven by solute-induced density gradients in the bulk.

Figure 6.4: Volume of single dissolving droplets as function of time until dissolution $t - \tau$. The black dashed line represents the expected diffusion-limited dissolution of a 20 nl 1-heptanol droplet Equation 6.1, to which the (purely diffusive) simulations (plotted as the open red diamonds) are compared. The experiments on individual droplets with of 1-heptanol and various initial volumes (solid lines of different colors) reveal an increased dissolution rate, due to a convective contribution to the dissolution [126]. We shift the x-axis by the droplet life time τ to overlap the individual measurements for comparison. The black arrows illustrate how the experiments can be used to find an empirical relation between the droplets initial volume and its dissolution time.

The experimental results from Figure 6.4 will be used in the next section, as they allow us to account for the variation in the initial droplet volumes: Despite the fact that great care is taken to create equally sized droplets, small differences in the initial droplet volume cannot be avoided. To allow for easy comparison between experiments with slight variations in the initial droplet volume, we correct for these deviations and compare the droplet volume to the desired initial volume of the droplets in the experiments (20 nl), namely by correcting the droplet volume V in each experiment according to

$$\tilde{V} = \frac{V}{V_0} \times 20 \text{ nl}, \quad (6.3)$$

where $\tilde{V}$ is the corrected droplet volume (in nl), and V and V_0 are the volume and the initial volume of the droplet, respectively. The differences in the initial droplet volumes (even though only a few nl) significantly affect the total droplet dissolution

time, thus obscuring the possible influence of collective effects. Therefore we must also correct the (dissolution) time based on the initial volume, which in diffusive problems is usually achieved by scaling with the appropriate time scale, namely the diffusive time scale $\tau_d = R_0^2 \rho / (\Delta c D)$, where R_0 is the initial droplet radius, and $\Delta c = c_s - c_\infty$. Scaling the time in such a way allows to compare purely diffusive droplet dissolution behavior, independent of the initial droplet size or the material [86, 88]. Unfortunately, the diffusive time scale τ_d cannot be used in the current system as the mass transport is not purely diffusive. On the other hand, purely convective dissolution with the associated convective time scale [126]

$$\tau_c = \frac{4}{5a} \left(\frac{\nu \rho_d^4 R_0^5}{g \beta_c \Delta c^5 D^3} \right)^{1/4}. \quad (6.4)$$

where β_c is the bulk expansion coefficient, g the acceleration of gravity, and a a prefactor of order 1. Equation 7.6 was shown to hold when the Rayleigh number

$$\text{Ra} \equiv \frac{g \beta_c \Delta c R^3}{\nu D} > 12. \quad (6.5)$$

The Rayleigh number expresses the ratio of the buoyant force to the damping force, and for the current 1-heptanol droplets with volumes ≤ 20 nl, we find $0.5 < \text{Ra} < 35$. This indicates droplet dissolution with contributions to mass transport from *both* convection and diffusion. This does neither allow for the use of the purely convective model, nor the purely diffusive model. Instead, both diffusion and convection play a role.

Therefore to proceed we exploit the single-droplet experiments to give an empirical relation between the initial volume of a single droplet and its dissolution time $\tau_{\text{single}}(V_0)$. Using this relation, we correct time in each experiment according to

$$\tilde{t} = \frac{t}{\tau_{\text{single}}(V_0)} \times 9100 \text{ s}, \quad (6.6)$$

where $\tilde{t}$ is the corrected time (in seconds), and $\tau_{\text{single}}(V_0)$ is the dissolution time of a single, isolated droplet, based on the droplets' initial volume $16 \text{ nl} \leq V_0 \leq 24 \text{ nl}$. $\tau_{\text{single}}(V_0)$ is obtained from the single-droplet experiments, as illustrated by the black arrows in Figure 6.4 for the case where $V_0 = 20$ nl. In Equation 6.6, 9100 s represents the dissolution time of a single, isolated droplet with an initial volume of 20 nl, which is the desired initial droplet volume. *

To obtain a reference time scale for the simulations we map the simulation units to physical units by fixing the initial drop volume to 20 nl and then choose a time scale by matching the diffusive dissolution time scale $\pi L D (c_s - c_\infty) / 2 \rho_d$, the coefficient in Equation 6.1, to its physical value. This corresponds to a dissolution time for a single drop of 13125 s. The scaled simulation results are shown as diamonds in

*Note that one cannot simply wait for a droplet with $V_0 > 20$ nl to dissolve down to $V = 20$ nl, as this would result in different waiting times, and with that variations in the volumes of the neighboring droplets.

Figure 6.4. Deviations from the theoretical curve occur because of the difficulty of separating time scales i.e., transient effects: for simulations of a reasonable duration (in terms of CPU-time), the dissolution time is not sufficiently long compared to the diffusive time and the system is not exactly in diffusive equilibrium at all times [128]. The use of a time scale in seconds, rather than a dimensionless time is preferred as it emphasizes that the simulations and experiments are subject to different physical processes: purely diffusive dissolution in the simulations versus a combination of diffusive and convective dissolution in the experiments. Therefore this comparison must be interpreted as qualitative, and not quantitative. The absence of convection in the simulations is mainly due to the fact that the two phases have equal densities, so no buoyancy is present. Currently, steps are being taken to also incorporate convection into the simulations, which opens the way to achieving quantitative agreement between the simulations and the experiments.

6.3.2 Droplet patterns: shielding mechanism

It has been proposed [64] that the enhanced dissolution time for collective droplets is caused by a larger solute concentration in the (liquid) environment in between the droplets, due to their dissolving neighbors, thus reducing the concentration gradient and thus the mass transport. We confirm this by simulating a pattern with $n = 5$ droplets, and measuring the concentration along a diagonal cross-section through this pattern as shown in Figure 6.5A and Figure 6.5B. The solid colored lines, shown in panel A, represent five iso-concentration lines measured at $t_1 = 1900$ s along the cross-section indicated by the dashed line in Figure 6.5B. They illustrate how the middle droplet primarily responds to a concentration gradient in the vertical direction, whereas the droplets at the perimeter of the pattern also experience a gradient in the lateral directions. This should result in a reduced mass loss rate for the center droplet, as compared to the outer ones, and thus a relatively faster dissolution of the outer droplets. This is indeed the case, as shown by the droplet cross-sections (plotted at subsequent times $t_1 = 1900$ s, $t_2 = 8500$ s, and $t_3 = 13200$ s by the black dashed lines in Figure 6.5A, by the top view images of the droplets (panels B-D), as well as by the evolution of the droplet footprint diameters in time (panel E). The cross sections in panel A also show that in the absence of pinning, the outer droplets dissolve asymmetrically, due to the higher mass loss rate at their exposed sides, i.e. fully consistent with recent findings [129].

Comparable behavior is observed in experiments on patterns of droplets, as shown in Figure 6.6. The droplets at the perimeter of the analyzed $n = 23$ pattern dissolve more quickly than the inner droplets. The outermost droplets (numbers 5 and 6) disappear first, followed by the droplets placed in the middle row (numbers 2, 3, and 4). The dissolution time of the center droplet (number 1) is extended by $\approx 20\%$ as compared to an equally sized, single droplet. However, it is surprising to see that the dissolution times of the outermost droplets (5 and 6) are in fact much *shorter* ($\tau < 9100$ s) as compared to a single droplet. We interpret that this is most likely caused by the increased convection over this droplet pattern, caused by the larger amount of droplets, and hence the larger volume of (lighter) alcohol-

Figure 6.5: (A) The iso-concentration profiles (colored lines, measured at $t_1 = 1900$ s) show how the concentration in between the droplets is increased due to the neighboring droplets. The profile is measured diagonally through a pattern with $n = 5$ droplets, as indicated by the dashed line in panel B. The (dashed) contours of the droplets correspond to times $t_1 = 1900$ s (outermost contours), $t_2 = 8500$ s, and $t_3 = 13000$ s (innermost contours). Panels B-D show the droplet footprints at simulation times $t_1 = 1900$ s (B), $t_2 = 8500$ s (C), and $t_3 = 13200$ s (D). The footprint diameters L are plotted as function of time in (E); the evolution of L cannot be analysed for $L < 0.1$ due to the diffuse interface nature of the numerical model. The times at which panels B-D are taken are indicated by the black arrows in panel (E).

Figure 6.6: Top view of a 23-droplet pattern ≈ 2 minutes after deposition (A), after 120 minutes (B), and after 170 minutes (C). The inset in (D) shows the original droplet pattern, the dashed box indicates the field of view. In (D) the footprint diameter is plotted as function of time, showing that the outer most droplets dissolve more quickly than the inner ones, and even more quickly than a single droplet ($\tau_{\text{single}}(20 \text{ nl}) = 9100 \text{ s}$). The red circles outline the droplets original footprint, revealing that the droplets are pinned by surface defects, as their centers of mass move during the dissolution. The correction scheme for volume and time as described in subsection 6.3.1 (Equation 6.3 and Equation 6.6) has not been applied here, in order to show the raw data.

saturated water. This stronger convection subjects the outermost droplets to an enhanced flow of clean water, increasing the dissolution rate and shortening the life time of the outermost droplets. Further inward in the pattern, the flow of water becomes progressively saturated by the dissolving droplets, reducing the dissolution rate from the innermost droplets and extending their dissolution time.

The initial footprints of the six droplets are indicated in red in panels A-C, illustrating that in contrast to the simulations, the droplet contact lines in the experiments are pinned by unavoidable local surface defects. This is especially visible for droplets 1 and 5, which are pinned to a point on their initial contact line throughout the entire

dissolution process.

6.3.3 Droplet patterns: collective behavior

Figure 6.7: Volume of the center droplet as function of time, as obtained from experiments (A) and numerics (B), for individual dissolving droplets and droplet patterns of various sizes. Volume and time in panel A have been rescaled (as described in subsection 6.3.1, see Equation 6.3 and Equation 6.6) to correct for small differences in the initial droplet volumes. Lines in (A) represent the mean of multiple experiments. The error bars indicate the spreading between different repetitions of the experiment.

We now proceed by changing the number of droplets in the system and experimentally study the dissolution behavior in patterns of $n = 5, 19, 41$, and 127 droplets, placed at distances $d = 700 \mu\text{m} \pm 100 \mu\text{m}$ apart (see Figure 6.1), such that $d/L_0 = 1.4 \pm 0.2$. The same spacing to diameter ratio is adopted in the simulations of patterns containing either 5, or an infinite number of droplets; shell boundary conditions (BC) are used for the single droplet, top BC for the infinite matrix and side BC for the 5 droplet matrix. As the camera used for these experiments (as discussed in subsection 6.2.1) could only produce a sharp image of a single droplet, the following sections discuss and present only the behavior of the center droplet in each pattern (as indicated in Figure 6.3). The volumes of the center droplets are plotted as function of time in Figure 6.7A and B for the experiments and simulations, respectively. Note that volume and time in Figure 6.7 are obtained using the respective scaling and conversion factors discussed in subsection 6.3.1. The dissolution of a single droplet is plotted as a reference in both figures and illustrates that the addition of extra droplets has a strong effect on the dissolution dynamics. More specifically, the slopes of the $V(t)$ curves (i.e., the volume loss rate) decreases upon the addition of more droplets, thus extending the droplet dissolution time.

To better appreciate the collective effect on the dissolution time, the experimentally and numerically measured dissolution times τ of the center droplets are plotted as function of $\log_{10}(n)$ in Figure 6.8. The competition between the collective convective effect (increasing the dissolution rate and reducing the life time) and the collective

Figure 6.8: Dissolution time τ of the center droplet vs $\log_{10}(n)$, where n is the number of droplets in the pattern. The experimental dissolution times are for the center droplet, and are corrected for variations of the initial volumes, as explained in subsection 6.3.1. Note that in the experiment the dissolution time for $n = 5$ droplets, is *smaller* than for a single one, due to convective effects.

diffusive effect (leading to an extended life time) is nicely visible in the experiments on small patterns ($n = 5, 19$): no significant increase of the life time as compared to a single droplet can be observed. In these small patterns, the effect of the convective flow is such that it counteract the shielding effect of the neighboring droplets. This shielding effect only becomes strong enough to counteract the effect of the collective convection in the larger patterns ($n = 41, 127$), where the dissolution time of the center droplet is extended significantly as compared to a single droplet ($\tau = 9100$ s). The effect of buoyancy driven convection is absent in the simulations, and hence a considerable increase of the droplet life time is already observed in the 5 droplet pattern.

6.3.4 Droplet patterns: effect of droplet spacing

So far, the droplets in all patterns, both in experiments and in numerics, were placed at a spacing to diameter ratio $d/L_0 = 1.4$. Still, for a given number of droplets in the experiments, the dissolution time of the center droplet is found to vary between experiments and we hypothesize that this is due to an unintentional variation in the

Figure 6.9: Volume of the center droplet as function of time for experiments (A) and numerics (B) on patterns with different ratios between the droplet-droplet distance d and the initial droplet diameter L_0 . Lines in (A) represent the mean of multiple experiments. The error bars indicate the spreading between different realizations of the experiments.

positioning of the droplets, possibly resulting in $d/L_0 \neq 1.4$. To test the influence of the (relative) droplet spacing on the dissolution process, we maintain the same droplet size ($V_0 = 20$ nl, $L_0 = 500$ μ m), but construct patterns with different droplet spacing: the droplets were placed in a $n = 41$ pattern at ratios $d/L_0 = 1.1, 1.4, 2$, and 2.8 which we compared to simulations on infinite patterns with $d/L_0 = 1.5, 2, 2.5, 3$, and 5 . Top boundary conditions were used in these simulations (Figure 3, panel E3).

The resulting droplet volumes are plotted as function of time in Figure 6.9, revealing that both in the experiments and in the simulations the dissolution time is considerably enhanced when the droplets are more densely packed. The dissolution time τ is plotted as function of d/L_0 in Figure 6.10 for both the experiments and simulations for direct comparison. It should be noted that in the limit $d/L_0 \rightarrow \infty$ (i.e., a single droplet), the simulations are not expected to result into the same behavior as the single droplet treated in subsection 6.3.1, due to the different boundary conditions used.

6.4 Conclusion

A three-dimensional diffuse interface numerical scheme and experiments were used to study collective effects in patterns of dissolving droplets. A single droplet was used as a test case for comparison of the dissolution time of droplets placed at the center of finite and infinite patterns of mono-disperse droplets. For patterns comprising many droplets simulations and experiments were in good qualitative agreement, both measuring dissolution times of the center droplet up to 60% longer than for a single droplet, with highest dissolution times measured for large, densely packed patterns.

Surprisingly, the experiments revealed a competition between an increased dissolu-

Figure 6.10: Droplet dissolution time τ as function of the relative droplet spacing. Both experiments and simulations show that the droplet dissolution time is increased in a denser packing.

tion due to enhanced convection, and the inhibition of dissolution due to shielding by the neighboring drops. The influence of the convective flow was noticeable at the outermost droplets of the pattern, which exhibited dissolution times shorter as compared to an equally sized, single isolated droplet. Also for the center droplet in small ($n = 5, 19$) patterns, the enhanced convection was found to inhibit the shielding mechanism, leading to no clear increase in the dissolution time. Only for larger patterns of droplets, the collective effect was such that it counteracted the enhanced convection, and resulted in an extended dissolution time of the center droplet.

Our simulations confirmed the earlier hypothesis [64] that the reduced dissolution rate is caused by an increased concentration in between the droplets, lowering the concentration gradient and thus the dissolution rate. This effect was weaker at the edge of the pattern, causing the outermost droplets to dissolve more quickly than the inner droplets, an effect found in both the simulations and experiments.

Future numerical work should incorporate the effect of natural convection, or future experimental work could eliminate convection, for example by reducing droplet sizes, or conducting the dissolution experiments in a micro-gravity environment [130]. Also, the current experimental system was limited by the fact that it could only measure the center droplet of the pattern. Future work could be improved by simultaneous volumetric measurements of all droplets in the pattern, for example through top view imaging combined with interferometry to obtain height profiles of the dis-

solving droplets [131].

Appendix: Numerical model

We describe the binary fluid by the Cahn-Hilliard free energy [132, 133]

$$\mathcal{F} = \int_V \left(\mathcal{F}_b + \frac{\kappa}{2} |\nabla \phi|^2 \right) dV + \int_S (h\phi_s) dS \quad (6.7)$$

where

$$\mathcal{F}_b = \frac{\rho}{3} \log \rho + \frac{a}{2} \phi^2 + \frac{b}{4} \phi^4 \quad (6.8)$$

is the bulk free energy. The first term in the bulk free energy is an ideal gas term, ρ the density field and a and b model parameters. With this choice of the free energy, phase separation occurs if $a < 0$ and $b > 0$ and the ϕ field in each phase takes the values $\phi_b = \pm \sqrt{-a/b}$. The second term in Equation 6.7 represents the surface tension, which takes the value $\gamma = \sqrt{-8ka^3/9b^2}$. This is a diffuse interface model and the interface width is $\sqrt{-2\kappa/a}$.

In the limit of negligible convection the concentration field evolves following to the diffusion equation

$$\frac{\partial \phi}{\partial t} = M \nabla^2 \mu, \quad (6.9)$$

where M is the mobility and the chemical potential

$$\mu \equiv \frac{\delta \mathcal{F}}{\delta \phi} = a\phi + b\phi^3 - \kappa \nabla^2 \phi. \quad (6.10)$$

We solve Eq (Equation 6.9) using a Lattice-Boltzmann algorithm. Details are given in ref. [134]. The parameters are $-a = b = 0.00305$, $\kappa = 0.0078$ and $M = 5$ and $\rho = 1$. The simulation domain was of size $(N_x, N_y, N_z) = (100, 100, 50)$ for the single drop and infinite pattern case, and $(N_x, N_y, N_z) = (200, 200, 50)$ for the five droplet pattern. Unless stated otherwise, the initial footprint diameter of the drop was $L_0 = 60$. This choice of parameters has already been validated in [128].

The chemical potential is fixed at the boundaries as described in subsection 6.2.2 by fixing the order parameter ϕ and using Equation 6.10. Details are given in ref. [128].

7 | Segregation in binary component droplets*

The dissolution of a single droplet, containing a mixture of oils, in water is experimentally studied. The oils in the droplets varied in terms of their solubility in water, and their hydrophobicity. We demonstrate that the polarity of the droplet constituents strongly influences the dissolution dynamics. A binary component droplet, containing two polar components (one soluble, one insoluble) exhibits a retarded dissolution as compared to a droplet containing only the soluble component. We argue that in this situation the mixture in the droplet can be assumed homogeneous, leading to a smaller effective contact area of the soluble liquid in the droplet with the bulk, and thus delayed dissolution. On the other hand, it is shown that this is not the case when a polar, soluble component is mixed with an insoluble, non-polar component, in which case segregation between the different liquids inside the droplet occurs, leading to Marangoni flows and superspreading of the droplet. The segregation is confirmed by volumetric measurements, and by the use of a solvatochromic dye in combination with confocal microscopy, which clearly showed that during dissolution local concentration differences occurred.

Figure 7.1: Three-dimensional confocal microscopy image, revealing segregation between the insoluble cyclohexane (yellow) and the soluble pentanol (purple).

*In preparation as: Erik Dietrich, Maaike Rump, Pengyu Lv, E. Stefan Kooij, Harold J. W. Zandvliet and Detlef Lohse, *Segregation in dissolving binary component sessile droplets*.

7.1 Introduction

The evaporation of a liquid droplet in air and the dissolution of gas bubbles or liquid droplets in water are comparable processes, that have received much attention in the past decades [17, 19, 87]. The topic of droplet evaporation and dissolution owes its popularity to its relevance in many applications. The first analytical description was given by Epstein and Plesset [102] in the context of diffusive transport from a spherical gas bubble in water, and has since then been extended to describe evaporating and dissolving sessile droplets [15, 19, 88, 91]. Especially the evaporation of sessile droplets has been studied in detail, revealing the influence of e.g. the effect of the thermal conductivity of the substrate [135, 136], substrate wettability [137], the behavior of the contact angle during evaporation [96, 123] and the influence thereof on the evaporation time [92, 110, 125], pinning of the contact line [103, 107, 138], natural convection around the droplet [111, 114, 126], cooling of the droplet surface [113], particles inside the droplet [90], and the effect of the droplet liquid on the evaporation process [139]. Despite the large number of publications on the topic, most of the experimental and theoretical effort by the (sessile) droplet community has been directed towards droplets containing only a single component.

The focus on single component sessile droplets is contrasted by a considerable body of research conducted on the vaporization and evaporation of multi-component (automotive) fuel sprays, which has been a topic of research for decades [140]. While this topic is dominated by different physical processes (for example a strong emphasis on non-isothermal processes, and forced convection [141]), similar approaches to the multi-component problem have been utilized as in the topic of the current work: dissolution of binary component sessile droplets in clean water. An example of a dissolving binary component sessile droplet is shown in Figure 7.2. Panels A-C show photographs of a droplet which contains a mixture of pentanol and cyclohexane, immersed in clean water in which it slowly dissolves.

When a droplet of a certain material a is placed in an immiscible, stationary bulk, an interface will form as shown in Figure 7.2A. If material a is soluble in the bulk and the bulk is clean (i.e. it does not contain any dissolved materials), molecules of a at the droplet side of the interface will cross the interface and dissolve into the bulk, saturating the bulk close to the interface of the droplet to $c_{s,a}$, the saturation concentration of material a in the bulk. Far away from the droplet, the bulk will still be clean ($c_{\infty,a} = 0$), which sets up a concentration gradient that drives the dissolved material away from the droplet, at a rate characterized by the diffusion coefficient D_a of a through the bulk. This 'makes room' at the droplet interface for more of the droplet material to dissolve, ultimately leading to dissolution of the droplet. When the droplet contains a second component b , miscible with a but immiscible with the bulk, the total droplet dissolution rate will be altered, depending on the properties and concentrations of a and b . Such a mixture can be described in multiple ways, for example by considering the mixture as a single, continuous

Figure 7.2: Panel A: Side view photograph of a sessile droplet, placed on a water-immersed hydrophobic substrate (indicated by the dashed line). A mirror image of the droplet is produced by shiny the substrate. The droplet, which has an initial volume $V_0 = 46$ nl contains pentanol mixed with cyclohexane in a 1:1 ratio (measured by volume). During the first ≈ 200 s, the soluble pentanol rapidly dissolves and the droplet volume V decreases while the footprint radius R_{fp} initially decreases slightly, after which it remains constant, leading to a decreasing contact angle θ , as illustrated by the photograph in panel B, and the graph in panel D. As the volume of the droplet decreased to ≈ 25 nl, the dissolution quickly slows down until only the insoluble cyclohexane remains, and V remains constant at $V = 23$ nl. In this final stage, θ slowly increases again, causing the droplet footprint to contract, as illustrated in panel C and the graph in D. The dashed lines in panels A-C mark the substrate.

liquid, the properties of which depend on the constituents [142–144]. Because this method does not explicitly consider the individual components and concentrations in the description of the dissolution of evaporation process, it makes this method a suitable approach to describe droplets which contain many components [145]. Other methods do treat the droplet components on an individual basis, and consider the contribution of each of the components with its respective properties. This is best illustrated by Brenn *et al.* [146], who explicitly considered the total evaporation rate of their (spherical) fuel droplets as the sum of the rates at which the individual components $i = a, b$ evaporate:

$$\frac{dm}{dt} = \sum_{i=a,b} \frac{dm_i}{dt}. \quad (7.1)$$

Instead of using the droplet diameter R in calculating dm_i/dt Brenn *et al.* [146] introduced the volume equivalent partial radius $R_{V,i} = R\phi_i^{1/3}$, using the instantaneous volume fraction ϕ_i of each of the components. To calculate dm_i/dt , the material properties ($c_{s,i}$, D_i , and liquid density ρ_i) must be known, as well as the concentrations of the materials on both sides of the droplet-bulk interface. In droplet vaporization, Raoult's law ($P_i = x_i P_i^*$, with P_i the partial vapor pressure of component i in the bulk, x_i the mole fraction of i in the liquid, and P_i^* the vapor pressure of the pure component) is commonly used to this purpose [147, 148]. However, this is an approximation, as Raoult's law relies on an ideal gas and thus neglects any interaction between the materials, and various methods have been presented to account for this [145, 149, 150].

In 2013, Su & Needham [151] presented one of the first studies on multi-component droplet dissolution in water. They assumed the instantaneous droplet-bulk interface composition of their spherical droplets, containing a mixture of two different types of acetates, to be directly related to the droplet volumetric composition:

$$\frac{V_a}{V_b} = \frac{A_a}{A_b} \quad (7.2)$$

where V_i and A_i are the volume and area fractions of the droplet-bulk interface respectively, occupied by components $i = a, b$ (denoted by the subscripts) such that the total droplet volume $V = V_a + V_b$, and interfacial area $A = A_a + A_b$. Instead of a volume equivalent partial droplet radius, Su and Needham calculated the dissolution rate of the individual components based on the total droplet radius, and multiplied this by the surface area fraction $A_i/A \leq 1$ occupied by the respective component, equivalent to the approach by Brenn *et al.* [146]. Note that while Equation 7.2 describes the composition at the *droplet* side of the droplet/bulk interface, it is equivalent to the use of Raoult's law to determine the partial gas pressures at the *bulk* side of the interface, in the sense that both approaches assume negligible interaction between a and b , and a homogeneous mixture inside the droplet.

Although Su and Needham obtained good agreement between their theoretical model and experiments, the assumption of perfect mixing and the absence of an interaction between a , b , and possibly the bulk, has been questioned. In fact, Su and Needham already noted that their approach could not be used in core-shell systems.

To overcome this limitation, the interaction between a , b , and the bulk has to be incorporated. A so-called activity coefficient γ_i for each component can be introduced to describe this interaction, and has been used to either correct Raoult's law [145, 146], or as shown very recently by Chu & Prosperetti [152], the surface area distribution. The activity coefficient expresses the interaction between the different species, based on their concentrations and the molecular structures.

In this paper we study the dissolution of oil droplets in clean water, to experimentally test the applicability of the approaches put forward by Su & Needham [151] and Chu & Prosperetti [152]. To this purpose, the droplets contain binary mixtures of water soluble long-chain primary alcohols (pentanol or heptanol), and compounds which

are fully miscible with the alcohol, but insoluble in water (cyclohexane or decanol). By using these combinations, we combine a polar, soluble compound with a water-insoluble material that is either also polar (decanol), or non-polar (cyclohexane). We compare the dissolution of these mixtures to existing theory, and to the dissolution dynamics of fully soluble single-component droplets.

7.2 Experimental Procedure

7.2.1 Preparation and Materials

Figure 7.3 provides a sketch of the experimental setup. The substrates were $\approx 1 \times 1$ cm² pieces of single side polished silicon wafer (P-type, boron doped (100) oriented, Okmetic) coated with PFODMS (1H,1H,2H,2H-Perfluorooctyldimethylchlorosilane 97%, ABCR GmbH, Karlsruhe Germany) following the procedure described earlier [107]. The PFODMS molecules bind covalently to the silicon substrate, forming a densely packed, hydrophobic monolayer. After the coating procedure, the samples were cleaned by insonication in chloroform for 10 minutes to remove any unbound silanes, and dried under a stream of nitrogen gas. Prior to each experiment, the samples were cleaned by insonication in acetone and dried under a stream of nitrogen. The sample was positioned at the bottom of cubical glass tank with dimensions $5 \times 5 \times 5$ cm³. Subsequently, the tank was filled with 100 ml water obtained several hours before the experiment from a Reference A+ system (Merck Millipore, at 18.2 M Ω cm). Finally, a droplet was placed on the immersed sample from a glass syringe through a thin (210 μ m outer diameter) needle. The syringe was vertically mounted in a computer controlled motorized pump, allowing to dispense droplets of controlled volumes.

All liquids were obtained from Sigma-Aldrich at $\geq 98\%$ purity, and used without further purification. The relevant material properties of the materials are listed in Table 7.1, together with the advancing and receding contact angles (θ_A and θ_R , respectively) as measured in multiple inflate-deflate cycles of a sessile droplet on water-immersed PFODMS-coated silicon substrates. Binary mixtures of the liquids were prepared by pre-mixing the two liquids at the desired volumetric ratios in clean glass-stopped flasks, from which the syringe was filled. As cyclohexane is very volatile, the 100 μ l syringe was refilled with a fresh mixture at the beginning of each experiment, subsequently flushed with ≈ 10 μ l, after which the droplet was quickly deposited to ensure a well-defined initial droplet composition.

7.2.2 Imaging

The droplet was illuminated by a collimated light emitting diode-light source (Thorlabs, wavelength $\lambda = 625$ nm) and imaged by a charge coupled device (CCD) camera (Pixelfly USB, PCO Germany), fitted with a long-distance microscope with adjustable magnification. The images were obtained at a typical rate of 1 frame per

Figure 7.3: Sketch of the experimental setup (not to scale) showing the droplet on the substrate in the glass tank. The syringe is mounted in a computer controlled pump (not drawn) to dispense the droplets. A LED source illuminates the droplet, and projects the image through a long-distance microscope onto a CCD-camera.

second, and post-processed using a Matlab routine to extract the droplet profile with sub-pixel accuracy [21].

7.2.3 Confocal Microscopy

To obtain insight into local concentration differences inside the dissolving droplet, confocal microscopy was employed. Confocal microscopy is an optical imaging technique which can increase the image resolution and contrast substantially. Compared with a normal optical microscope, a confocal microscope can eliminate the out-of-focus light by crucially adding a pinhole on the confocal plane of the lens which acts as a filter for light from the focal plane. Three-dimensional information can be obtained by reconstruction from a series of images, taken at various focal positions. Confocal, real-time observation of the dissolution process was carried out in three-dimensional view using a $10\times$ dry objective (Plan Fluor $10\times/0.3$ DIC, numerical aperture = 0.3, working distance = 16 mm). The confocal microscope (Nikon A1 confocal laser microscope system, Nikon Corporation, Tokyo, Japan) was operated in the bottom view mode, so transparent substrates had to be used. WillCo-Dish (WillCo-Dish, The Netherlands) glass bottom dishes were used for this purpose. These dishes have a $170\text{ }\mu\text{m}$ thick borosilicate glass bottom, on which a circular polystyrene rim is glued. The dishes were cleaned by insonication in isopropyl alcohol, ethanol and water, dried under a stream of nitrogen, and then coated with PFODMS, using the process described earlier. The polystyrene rim excludes the application of more aggressive cleaning steps. Pentanol or heptanol was pre-mixed with cyclohexane to create a binary mixture, and a small amount of Nile red (micro-

scopy grade, Sigma-Aldrich, the Netherlands) was added. Nile red is a hydrophobic, solvatochromic dye, which can absorb light at various wavelengths (both in the ultra-violet and visible range) and emits light at a wavelength that depends on the solvent polarity. Detecting the emitted wavelength allows us to determine if the dye is in a polar or non-polar environment, as illustrated by Figure 7.5.

For the confocal measurements, the dish was filled with water, a single droplet of the alcohol mixture was placed on the glass bottom after which the dish was mounted in the microscope. The Nile red dye, labeling the binary mixture, was simultaneously excited at two wavelengths $\lambda = 488$ nm and $\lambda = 561$ nm. The dye emitted light in two separate ranges: $\lambda = 500 - 550$ nm and $\lambda = 663 - 738$ nm in the pentanol-rich and cyclohexane-rich phases, respectively, which can be displayed as two different colors to visualize local concentration differences. Recording of time-series three-dimensional images was started after the microscope view and focus were set, which was a few minutes after deposition of the droplet. Each vertical scan loop, starting just below the droplet and scanning upward until it reaches the droplet apex, took approximately 30 s in the resonant scan mode. This time scale is much shorter than the droplet dissolution process, so that variations of the droplet morphology during each scan loop were small.

7.3 Volumetric measurements

As explained in the introduction, the dissolution rate dV/dt in a multicomponent droplet depends on the properties of its constituents, and the composition of the droplet interface. Therefore, we can obtain information on the composition of the droplet interface by measuring the dissolution process. To this purpose, 5 different mixtures were prepared, listed in Table 7.2. The first four mixtures initially contain equal amounts by volume of a soluble component (pentanol or heptanol), and a (practically) insoluble component (decanol or cyclohexane, see Table 7.1). The fifth mixture contained two soluble components: pentanol and heptanol, also initially mixed in a 1 : 1 ratio. Besides these mixtures, single-component droplets containing either pure pentanol or pure heptanol were measured to provide a reference. All droplets had an initial volume $V_0 \approx 100$ nl. It is important to realize that pentanol, heptanol and decanol are all alcohols, and have comparable dipole moments and structures (see Table 7.1 and Figure 7.4), whereas cyclohexane is completely apolar and has a cyclic shape.

Figure 7.4: Molecular structures of the primary alcohols pentanol (A), heptanol (B), and decanol (C), and cyclohexane (D). Gray, red, and white spheres represent carbon, oxygen and hydrogen atoms, respectively.

Figure 7.5: The emission wavelength of Nile red depends on the polarity of the solvent. It appears yellow in a non-polar solvent such as cyclohexane (left tube), but purple when a polar compound is added, as visible in the pentanol/cyclohexane mixture (right tube).

Table 7.1: Properties of the various materials used in this work (measured at 25°C): Chemical composition, density ρ of the pure liquid, diffusion constant D of the material in water, saturation solubility c_s in water, interfacial tension γ of the liquid-water interface, dipole moment of the molecule, and the advancing (θ_A) and receding contact angles (θ_R) for a sessile droplet of the material on a PFODMS-coated Si-substrate, immersed in clean water. The density difference $\Delta\rho = \rho_{H_2O} - \rho_{sat}$ between clean water and water saturated with the respective alcohol was calculated using the data from [115]. No values for $\Delta\rho$ of decanol and cyclohexane could be found, and given their negligible solubility it is save to assume $\Delta\rho \approx 0$. Other data were obtained from [13][†], [14]^{*}, [153][♣], [100][♣], [99][†], [154]^{*}, [155][♣], [156][¶], [157][•], [158][‡], and [159][◆].

Material	ρ [kg m ⁻³]	D [10 ⁻⁹ m ² s ⁻¹]	c_s [kg m ⁻³]	$\Delta\rho$ [kg m ⁻³]	γ mN m ⁻¹	Dipole moment [Debye]	θ_A [°]	θ_R [°]
pentanol	811	0.888 [†]	22 ^{‡,*}	3.42	4.4 [♣]	1.7 [•]	50 ± 7	43 ± 6
heptanol	822	0.800 [†]	1.67 [*]	0.29	7.7 [♣]	1.739 [‡]	60 ± 1	50 ± 2
decanol	830	0.475 [*]	0.036 [*]	≈ 0	8.97 ^b	1.6 [¶]	68 ± 1	53 ± 1
cyclohexane	778	0.839 [◆]	0.043 [♣]	≈ 0	50 [♣]	0 [•]	89 ± 6	69 ± 8

Table 7.2: Overview of the various mixtures considered in this chapter. Each case represents a droplet containing materials a and b mixed with initial volumes $V_{0,a}$ and $V_{0,b}$, such that the total initial droplet volume $V_0 = V_{0,a} + V_{0,b}$.

Mixture	Material a	Material b	$\frac{V_{0,a}}{V_0} : \frac{V_{0,b}}{V_0}$
1	pentanol	decanol	0.5 : 0.5
2	pentanol	cyclohexane	0.5 : 0.5
3	heptanol	decanol	0.5 : 0.5
4	heptanol	cyclohexane	0.5 : 0.5
5	pentanol	heptanol	0.5 : 0.5

The resulting volume of the droplets are plotted as function of time in Figure 7.6A. Here, it can be seen that the single-component droplets are completely soluble. Mixtures 1 – 3, which contain an insoluble component (cyclohexane or decanol), do not completely dissolve. These mixtures show an initial dissolution stage in which the soluble component dissolves and the volume of the droplets decreases. When most of the soluble material has dissolved, the dissolution rate rapidly decreases, visible as a ‘kink’ in the $V(t)$ curves. In the final stage, only the insoluble component remains, and the volume is constant. The heptanol/cyclohexane mixture is a surprising exception, as it appears that in this mixture also the cyclohexane slowly dissolves, for which a possible explanation will be given later. The pentanol/heptanol mixture shows a more complex behavior, comprising a fast and a slow dissolution stage, as both of the constituents are soluble, but have one order of magnitude difference in solubility (see Table 7.1).

The large difference in solubility between pentanol and heptanol results in an order of magnitude spread in the dissolution time scale, making it difficult to compare the measurements. Moreover, small differences in the initial size of the droplets affect the dissolution time. At this point it should be noted that the dissolution process described in the introduction, as well as that in the work of both Su & Needham [151] and Chu & Prosperetti [152] assumes a static water phase, and thus purely diffusive mass transport. In this limit, the dissolution time τ of a droplet with initial radius R_0 is approximately given by the diffusive time scale $\tau_c \equiv R_0^2 \rho_d / (2D\Delta c)$ [88], where $\Delta c = c_s - c_\infty$. However, it has been shown, in the context of both growing bubbles and dissolving droplets [108, 126], that a convective flow can develop, driven by solute-induced differences in the bulk density. This convective flow increases the mass exchange rate, rendering diffusive approaches inaccurate. We have shown in our recent work [126] that the effect of this convective flow on the dissolution rate is relevant when the Rayleigh number,

$$Ra \equiv \frac{g\beta_c \Delta c R^3}{\nu D} \quad (7.3)$$

is larger than the transition Ra-number $Ra_t = 12$. Here ν is the bulk viscosity, $\beta_c \equiv \frac{\partial \rho}{\partial c} / \rho_b$ is the solutal expansion coefficient of the bulk, g is the acceleration of

Figure 7.6: Volume of the droplets as function of time. All mixtures initially contain two components mixed at a 1 : 1 by volume ratio. The orange and green lines represent single component pentanol or heptanol droplets, respectively. Panel B shows $(V/V_0)^{5/12}$, resulting in straight curves for the single component droplets, showing that they dissolve mainly through convective transport. The prefactor χ was extracted from the slope of the curves for pure pentanol and heptanol droplets, and used to plot the dashed black lines in panel A, which represent the convective dissolution model, Equation 7.5.

gravity, and the equivalent radius of the droplet $R = (3V/(2\pi))^{1/3}$ is chosen as its characteristic size. The initial Ra-numbers of 100 nl pentanol and heptanol droplets are $Ra = 1705$ and $Ra = 170$, respectively, indicating convective dissolution.

In the convective regime, the dissolution rate of a droplet is given by [126]

$$\frac{dV}{dt} = -\chi(3V)^{7/12} (2\pi)^{5/12} \left(\frac{g\beta_c \Delta c_s^5 D^3}{\nu \rho_d^4} \right)^{1/4}, \quad (7.4)$$

where χ is a constant prefactor of order 1, whose value depends on the exact shape of the droplet. Indeed it was found [126] that χ changed with the droplet contact angle. The ODE (7.4) can be solved to find

$$V^{5/12} = V_0^{5/12} - \frac{5\chi}{4} \left(\frac{2\pi}{3} \right)^{5/12} \left(\frac{g\beta_c \Delta c_s^5 D^3}{\nu \rho_d^4} \right)^{1/4} t. \quad (7.5)$$

If we plot $(V/V_0)^{5/12}$ as function of time for the droplets shown in Figure 7.6A, we obtain Figure 7.6B, where indeed the single component droplets produce a straight line throughout the largest part of the dissolution process, confirming that their dissolution is described by the convective mechanism. Furthermore, we can extract the value of χ for the pure pentanol and heptanol droplets by measuring the slope of the dissolution curves in Figure 7.6B. The thus obtained values for χ are listed

Table 7.3: Values for the prefactor χ for dissolving droplets of pure pentanol and pure heptanol.

Liquid	χ
Pentanol	0.65
Heptanol	0.85

in Table 7.3, and for the remainder of this work we will assume these values to be a material property, rather than a geometric which is only fully correct in the limiting cases of the pure liquid droplets. The black dashed curves in Figure 7.6A represent Equation 7.5, evaluated using the material properties and the found values for χ for pure pentanol and heptanol droplets, showing good agreement with the experimental data.

Using the thus obtained values for χ and the respective material properties one can easily calculate the convective dissolution time τ_c of a droplet with initial volume V_0 from Equation 7.5, giving:

$$\tau_c = \frac{4}{5\chi} \left(\frac{3V_0}{2\pi} \right)^{\frac{5}{12}} \left(\frac{\nu\rho_d^4}{g\beta_c\Delta c^5 D^3} \right)^{1/4}. \quad (7.6)$$

If we use the convective dissolution time to scale time in the experiments as

$$\tilde{t} = \frac{t}{\tau_c}, \quad (7.7)$$

and rescale the droplet volume by its initial volume

$$\tilde{V} = \frac{V}{V_0}, \quad (7.8)$$

and replot the data of Figure 7.6, we obtain Figure 7.7A and B, where indeed the $\tilde{V}(\tilde{t})$ curves of the pure pentanol and heptanol droplets collapse, demonstrating the universality of the convective dissolution model.

For the mixtures, τ_c was calculated using the properties of material a , listed in Table 7.2 and the corresponding value of χ , listed in Table 7.3 which was assumed to be constant. Figure 7.7B provides a detailed view at small $\tilde{t}$, and shows that the scaled data of the single-component droplets collapse onto a single curve. Furthermore, we see that by scaling the volume according to Equation 7.8, the residual volumes of mixtures containing either decanol or cyclohexane approximately equal $V_{0,b}/V_0$, as one expects. However, if we focus on the dissolution rate $d\tilde{V}/d\tilde{t}$, we see that mixtures of pentanol/decanol, heptanol/decanol and pentanol/heptanol, show a *retarded* dissolution as compared to the single-component droplets, owing to the addition of an insoluble or less soluble alcohol. The heptanol/cyclohexane also shows a retarded dissolution as compared to a pure heptanol droplet, however, the dissolution rate is surprisingly faster as compared to the heptanol/decanol mixture, indicating that changing decanol for cyclohexane as the insoluble compound alters

the dissolution dynamics. The retarded dissolution is not observed at all for the pentanol/cyclohexane mixture: the dissolution process of this mixture perfectly follows the $\tilde{V}(\tilde{t})$ trace of the single component droplet. Since dissolution occurs at the droplet-bulk interface, their similar dissolution dynamics suggests that the interface of a pure pentanol droplet is identical to the pentanol/cyclohexane mixture, i.e. comparable to a surfactant. In fact, the pentanol/cyclohexane mixture in water has been used before to study emulsions [160]. This behavior is consistent, for example when pentanol and cyclohexane are mixed at different initial ratios, or when the droplet is ten times larger ($V_0 = 1$ μl , instead of $V_0 = 100$ nl), as shown in Figure 7.8.

Figure 7.7: Scaled droplet volume $\tilde{V}(\tilde{t}) = V(t)/V_0$ as function of scaled time $\tilde{t} = t/\tau_c$ for the various mixtures, and the two single-component droplets. The single-component droplets collapse onto a single curve, illustrating universality of the convective dissolution mechanism [126]. The residual volumes of each of the mixtures approximately equals $V_{0,b}/V_0$, so the amount of insoluble material. Panel B gives a more detailed view of the interval $0 \leq \tilde{t} \leq 1$, clearly revealing that the mixtures containing two types of alcohol show retarded dissolution, whereas the mixtures containing cyclohexane do not.

To get a more quantitative view on the segregation in the mixtures, we proceed by trying to apply the same approach as used by Su & Needham [151], and regard the total droplet dissolution rate as the sum of the dissolution rates of the individual components. Therefore we modify Equation 7.4 to,

$$\frac{dV}{dt} = \sum_{i=a,b} \frac{dV_i}{dt} = (2\pi)^{\frac{5}{12}} \sum_{i=a,b} -A_{\text{frac},i} \chi_i (3V)^{\frac{7}{12}} \left(\frac{g\beta_{c,i} \Delta c_{s,i}^5 D_i^3}{\nu \rho_{d,i}^4} \right)^{1/4}, \quad (7.9)$$

where the sum over $i = a, b$ indicates the summation of the contribution of the individual materials, where the material properties and values for χ as listed in

Table 7.1 and Table 7.3 are used. $A_{\text{frac},i} = A_i/A$ is the fraction of the interface occupied by component i at each instant in time. Since both decanol and cyclohexane are effectively insoluble, we can safely assume that in mixtures containing either of these components, all the changes in the volume of the droplet can be attributed to dissolving pentanol or heptanol. In the pentanol/heptanol mixture we use the fact that $A_{\text{frac, heptanol}} = 1 - A_{\text{frac, pentanol}}$. Equation 7.9 is fitted to the experimental data using $A_{\text{frac},a}$ as the only fitting parameter where again, a corresponds to the materials listed in Table 7.2. The obtained results are plotted as function of $\tilde{V}$ in Figure 7.9. From this figure, we can distinguish two types of behavior.

The mixtures that contain two types of alcohol are characterized by $A_{\text{frac},a} = 0.5$ at $\tilde{V} = 1$, where a indicates pentanol or heptanol. This initial state is followed by a continuous decreases to $A_{\text{frac},a} = 0$ at $\tilde{V} \approx 0.5$, signaling that Equation 7.2 provides a good representation of the interface composition. The pentanol/heptanol mixture is somewhat more complicated to interpret, as both constituents dissolve and we can not directly relate $\tilde{V}$ to the droplet composition. Nevertheless, as the droplet dissolves, $A_{\text{frac,pentanol}}$ (plotted as the blue solid line in Figure 7.9) and $A_{\text{frac,heptanol}}$ (plotted as the blue-dashed line in Figure 7.9) show a continuous decrease or increase, respectively. At $\tilde{V} = 0.4$, $A_{\text{frac,pentanol}} = 0$, which is consistent with the position of the 'kink' in the dissolution curve shown in Figure 7.7, which is followed by a decreased dissolution rate, signaling depletion of the more soluble pentanol from the droplet.

A completely different behavior is observed for the alcohol/cyclohexane mixtures, which display an approximately constant value for $A_{\text{frac},a}$, followed by a steep decrease once the droplet is depleted from soluble material (at $\tilde{V} = V_b/V_0 = 0.5$). Note that $A_{\text{frac,pentanol}} > 1$, as observed for the pentanol/cyclohexane mixture, obviously does not reflect an increase in interface area, but represents a dissolution rate larger than expected from Equation 7.4, possibly caused by increased convection, which we will demonstrate later on. The behavior of $A_{\text{frac, heptanol}}$ in the heptanol/cyclohexane mixture is consistent with the dissolution dynamics observed in Figure 7.7, where the dissolution of the heptanol/cyclohexane mixture was slower than the pure heptanol droplet, but did show a sharp kink, marking the point at which heptanol was depleted from the droplet. This heptanol/cyclohexane mixture displays some more surprising features. Figure 7.7 shows that for $\tilde{V} < 0.5$ the cyclohexane does in fact dissolve. A similar behavior was observed in preliminary measurements on pentanol/cyclohexane droplets in water pre-saturated to $0.5 \times c_s$ pentanol. We hypothesize that heptanol, and to a lesser extent pentanol, acts as a surfactant that helps to disperse cyclohexane in water. A large affinity between heptanol and cyclohexane could also explain the reduced dissolution rate of this mixture, observed in Figure 7.7. However, more work is required to verify this.

Although Chu & Prosperetti [152] treated binary droplets of different materials than in the current work, it is striking to see that their theoretical predictions for the surface density of the soluble species during dissolution are qualitatively similar to the $A_{\text{frac}}(\tilde{V})$ curves extracted from our experiments. Clearly, future work should involve direct comparison between the theoretical method used by Chu & Prosperetti [152], and experiments such as those in the current work.

Figure 7.8: Scaled droplet volume $\tilde{V}(\tilde{t}) = V(t)/V_0$ as function of scaled time $\tilde{t} = t/\tau_c$ for pentanol/cyclohexane mixtures, and a pure pentanol droplet. Here $V_0 = 100$ nl. The mixtures are prepared at different initial compositions $V_a/V_0 : V_b/V_0$. One droplet with $V_0 = 10 \times 100$ nl = $1 \mu\text{l}$ was studied as well, showing identical behavior in the rescaled variables. Each mixture, regardless its initial composition and initial volume, collapses onto the pure pentanol droplet curve during the dissolution stage, which abruptly stops at V_b/V , indicating depletion of the soluble pentanol from the droplet.

7.4 Segregation, contact angle, and Marangoni flow

Given the difference in surface tensions for the liquids, the change in interface composition should result in a change of the contact angle θ . This change is easily confirmed by plotting θ as function of $\tilde{t}$, as done in Figure 7.10. Figure 7.10 again shows distinctive behavior between droplets containing mixtures of alcohols, and the droplets containing cyclohexane: contact angles for mixtures of pentanol/decanol, heptanol/decanol, and pentanol/heptanol are always limited by the values of the pure components (listed in Table 7.1). The pentanol/cyclohexane mixture shows a sharp decrease towards $\theta < 30^\circ$, far below the value for either pure pentanol or cyclohexane.

Figure 7.9: Interface fraction A_{frac} of the soluble component (pentanol or heptanol), as function of scaled droplet volume $\tilde{V}$. Note that the dissolution time runs from right to left and that $A_{\text{frac},a} > 1$ does not reflect an increase in interface area, but represents a dissolution rate larger than expected from Equation 7.4. For the pentanol/heptanol mixture, the interface fractions of pentanol $A_{\text{frac}, \text{pentanol}}$ is plotted as the blue solid line, and the interface fraction of heptanol $A_{\text{frac}, \text{heptanol}} = 1 - A_{\text{frac}, \text{pentanol}}$ is plotted as the blue dashed line.

lohexane. This decrease in θ could be the result of initial spreading of the droplet, during which the footprint radius increases and θ slowly decreases to an equilibrium value. However, if we look at Figure 7.2D, we see that an increase in the footprint radius is not observed, and therefore cannot explain the decrease in θ . Moreover, the values of the receding contact angles θ_R , as listed in Table 7.1, are all $> 30^\circ$, excluding contact line pinning as an explanation for the low contact angle. Also the (initial) volume of the droplet does not affect the contact angles, as demonstrated by Figure 7.11, where θ is plotted as function of time for pentanol/cyclohexane droplets with varying initial volumes.

Figure 7.10: Contact angle θ as function of scaled time $\tilde{t}$ (A) and scaled droplet volume $\tilde{V}$ (B), during dissolution of the various mixtures. They can be compared to the values of the pure components: $43^\circ \leq \theta \leq 50^\circ$ and $50^\circ \leq \theta \leq 60^\circ$ for pentanol and heptanol, respectively.

Figure 7.11: Contact angle θ as function of time $\tilde{t}$, during dissolution of mixture 2 droplets, initially containing a mixture of equal amounts of pentanol and cyclohexane. The dashed lines indicate the receding contact angles θ_R for pure droplets of pentanol ($\theta_R = 43^\circ$) and cyclohexane ($\theta_R = 69^\circ$).

As the decrease in θ is not observed in immersed sessile droplets of either pure pentanol or cyclohexane, it is possible that this remarkable behavior of θ is related to either mixture or segregation of the two components. Segregation between the components can be visualized by adding a small amount of solvatochromic dye to the pentanol/cyclohexane mixture, and visualize the droplet during dissolution using confocal microscopy. From this, we obtain a three-dimensional profile of the droplet surface, where the color of the dye represents the composition, as shown in Figure 7.12. In this figure, the purple color (representing pentanol-rich regions) initially covers the entire surface, as shown in Figure 7.12A. During dissolution (Figure 7.12B), the perimeter of the droplet turns yellow, representing an increase of the cyclohexane concentration in this region. The depletion of soluble material and the enrichment of cyclohexane near the contact line indicates that, similar to diffusive dissolution [15, 86, 89], convective dissolution in this case leads to an increased flux of the soluble material at the droplet perimeter. As dissolution progresses and more pentanol dissolves, the cyclohexane rim rapidly expands inward (Figure 7.12, panels B-C), until ultimately all pentanol has dissolved (Figure 7.12D). Depletion of the soluble component from the droplet interface is not readily observed when we perform the same measurement for a droplet of heptanol/cyclohexane mixture, shown in Figure 7.13. The surface of this droplet shows a continuous, uniform transition from blue/green (representing a high heptanol concentration), to yellow.

The difference in concentration over the droplet interface, combined with the large difference in surface tension of the two liquids, leads to an interfacial tension gradient over the interface. This gradient results into a Marangoni flow across the interface, directed from the droplet apex towards the rim. It is this flow that results in the so-called superspreading of the droplet [161–163]. We can confirm the presence of this interfacial flow by two experiments. Firstly, the bulk flow can be visualized by adding a small amount of tracer particles (3 μm diameter, fluoromax Thermoscientific) to the water. Figure 7.14 shows a streak image which readily demonstrates that while the bulk flows towards the droplet apex (consistent with convective droplet dissolution [126]), particles close to the droplet interface swirl around and move in the opposite direction, as indicated by the arrows.[†] Secondly, by slightly defocussing the microscope, a shadowgraph image is recorded, which shows local differences in optical index (caused by dissolved alcohol) as brighter/darker regions. Such a shadowgraph is shown in Figure 7.15: The large plume above the droplet is the alcohol-rich convective plume, originating from the buoyancy of the alcohol-saturated water surrounding the droplet moves upwards, drawing in fresh water from the sides. The smaller flame-like features visible just above the interface are small swirls, which propagate in the opposite direction from the bulk, as indicated by the arrows. These swirls create an extra convection in the solute-rich boundary layer that develops over the dissolving droplet.

As the convective dissolution model assumes a laminar flow in this boundary layer, it is to be expected that this increased convection increases mass transport to val-

[†]Unfortunately, the low particle concentration near the droplet interface prohibited detailed particle image velocimetry (PIV) or particle tracking.

Figure 7.12: Three-dimensional confocal image of a droplet containing a pentanol/cyclohexane mixture. Panels show the surface at $t = 0$ s (A), $t = 270$ s (B), $t = 360$ s (C), and $t = 420$ s (D). Purple indicates the polar solvent (pentanol), yellow indicates the non-polar solvent (cyclohexane). The surface is covered with pentanol during a large fraction of the dissolution process, with depletion starting from the rim (figures B and C).

Figure 7.13: Three-dimensional representation of the droplet surface at $t = 0$ s (A), $t = 2000$ s (B), $t = 3300$ s (C), and $t = 6000$ s (D). Blue indicates heptanol, yellow indicates cyclohexane. The uniform green appearance in panels B and C indicates a well-mixed interface during dissolution.

Figure 7.14: Streak image, showing the motion of tracer particles added to the bulk, surrounding a dissolving droplet containing a mixture of pentanol and cyclohexane. Arrows are drawn to indicate the direction of the particle trajectories. Most of the particles flow right-to-left, accumulating in a single convective plume, rising upward from the droplet apex. Some particles, close to the droplet-bulk interface, recirculate, due to the Marangoni flow across the droplet interface.

ues above those expected based on Equation 7.5, and from that the fitted value $A_{\text{frac, pentanol}} > 1$ for the pentanol/cyclohexane mixture. Figure 7.15 illustrates another effect caused by the depleted rim, which only becomes clear for this large droplet ($V \approx 1 \mu\text{l}$): locally varying surface tensions and the Marangoni flow cause the droplet shape to deviate from a spherical cap, with an increased radius of curvature near the contact line [161].

7.5 Discussion and conclusion

In the current work we have shown that dissolving droplets containing a binary mixture of liquids can exhibit markedly different behavior depending on the droplet's constituents. We have shown that the approach of Su & Needham [151] is justified for some, but not for all mixtures: in the case of mixtures containing two comparable liquids, such as two different types of alcohols, the interfacial composition of the droplet indeed depends on, and varies continuously with the droplet composition. However, this does not hold for all mixtures, like the alcohol/cyclohexane mixtures

Figure 7.15: Shadowgraphy image (filtered and contrast-enhanced) of a dissolving droplet containing a mixture of pentanol and decanol. Deformation of the droplet, caused by Marangoni flow and local differences in surface tension, is visible as the non-spherical shape of the droplet.

in this work. It thus appears that the assumption, reflected in Equation 7.2 is only valid for mixtures of components with comparable material parameters, such as polarity and surface tension with the bulk. More work is required to explore to which limits Equation 7.2 is valid, and a description of the dissolution process such as Equation 7.9 is applicable.

Clearly, the alcohol/cyclohexane mixtures in this work showed segregation of the droplet constituents: In these cases, a constant surface composition was measured during dissolution, regardless of the droplet composition, and in these situations the method proposed by Chu & Prosperetti [152] is likely to be more accurate. The next step forward would therefore consists of experiments involving experiments and matching simulations to allow for a direct comparison. However, we have also shown that more complicated processes should be considered, as strong dynamic effects can occur. Our confocal microscopy measurements have revealed that local depletion of the soluble compound occurs, which in turn fuels a Marangoni flow. Especially this last observation can have huge implications, either undesirable or advantageous, for example for ink droplets containing pigments which should be distributed evenly over the substrate. Lastly, our measurements hints at the possibility that the soluble component can act as a surfactant to the non-soluble component, likely compromising the accuracy of current theories. These effects illustrate the finding that in many applications, the interaction between the droplet constituents and the bulk can not be neglected.

8

Summary and outlook

The introduction explains how one can form three different, yet physically equivalent systems: gas filled bubbles in a liquid environment, droplets in a gas environment, or droplets in a liquid environment. All experiments in this thesis have been conducted on liquid surface droplets in water, hence the title of this thesis: Dynamics of dissolving surface droplets. While the experiments presented in this thesis are not much different from the (undervalued) activity of watching paint dry, each of the chapters reveals how seemingly simple and everyday processes can be amazingly complex and rich from a physical point of view. This last chapter highlights the main results of this thesis, and gives an outlook towards future research and possible applications.

8.1 Droplets and bubbles

At various points throughout this thesis we have shown that oil droplets dissolving in water could display the same behavior as evaporating droplets in air, or bubbles growing or dissolving in water. The fact that bubbles and droplets are sometimes hard to distinguish was encountered in chapter 3, where we set out to measure a recirculation flow around surface nanobubbles. The detected spherical cap-shaped objects later turned out to be liquid droplets, rather than gaseous bubbles. In retrospect, it is not surprising that the nanobubble-like objects in chapter 3 were found to be stable: the droplets were filled with a (practically) insoluble silicon oil, resulting in dissolution times beyond the duration of any of the experiments. With the challenges of small gas bubbles in mind, the experiments in the following chapters relied on the much more controllable and versatile system of droplets containing various long-chain alcohols, dissolving in water.

As said, the system of a dissolving oil droplet is only seemingly straight forward, and aspects of even the simplest case (a single, isolated droplet) are not fully understood. For example, preliminary experiments and simulations reveal that not only the alcohol dissolves in the water, but a counter-diffusive flow is set up as well, where water diffuses into the droplet. In some cases this water was observed to condense as water droplets inside the alcohol droplet. In turn, these water droplets moved around inside the droplet, revealing the existence of a flow inside the droplet. None of these three effects have been studied in detail and might be a topic of future research.

Chapters 4, 5, and 6 focused on droplets containing a single type of liquid, which meant that the droplet composition remained constant during the dissolution. In chapter 7, we extended the scope by mixing two types of oil and measuring the dissolution. In this chapter it was found that not only the solubility of the oils plays

a role in the dissolution, but also the hydrophobicity of the molecule. Because of this, the droplet did not dissolve according to a simple sum of the two components, and more sophisticated processes should be considered in order to describe such a mixture. In addition to that, we showed that another effect emerged: depletion of one of the two components from the droplet contact line, resulting in super-spreading of the droplet. Application-wise, this last finding could be particularly promising, as it causes the droplet to flatten well below its normal equilibrium contact angle. In processes such as spray-painting, spray-cooling or deposition of small particles, this could result in an enhanced wetting (and thus coverage of e.g., pigments) of the substrate without the necessity of a patterned substrate to facilitate pinning, and it could reduce the coffee-stain effect [85]. The rich behavior of the dissolving binary component droplets points out that chapter 7 only scratched the surface of this topic, and that a complete, unexplored field lies ahead. For example the shape of the molecule, which might influence the occupied interfacial area per molecule has not been addressed.

8.2 Surfaces

This thesis focusses on surface droplets, and it is thus logical that some emphasis was placed on the interaction between the surface and the droplet. This was most elaborately done in chapter 4, where we studied the stick-jump mode. In this study, intrinsic roughness of the substrate caused the droplet contact line to stick to the substrate. Only when the depinning force became large enough, i.e., when the contact angle decreased below a certain value, the contact line depinned and the droplet quickly 'jumped' to a new geometry. The roughness of the samples used in this thesis originated from imperfections of the substrates and the coating procedure, explained in more detail in chapter 2. Attempts were made to vary the roughness of coated silicon substrates by anisotropic etching [164,165], which resulted in a silicon surface covered by pyramid shaped hillocks, as shown in figure 8.1. However, these etched substrates did not result in any consistent results in terms of contact angles and pinning behavior.

The step forward is therefore to position droplets on patterned substrates, where local variations in geometry or wettability create controlled pinning sites for the droplet. This opens the way to study the influence of pinning on the dissolution or stabilization of droplets and bubbles. Especially the latter is interesting, as it could confirm a new theory that explains the stability of surface nanobubbles based on the stabilizing effect of contact line pinning [69].

8.3 Mass transport

An intuitive guess about the dissolving droplets of oil, is to assume that all mass transport is governed by diffusion, since the droplets are small, and the dissolution is very slow. This was also the approach in chapter 4 where, nevertheless, it was

Figure 8.1: Scanning electron microscopy (SEM) images of a silicon surface, etched through an anisotropic wet etching process [164, 165]. The etching rates along each of the crystal planes is different, resulting in pyramid shaped hillocks. The size and density of these hillocks depend on parameters such as temperature of the etching liquid, and etching time. The two panels do not show part of the same sample.

noted that dissolution occurred faster than expected. This discrepancy could be corrected by assuming an effective diffusion constant, twice as high as the literature value, which accounted for the discrepancy in mass transport. In chapter 5, the origin of this discrepancy was explored in detail, and it was shown here that the dissolved alcohol locally reduced the density of the bulk, inducing a buoyancy driven convection, which in turn increased the mass transport and hence the dissolution rate. A convective dissolution model was derived, based on the scaling between the droplet properties and the dissolution rate, which takes the dimensionless form $Sh \sim Ra^{\frac{1}{4}}$. It was especially here that the versatility of the oil-in-water system stood out, as the various alcohols and their respective solubilities allowed for a variation of the Rayleigh number by four orders of magnitude, while still keeping the droplet size below the capillary length. The similarities between the $Sh - Ra$ relation for our droplets and the growing gas bubbles presented in [108] is a fine example of both the universality of the convective dissolution model, and the fact that bubbles and droplets are much alike.

The convective dissolution model contains a prefactor, the value of which can be determined from the experiments. The hypothesis that the prefactor in the model is influenced by the contact angle of the droplet, can easily be tested by taking droplets of a certain (initial) Rayleigh number and place them on substrates that differ in hydrophobicity. This could then be extended by changing the geometry of the droplet's surroundings, or orientation with respect to gravity. This would be a crucial step to make the findings from chapter 5, which is more fundamental, applicable for practical situations where droplets might be sitting on a vertical wall, or hanging from a ceiling. An ultimate test of the universality of the convective

model would be to create bubbles, dissolving droplets, and evaporating droplets with matching Rayleigh numbers and compare the mass exchange of each of these objects.

Another (arguably more complex) mass transport problem was addressed in chapter 6, where not one, but multiple dissolving droplets were placed in an ordered pattern. The experiments showed that a competition between collective and convective effects caused either a decrease or increase of the droplet dissolution time, strongly depending on the actual position in the pattern. A crucial step to obtain fundamental insight is to expand the simulations from this chapter to incorporate convective effects, while the experiments should be extended to simultaneously measure the volume of all droplets inside the pattern. Possible methods to achieve this would be through confocal microscopy, top view microscopy combined with an interference technique, or other methods where a three-dimensional profile of the pattern can be obtained.

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Samenvatting

Hoewel druppels en bellen een alledaags verschijnsel zijn, worden zowel hun verschijningsvorm als hun levensloop bepaald door vele intrigerende aspecten. De alomtegenwoordigheid van druppels en bellen in verschillende (industriële) toepassingen onderstreept het belang van een goed begrip van de relevante fysische aspecten. Hoofdstuk 3 behandelt de resultaten van experimenten aan oppervlakte nanobellen, kleine gasvormige domeinen op het grensvlak waar water in aanraking komt met een vaste ondergrond. Deze nanobellen zijn interessant, aangezien hun levensduur vele malen groter blijkt te zijn dan op basis van klassieke kennis over bellen verwacht kan worden. Een van de verklaringen voor deze discrepantie gaat uit van een stabiliserend mechanisme op basis van een circulerende stroming rondom de bel. In hoofdstuk 3 van deze thesis wordt de validiteit van deze theorie getest door het volgen van de bewegingen van kleine deeltjes die zijn toegevoegd aan het water dat de nanobellen omringt. Echter, de metingen maken het niet aannemelijk dat een circulerende stroming rondom de oppervlakte nanobellen bestaat. Het laatste deel van hoofdstuk 3 bediscussieert het risico van onbedoelde vervuiling in de context van oppervlakte nanobellen. Het is namelijk gebleken dat minieme hoeveelheden vervuiling, afkomstig van verschillende bronnen, druppeltjes kunnen vormen. Deze druppels zijn op grond van hun vorm en mechanische eigenschappen niet te onderscheiden van gasgevulde nanobellen. Het is daarom waarschijnlijk dat de metingen aan de recirculatie stroming zijn uitgevoerd boven druppels, in plaats van bellen. Omdat oppervlakte nanobellen moeilijk te meten en te controleren zijn, wordt na hoofdstuk 3 de stap gemaakt van gasgevulde bellen naar druppels gevuld met zogenoemde lange-keten alcoholen. Deze druppels zijn gemakkelijk te vormen en te bestuderen, waarbij parameters zoals druppel grootte, verzadiging en de positionering van de druppels nauwkeurig te bepalen zijn.

Hoofdstuk 4 beschrijft het oplossen van druppels, in de zogenoemde "plak-sprong" oplosmodus. De modus wordt gekenmerkt door relatief lange periodes waarin de druppel oplost terwijl de contactlijn vastgeplakt zit aan het substraat (de plak-periode), afgewisseld met een veel kortere periode waarin de contactlijn loslaat, en de druppel naar een nieuwe vorm 'springt'. Hoofdstuk 4 behandelt de oorzaak van het plakken van de contactlijn, en beschrijft de oplostijd van druppels in deze modus. De theoretische beschrijving voor deze oplostijd komt overeen met de experimenten wanneer een 'effectieve diffusie constante' wordt aangenomen. Dit is nodig om te corrigeren voor het toegenomen massatransport ten opzichte van de theoretische waarde voor diffusief massatransport. In hoofdstuk 4 wordt gehypothetiseerd dat de toename in massatransport toegeschreven kan worden aan de ontwikkeling van een convectie stroming rondom de oplossende druppel.

Deze hypothese wordt bevestigd in hoofdstuk 5, waarin micro-deeltjes beeld snelheidsmetingen het bestaan van een convectiestroom aantonen, welke wordt gemeten rondom oplopende druppels van verschillende types lange-keten alcoholen. Met de inzichten die op zijn gedaan aan de hand van de snelheidsmetingen wordt het systeem beschreven in dimensie loze getallen, waarmee aangetoond kan worden dat het oplosgedrag wordt bepaald door een diffusieve en een convectieve bijdrage. Welke van de twee bijdragen dominant is, wordt bepaald door de waarde van het Rayleigh getal. Voor kleine Rayleigh getallen (kleiner dan 12) is het oplosgedrag diffusie-gelimiteerd, terwijl het gedrag wordt bepaald door convectie in geval van grotere Rayleigh getallen. Met deze kennis is een theoretisch model opgesteld dat de druppel dynamica schrijft in het convectieve regime. Toetsing van het model aan experimentele data laat goede overeenkomsten zien.

Waar hoofdstukken 4 en 5 zich toediepen op het gedrag van een enkele druppel, bestaande uit een enkel materiaal, wordt in hoofdstukken 6 en 7 het onderzoek verbreed naar meer complexe situaties. In hoofdstuk 6 wordt de situatie waarin een druppel is omringd door meerdere druppels beschouwd. De naburige druppels zullen het water verzadigen met oplosbaar materiaal, waardoor het massatransport afneemt, en de afzonderlijke druppels langzamer oplossen, resulterend in een extensie van de levensduur. Experimenten en computer simulaties aan druppel patronen worden vergeleken, en tonen beiden aan dat de oplostijd van een druppel in een patroon kan worden verlengd met 60%, ten opzichte van een alleenstaande druppel. Echter, de experimenten tonen aan dat een patroon van druppels een sterkere convectie stroming op kan wekken, welke op zijn beurt resulteert in een toename van het massatransport, en een gereduceerde oplostijd. Het blijkt af te hangen van de patroon grootte en de positie van de druppel, of de oplostijd van een druppel toeneemt of afneemt.

Hoofdstuk 7 tot slot behandelt metingen aan twee-component oppervlakte druppels: druppels die bestaan uit een mengsel van twee verschillende stoffen. Elk van deze stoffen heeft specifieke oplosbaarheid in water. Eerdere publicaties beargumenteerden dat zo een druppel beschouwd kan worden als een ideaal mengsel, en dat het totale gedrag van de druppel kan worden voorspeld door de bijdragen van de individuele stoffen naar rato op te tellen. De experimenten zoals die gepresenteerd zijn in hoofdstuk 7 tonen aan dat dit niet altijd het geval is, en dat separatie tussen de twee stoffen op kan treden. Volumetrische metingen en chemisch sensitieve metingen met een zogenaamde confocaal microscoop geven meer inzicht in de verdeling van de twee stoffen over de druppel, en demonstreren dat het gedrag van twee-component oppervlakte druppels dynamisch en complex is.

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Dynamics of dissolving surface droplets